



รายงานวิจัยฉบับสมบูรณ์

โครงการ “การสังเคราะห์ พิสูจน์เอกลักษณ์ สมบัติเชิงความร้อน
และฟังก์ชันของโครงข่ายโลหะอินทรีย์”

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กรกฎาคม 2555

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โครงการ “การสังเคราะห์ พิสูจน์เอกลักษณ์ สมบัติเชิงความร้อน
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Abstract

Porous coordination polymers (PCPs), also known as metal organic frameworks (MOFs) recently have received great attention because of their diverse and fascinating architectures with promising functional properties such as molecular adsorption and separation processes, ion-exchange, catalyst, sensor technology, optoelectronics and magnetism. Particularly, the guest removal and re-adsorption in flexible and dynamic molecular solids are of interest for many potential applications especially in the areas of gas storage and sensors. This research discusses functional properties toward catalysis, anion-exchange and dynamic behaviors in Zn(II)-4,4'-bipyridine-carboxylato compounds exhibiting 1D, 2D and 3D structural frameworks. More recently, we have synthesized the flexible and dynamic non-coordination supramolecular Co(II)/Fe(II)-2-aminopyrazine-sulfate frameworks supported by weak molecular interactions such as hydrogen bonds and π - π stacking. These compounds exhibit water-induced reversible crystal-to-amorphous transformations with chromotropism which is uncommon for the non-coordination frameworks to maintain their structures. Contradictory, a related coordination polymer is obtained for Cd(II) which also shows water-induced reversible structural phase transition. Furthermore, the azido Co(II) complex system yielded four coordination polymers with interesting molecular magnetic phenomena.

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บทคัดย่อ

สารประกอบโคออร์ดิเนชันพอลิเมอร์ที่มีรูพรุน (PCP) หรือโครงข่ายโลหะอินทรีย์ (MOF) ได้รับความสนใจเป็นอย่างยิ่งในปัจจุบัน เนื่องจากมีโครงสร้างที่หลากหลายและน่าทึ่ง ร่วมกับแสดงสมบัติหน้าที่ที่ดี ได้แก่ การดูดซับและกระบวนการแยกเชิงโมเลกุล การแลกเปลี่ยนไอออน การเร่งปฏิกิริยา เทคโนโลยีเซนเซอร์ ออปโตอิเล็กทรอนิกส์ และสมบัติทางแม่เหล็ก โดยเฉพาะอย่างยิ่งในกระบวนการกำจัดและดูดซับกลับคืนของแก๊สในโครงข่ายโลหะอินทรีย์ที่มีความยืดหยุ่นและมีสมบัติเชิงพลวัตนั้น กำลังได้รับความสนใจอย่างมาก ซึ่งเหมาะแก่การประยุกต์ในการกักเก็บแก๊สและเซนเซอร์ ในงานวิจัยฉบับนี้อภิปรายสมบัติหน้าที่ของโครงข่ายโลหะอินทรีย์ ได้แก่ การเร่งปฏิกิริยา การแลกเปลี่ยนไอออนลบ และพฤติกรรมเชิงพลวัตของสารเชิงซ้อน $\text{Zn(II)-4,4'-bipyridine-carboxylato}$ ซึ่งแสดงโครงข่ายตั้งแต่หนึ่งมิติ สองมิติ และสามมิติ และสามารถสังเคราะห์โครงข่ายซูปราโมเลกุลที่ไม่มีการโคออร์ดิเนชันในระบบ $\text{Co(II)/Fe(II)-2-aminopyrazine-sulfate}$ ซึ่งประกอบขึ้นมาจากอันตรกิริยาแบบอ่อน ได้แก่ พันธะไฮโดรเจนและอันตรกิริยา $\pi-\pi$ และสารกลุ่มนี้แสดงการเปลี่ยนแปลงเฟสโครงสร้างแบบผันกลับได้จากโครงร่างผลึกเป็นอสัณฐานเมื่อถูกเหนี่ยวนำโดยโมเลกุลน้ำร่วมกับการเปลี่ยนแปลงสี ซึ่งพฤติกรรมนี้พบได้ยากในโครงข่ายที่ไม่มีการโคออร์ดิเนชัน ขณะที่เปลี่ยนชนิดโลหะเป็น Cd(II) ทำให้เกิดโคออร์ดิเนชันพอลิเมอร์สองมิติและแสดงการเปลี่ยนเฟสโครงสร้างผลึกแบบผันกลับได้เมื่อถูกเหนี่ยวนำโดยโมเลกุลน้ำ นอกจากนี้ ในระบบสารเชิงซ้อน Co(II) azido ทำให้ได้โคออร์ดิเนชันพอลิเมอร์ 4 ชนิดที่มีปรากฏการณ์ทางแม่เหล็กเชิงโมเลกุลที่น่าสนใจ

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และฟังก์ชันของโครงข่ายโลหะอินทรีย์”

รายงานสรุปความก้าวหน้าของโครงการประจำปี

Executive Summary

Metal-organic frameworks (MOFs) have attracted intensive attention for the past decade owing to their diverse topologies and enormous potential applications for molecular adsorption and separation, catalysis, ion exchange, optoelectronics and sensor technology. MOFs have advantages in that they provide not only light materials with high porosity, but also desirable regular networks. One of the more prominent applications pursued for these materials has been their possible use in high-density hydrogen storage. The field of metal-organic frameworks has been extensively investigated with a focus on functional material research and crystal engineering. In material research, the coordination networks with interesting properties are constructed for fine-tuning the properties and creating new functional materials. On the other hand, crystal engineering is attracting interest from both the synthetic routes and the art of structural design.

The present research deals with the systematic synthesis, structural characterization and magnetic properties of novel metal-organic framework materials based on the coordination chemistry of carboxylates, sulfate, azide and *N,N'*-ditopic organic spacers. The central aim is to generate new compounds of this interesting family which is focused on the core features of crystal engineering and their functions toward anion-exchange, catalysis, dynamic structural transformation with chromotropism and molecular magnetism. An emphasis is therefore given to the analysis of the crystal structures and functional properties of many product systems. This research can be separated into two parts:

Part I addresses the syntheses, structural characterization, anion exchange and catalytic properties of a series of 4,4'-bpy-carboxylato metal-organic frameworks. The combination of framework-builder coordination moiety (zinc(II)-4,4'-bpy and copper(II)-4,4'-bpy) with respectively formate, acetate and propionate ligands provides two series of novel metal organic frameworks. Eleven zinc(II)-4,4'-bpy-carboxylato coordination polymers, i.e. the 3D frameworks $\{[\text{Zn}_3(4,4'\text{-bpy})_{3.5}(\mu\text{-OOCH})_4(\text{H}_2\text{O})_2](\text{X})_2\}_n$ when $\text{X} = \text{ClO}_4 \cdot \text{H}_2\text{O}$ (1), PF_6^- (2), $\text{BF}_4 \cdot \text{H}_2\text{O}$ (3), the 2D layer $\{[\text{Zn}_4(4,4'\text{-bpy})(\mu\text{-OOCH})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})\}_n$ (4), the 2D zig zag layer $\{[\text{Zn}_4(4,4'\text{-bpy})_4(\mu\text{-OOCH})_5(\text{H}_2\text{O})_5](\text{NO}_3)_3(4,4'\text{-bpy})_2(\text{H}_2\text{O})_3\}_n$ (5), the 1D three-leg ladder $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-OOCCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (6), the 2D layer $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-OOCCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(4,4'\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (7), the double-stranded zig zag chain $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-OOCCH}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (8), the 2D layer $\{[\text{Zn}_2(4,4'\text{-bpy})_2(\mu\text{-OOCCH}_2\text{H}_5)_2(\text{OH})(\text{H}_2\text{O})](\text{BF}_4)(\text{H}_2\text{O})_2\}_n$ (9), the double ladders chain $\{[\text{Zn}_2(4,4'\text{-bpy})_2(\mu\text{-OOCCH}_2\text{H}_5)_2(\text{H}_2\text{O})_2]$

(CF₃SO₃)₂]_n (**10**) the double-stranded zig zag chain {[Zn₃(4,4'-bpy)₄(μ-OOCC₂H₅)₄(H₂O)₂](NO₃)₂(H₂O)₃]_n (**11**) and nine copper(II)-4,4'-bpy-carboxylato coordination polymers, the triple-stranded layers {[Cu₃(4,4'-bpy)₂(μ-OOCH)₄(H₂O)₂](X)₂(H₂O)₆]_n when X = ClO₄⁻ (**12**), PF₆⁻ (**13**), BF₄⁻ (**14**), CF₃SO₃⁻ (**15**), the zig zag 2D layer {[Cu(4,4'-bpy)(μ-OOCH) (NO₃)]_n (**16**), the quadruple-stranded layers {[Cu₂(4,4'-bpy)₂(μ-OOCCH₃)₃](X) (H₂O)]_n when X = ClO₄⁻ (**17**), PF₆⁻ (**18**), BF₄⁻ (**19**), CF₃SO₃⁻ (**20**) are obtained and have been crystallographically characterized. This study shows that the change from a formate ligand to an acetate and a propionate ligand gives rise to the formation of drastically distinct metal organic frameworks, as the result of the different steric bulk of the carboxylato unit involved.

The thermal and optical properties, ion-exchange with structure retention and catalytic reactivity, as well as dynamic structural transformation have been investigated. Compounds **6-9** and **11** show a crystalline-to-crystalline structural transformation up on removal/reintroduction of water guest molecules. The anion exchange among zinc(II) and copper(II) compounds is found to be highly selective while anion-sensing properties in an aqueous solution is found only in **1**. Interestingly, these zinc(II) compounds are effective heterogeneous catalysts for the high-yielding cyanosilylation of acetaldehyde in dichloromethane with size-selective. Contradictory, all copper(II) compounds are less active and less selective catalysts for cyanosilylation of aldehydes.

Part II addresses the syntheses, structural characterization and their functional properties toward dynamic structural transformation with chromotropism and magnetism. Novel fifteen metal(II) polymeric complexes were successfully synthesized and structurally characterized, as following: firstly, five Cu^{II} coordination networks containing 2-aminopyrazine and various carboxylate anions, 2D wavy sheet [Cu(ampyz)(O₂CH)₂]_n (**III-1**), 1D chains [Cu₂(ampyz)(O₂C₂H₃)₄]_n (**III-2**) and [Cu₂(ampyz)(O₂C₃H₅)₄]_n (**III-3**), 2D layer [Cu₂(ampyz)(O₄C₄H₄)₂]_n(H₂O)_n (**III-4**) and 2D stairlike layer [Cu(ampyz)(O₄C₃H₂)₂]_n(H₂O)_{2n} (**III-5**), secondly, three isostructural flexible metal-supramolecular architectures [M(H₂O)₄(ampyz)₂][M(H₂O)₆](SO₄)₂(H₂O)₂ (M are Co^{II} (**IV-1**), Fe^{II} (**IV-2**) and Co^{II}/Fe^{II} (**IV-3**)) and a flexible 2D Cd^{II} coordination network [Cd(ampyz)(H₂O)₂(SO₄)_n](H₂O)_n (**IV-4**), thirdly, two flexible metal-organic frameworks [Co(pydc)(H₂O)₂]_n (**IV-5**) and [Co(pydc)(H₂O)₄]_n(H₂O)_n (**IV-6**), (pydc = 3,5-pyridinedicarboxylate) and lastly, four azido Co^{II} magnetic hybrid frameworks, i.e. 1D chain of [Co₃(N₃)₆(OH)₂](2,2'-bpe)₂]_n(2,2'-bpe)_n (**V-1**), 2D layer [Co(N₃)₂(2,2'-bpe)]_n (**V-2**) and 2D sheet [Co(N₃)₂(ampyz)]_n (**V-3**) and 3D framework [Co(N₃)₂(ampyz)]_n (**V-4**) of [Co(N₃)₂(ampyz)]_n.

Compound **III-1** reveals a 2D wavy sheet structure. Both **III-2** and **III-3** consist of polymeric chains constructed from paddle-wheel (CuNO₄)₂ chromophores. The structure of **III-4** consists of a 2D layer built from double-stranded chain of paddle-wheel units connecting ampyz spacers. Compound **III-5** exhibits a 2D stairlike layer built from malonate anions and μ₂-ampyz. Beside the various coordinative modes of carboxylates, the ampyz spacer has an influence on the molecular structures *via* either the ditopic bridging mode, or by other weaker interactions, such as hydrogen bonding and π-π stacking, which mainly

contribute to the stabilization of the overall supramolecular structures. All compounds emphasize the effect of the ampyz spacer in building the copper(II) networks and are compared with the same carboxylate coligands in the μ_2 -pyz Cu^{II} systems. Magnetic properties of **III-1** and **III-5** reveal weak ferromagnetic and weak antiferromagnetic spin exchange interactions between adjacent Cu^{II} ions *via* μ_2 -syn-anti carboxylates and μ_2 -ampyz with the spin exchange parameters of $J_{\text{inter}}/k = +6.9$ K and $J_{\text{intra}}/k = -2.3$ K, for **III-1** and $J_{\text{inter}}/k = +7.4$ K and $J_{\text{intra}}/k = -2.2$ K for **III-5**, respectively. Magnetic behaviors of **III-2-4** exhibit very strong antiferromagnetic interactions *via* four μ_2 -syn-syn carboxylates bridging between Cu^{II} ions which is well-known for the classical paddle-wheel Cu^{II} complexes.

Compounds **IV-1-3** are isomorphous series. Monomeric complex units $[\text{M}(\text{H}_2\text{O})_4(\text{ampyz})_2]^{2+}$ are assembled by intermolecular hydrogen bonding and π - π stacking *via* ampyz moieties to build 2D sheets. These layers are linked by intermolecular hydrogen bonding *via* ampyz ligand, $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ unit, sulfate anion and lattice and coordinated water molecules to stabilize 3D supramolecular structure. Whereas **IV-4** shows a 2D coordination network where the sulfato connector and the bridging ampyz link Cd^{II} ions. Lattice water molecules are filled in between the layers *via* the hydrogen bonds stabilizing 3D supramolecular network of **IV-4**. Interestingly, compounds **IV-1-3** exhibit water-induced reversible crystal-to-amorphous transformations with chromotropism and compound **IV-4** also shows water-induced reversible structural phase transformation confirmed by spectroscopic techniques, elemental analyses, TGA, and XRPD. These results demonstrate the significant role between coordination bridges and weaker intermolecular interactions for the structural conversion even though **IV-1-3** are lack of coordination bridges for maintenance of their structures, however, the weak intermolecular interactions, especially hydrogen bonding, play a key role to the recovery of the crystalline phase. Moreover, the selective methanol accommodation with chromotropism in dehydrated **IV-1A** is observed which could be attributed to the proper size of methanol and weak host-guest interactions causing the changes of the *d*-orbital energy in distorted octahedral geometry. However the **IV-1A·MeOH** is unstable in air. The original crystalline phase **IV-1''** is easily recovered after the evaporation of methanol at room temperature which is indication of high selective recognition of **IV-1A** to water molecules. This work is beneficial to expand the field of the crystal engineering by controlling the weak interaction of coordination moieties.

By utilizing a flexible coligand 1,2-bis(2-pyridyl)ethylene (2,2'-bpe), two new azido-bridged cobalt(II) coordination networks **V-1** and **V-2** have been obtained. Compound **V-1** shows uncommon 1D chain comprised of double EO azido bridged five- and six-coordinated Co^{II} geometries in a unique $(-5-5-6-)_n$ sequence of the coordination number. The 2,2'-bpe acts as terminal co-ligand and uncoordination molecule in the crystal lattice. Moreover the adjacent 1D chain is assembled by C-H $\cdots\pi$ interactions and the intermolecular hydrogen bonding between uncoordination 2,2'-bpe and coordination water molecules building 2D layer. Whereas compound **V-2** is 2D coordination network containing the alternating double EO and double EE bridging modes of azides and ditopic 2,2'-bpe bridges. The magnetic

investigation of **V-1** reveals dominant intrachain ferromagnetic interactions with double EO azide-bridge and weak interchain antiferromagnetic interactions with overall metamagnetic behavior having magnetic ordering at 6 K. The magnetic behavior of **V-2** shows spin-canted antiferromagnetism below T_N of 12 K. In case of the versatile ampyz spacer, two high dimensional cobalt(II) azido inorganic-organic hybrid frameworks, which contain similarly alternating double EO and double EE azido-bridged Co^{II} chain were obtained from the different preparative methods. The high symmetric square-grid structure of **V-3** from layer diffusion method which consists of *trans*-ampyz bridging between octahedral Co^{II} centers in axial positions, presents the coexistence of a big spin canting angle and metamagnetism below 10 K. The canting angle is estimated to be 7.7° and the critical field for metamagnetic phase transition is ≈ 600 Oe at 2 K. The interlayer hydrogen bonding between amino group of ampyz spacer and symmetric double EE azido bridges plays an important role on the field-induce metamagnetic phase transition. The spin canting of **V-3** could be attributed to the significant antisymmetric exchange arising from the structure phase transition at low temperature and the great role of magnetic anisotropy of Co^{II} ion. Whereas 3D framework containing *cis*-ampyz bridging among Co^{II} centers of **V-4** was synthesized from hydrothermal technique. It was crystallized in lower space group and exhibited only small spin-canted antiferromagnetism below 16 K. It is suggests that the large magnetic anisotropy in **V-4** might contribute a spin canting together with small antisymmetric coupling between Co^{II} ions, arising from a distortion in the crystal net at low temperature, which is frequently found in the related complexes containing the same bridging mode of azide. These results will provide the merit for future investigations and demonstrate the importance of the crystal engineering of inorganic-organic hybrid framework in the field of molecular-based magnetic materials.

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LIST OF ABBREVIATIONS

ampyz	2-aminopyrazine
bpy	4,4'-bipyridine
dpe	1,2-di(4-pyridyl)ethylene
MeOH	Methanol
EtOH	Ethanol
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EPR	Electron paramagnetic resonance
pyz	pyrazine
T	Tesla
G	Gauss
FC	field-cooled
SBU	secondary building unit
ZFC	zero-field cooled
kK	KiloKeyser (1000 cm ⁻¹)
χ_m	Molar magnetic susceptibility
J	exchange energy
h	Plank's constant
β, μ_B	Bohr magneton
N	Avogadro's number
k	Boltzmann constant
H	the magnetic field strength
g	Lande' splitting factor
θ	Weiss constant
α	canting angle

Part II

Metal-Organic Frameworks and Their Functions
Toward Dynamic Structural Transformation
with Chromotropism and Magnetism

Metal-Organic Frameworks and Their Functions Toward Dynamic Structural Transformation with Chromotropism and Magnetism

1. Introduction

A great interest of transition metal complex-assemblies in inorganic-organic hybrid framework materials has recently been devoted to the development of rational synthetic routes to novel one-, two- and three-dimensional crystal frameworks, due to their potential applications in many areas. The molecule-based crystal is a characteristic of the assemblage which is dissimilar to inorganic assemblage. This is ascribed to a variety of coordination geometries of building blocks and the coordination numbers. Furthermore, the functionality of organic and inorganic ligands as a connector is essential for the formation of coordination network structures and the intermolecular interactions involving hydrogen bonding and π - π stacking which all are necessary to rational design of crystal frameworks together with the fine tuning their functional properties.

The work described in this topic was started with the intention of developing in a field of crystal engineering of inorganic-organic hybrid framework materials as well as expanding and learning the insights of fundamental molecule-based magnetic materials. The three main purposes of this work are described in the terms of “*structural diversity*”, “*structural dynamic*” and “*magnetic ordering*”. In the diversity of structural frameworks the influences of flexibility, functional group and versatile coordination modes of bridging ligands on the structural architectures are demonstrated in all compounds. In addition, the effects of metal ions and reaction temperature are also observed. In the feature of structural dynamic behaviors, by employing the versatile aminopyrazine spacer with sulfate anion, the reversible structural phase transformations with chromotropism in the characteristic 3rd generation flexible metal-supramolecular frameworks and coordination polymer are demonstrated, in which all compounds are supported by weak intermolecular interactions, such as hydrogen bonds, π - π stacking, and electrostatic forces. It is interesting that these phenomena are not common in non-coordination supramolecular systems. Furthermore, this behavior with the color change is also found in the 1D and 2D coordination polymers of the Co(II)-3,5-pyridinedicarboxylate system. Lastly, the crystal engineering of molecular magnetism which aims to control the spins in molecules and molecular assemblies has been developed. The final part mainly deals with the investigation of long-range magnetic orders in extended inorganic hybrids of cobalt(II) azido complexes. This part various interesting molecule-based magnetic phenomena (ferromagnetism, canted antiferromagnetism and metamagnetism) in highly anisotropic Co^{II} complexes along with their diversity of structural dimensions and coordination geometries are studied.

First part, the structural characterization and magnetic measurement in series of Cu^{II} coordination polymers containing 2-aminopyrazine (ampyz) and different carboxylato ligands are presented. It has been known that crystal engineering is attracting much interest from both the synthetic routes and the state of art in structural design. This chapter focuses on the structural diversity of Cu^{II} coordination polymers caused by the effect of functional group (amine) in ampyz spacer and versatile coordination modes of carboxylate bridges. No compounds in this system have been reported as yet. Thus five new Cu^{II} coordination networks containing both μ_2 -ampyz and the bridging carboxylate anion, *i.e.* 2D layer [Cu(ampyz)(O₂CH)₂]_n (**III-1**), 1D chains [Cu₂(ampyz)(O₂C₂H₃)₄]_n (**III-2**) and [Cu₂(ampyz)(O₂C₃H₅)₄]_n (**III-3**), 2D layer [Cu₂(ampyz)(O₄C₄H₄)₂](H₂O)_n (**III-4**), 2D layer [Cu(ampyz)(O₄C₃H₂)₂](H₂O)_{2n} (**III-5**) were reported (when HCO₂⁻ = formate, CH₃CO₂⁻ = acetate, C₂H₅CO₂⁻ = propionate, CH₂C₂O₄²⁻ = malonate and C₂H₄C₂O₄²⁻ = succinate anions). The structures of all compounds are compared with compounds containing the same carboxylate ligands in the μ_2 -pyrazine Cu^{II} systems. The EPR and magnetic measurements at low temperature of all the compounds have also been investigated and briefly discussed.

The second deals with the structural dynamics with chromotropism in metal supramolecular frameworks and coordination polymer. Since the role of many interaction sites of ampyz spacer was observed from previous chapter and the structural diversity in metal sulfate chemistry was known, therefore, series of metal(II) supramolecular structures and Cd^{II} coordination polymer containing ampyz and sulfate anions, which exhibit significant chromotropism associated with reversible water-induced structural phase transformations, have been studied. The effect of 3d- and 4d- transition metal centers on the molecular assemblies were observed, leading to the differences in structural dynamics behaviors. Many techniques (thermal analysis, X-ray powder diffraction, elemental analysis, IR and UV-vis spectroscopic techniques) have been employed to study the reversible structural phase transformations. In this series three new supramolecular metal-coordination architectures [M(H₂O)₄(ampyz)₂][M(H₂O)₆](SO₄)₂(H₂O)₂ (M = Co (**IV-1**), Fe (**IV-2**), and mixed Co/Fe (**IV-3**) and a Cd^{II} coordination polymer [Cd(ampyz)(H₂O)₂(SO₄)_n](H₂O)_n (**IV-4**) are demonstrated. In addition this behavior with the color change is also found in the 1D and 2D coordination polymers of the Co(II)-3,5-pyridinedicarboxylate system. The 3,5-pyridinedicarboxylate (pydc) is chosen as an organic spacer since this molecule has proven to be able to establish a bridge between metal centers. Therefore [Co(pydc)(H₂O)₂]_n (**IV-5**) and [Co(pydc)(H₂O)₄]_n(H₂O)_n (**IV-6**), (pydc = 3,5-pyridinedicarboxylate) are reported, which exhibit significant chromotropism associated with water-induced crystal-to-amorphous phase transformations.

Last part demonstrates the importance of the crystal engineering of inorganic-organic hybrid framework in the field of molecular-based magnetic materials. The structural diversity and the comprehensive study of long-range magnetic orders of four new azido cobalt(II) extended inorganic hybrids are described, which show various structural dimensionalities from 1D chain, 2D layer to 3D framework structures. In this chapter, two compound systems are divided according to the organic coligands. The former shows two

azido Co^{II} complexes with 1,2-bis(2-pyridyl)ethylene (2,2'-bpe), *i.e.* 1D chain $[\text{Co}_3(\text{N}_3)_6(\text{OH}_2)_2(2,2'\text{-bpe})_2]_n(2,2'\text{-bpe})_n$ (**V-1**) and 2D layer $[\text{Co}(\text{N}_3)_2(2,2'\text{-bpe})]_n$ (**V-2**). This work is the first report of azido complexes containing 2,2'-bpe flexible coligand. The last part presents two azido Co^{II} complexes with ampyz spacer, *i.e.* 2D sheet $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (**V-3**) and 3D framework $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (**V-4**). It is interesting that they were obtained from the different preparative methods and similarly contain alternating double EO and double EE azido-bridged Co^{II} chain. The magnetic properties of **V-1-4** are discussed and compared with the related azido complex systems.

2. Experimental

2.1 Series of copper(II) coordination polymers containing ampyz and different carboxylato

ligands

[Cu(ampyz)(O₂CH)₂]_n (III-1). An ethanolic solution (5 mL) of ampyz (0.5 mmol, 48 mg) was carefully layered on an aqueous solution (5 mL) of $\text{Cu}(\text{HCO}_2)_2$ (0.5 mmol, 76 mg) with 0.1 mL (2.6 mmol) of formic acid in 20 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After four days, blue-green rod-shaped crystals of **III-1** were obtained. Yield 84 mg (68%) based on copper salt. Anal. Calcd for $\text{CuC}_6\text{H}_7\text{N}_3\text{O}_4$: C, 28.98; H, 2.82; N, 16.90 %. Found: C, 28.81; H, 2.91; N, 16.89 %. IR (KBr, cm^{-1}): 3364w, 3127w, 1639m, 1587s, 1329m, 1236w, 1076w, 1030w, 811w, 572w. UV-vis (diffuse reflectance, cm^{-1}): 15670.

[Cu₂(ampyz)(O₂C₂H₃)₄]_n (III-2) was synthesized similarly to compound **III-1** using $\text{Cu}(\text{CH}_3\text{CO}_2)_2$ (0.5 mmol, 91 mg) instead of $\text{Cu}(\text{HCO}_2)_2$ with 0.1 mL (1.7 mmol) of acetic acid. After three days, green rod-shaped crystals of **III-2** were obtained. Yield 190 mg (83%) based on copper salt. Anal. Calcd for $\text{Cu}_2\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_8$: C, 31.45; H, 3.71; N, 9.17 %. Found: C, 31.33; H, 3.77; N, 9.18 %. IR (KBr, cm^{-1}): 3387w, 3342w, 3224w, 1655m, 1608s, 1435m, 1349w, 1219w, 1017w, 685w, 628w. UV-vis (diffuse reflectance, cm^{-1}): 14270.

[Cu₂(ampyz)(O₂C₃H₅)₄]_n (III-3). An ethanolic solution (5 mL) of ampyz (0.5 mmol, 48 mg) was added to a stirring 5 mL of aqueous solution containing $\text{Cu}(\text{OH})_2$ (0.5 mmol, 49 mg) and propionic acid (1 mL, 13 mmol). The resulted solution was stirred at 50 °C for an hour and then a small amount of precipitates was filtered off. The green filtrate was allowed to stand for four days at room temperature to yield green rod-shaped crystals of **III-3**. Yield 132 mg (51%) based on copper salt. Anal. Calcd for $\text{Cu}_2\text{C}_{16}\text{H}_{25}\text{N}_3\text{O}_8$: C, 37.36; H, 4.86; N, 8.17 %. Found: C, 37.13; H, 4.96; N, 8.17 %. IR (KBr, cm^{-1}): 3427w, 3229w, 1645m, 1602s, 1541w, 1427m, 1381w, 1301w, 1217w, 1070w, 1018w, 813w. UV-vis (diffuse reflectance, cm^{-1}): 14280.

[Cu₂(ampyz)(O₄C₄H₄)₂]_n(H₂O)_n (III-4). An ethanolic solution (3 mL) of ampyz (0.5 mmol, 48 mg) was carefully layered on a solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 mmol, 121 mg) and succinic acid (0.5 mmol, 59 mg) in a mixture of water (4 mL) and ethanol (1 mL). The vial was sealed and allowed to stand

undisturbed at room temperature. After four days, blue-green rod-shaped crystals of **III-4** were obtained. Yield 79 mg (34%) based on copper salt. Anal. Calcd for $\text{Cu}_2\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_9$: C, 30.52; H, 3.18; N, 8.90 %. Found: C, 30.68; H, 3.32; N, 8.85 %. IR (KBr, cm^{-1}): 3368br, 3172w, 1624s, 1544w, 1428s, 1403w, 1301w, 1219w, 1070w, 1021w, 577w. UV-vis (diffuse reflectance, cm^{-1}): 14450.

[Cu(ampyz)(O₄C₃H₂)_n(H₂O)_{2n} (III-5) was synthesized similarly to compound **III-4** using disodium malonate monohydrate (0.5 mmol, 83 mg) instead of succinic acid. After four days, green rod-shaped crystals of **III-5** were obtained. Yield 44 mg (15%) based on copper salt. Anal. Calcd for $\text{Cu}_2\text{C}_{14}\text{H}_{22}\text{N}_6\text{O}_{12}$: C, 28.34; H, 3.74; N, 14.16 %. Found: C, 29.06; H, 3.02; N, 14.45 %. The microanalysis is slightly deviated. Presumably this is from the loss of solvent. IR (KBr, cm^{-1}): 3342br, 3220w, 1665m, 1578s, 1547m, 1421m, 1362m, 1270w, 1229w, 1081w, 1031w, 810w, 744w. UV-vis (diffuse reflectance, cm^{-1}): 15675.

2.2 Series of metal(II) supramolecular frameworks containing ampyz and sulfate anions

[Co(H₂O)₄(ampyz)₂][Co(H₂O)₆](SO₄)₂(H₂O)₂ (IV-1). An ethanolic solution (5 mL) of ampyz (1.0 mmol, 96 mg) was carefully layered on an aqueous solution (5 mL) of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mmol, 141 mg) in a glass vial (20 mL). This vial was sealed and allowed to stand undisturbed at room temperature. After four days, orange crystals of **IV-1** were obtained. Yield 92 mg (26%) based on metal salt. Anal. Calcd for $\text{Co}_2\text{C}_8\text{H}_{34}\text{N}_6\text{O}_{20}\text{S}_2$: C, 13.41; H, 4.78; N, 11.73%. Found: C, 13.48; H, 4.39; N, 11.79%. IR (KBr, cm^{-1}): 3450s, 3335s, 3257s, 1644m, 1603w, 1540m, 1444m, 1216w, 1108s, 1074s, 1022m, 983w, 825w, 642m. UV-vis (diffuse reflectance, cm^{-1}): 31000, 22300, 19800, less than 9000.

[Fe(H₂O)₄(ampyz)₂][Fe(H₂O)₆](SO₄)₂(H₂O)₂ (IV-2) was synthesized in a similar manner to that of compound **IV-1** by using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mmol, 139 mg) instead. After four days, yellow crystals of **IV-2** were obtained. Yield 80 mg (23%) based on metal salt. Anal. Calcd for $\text{Fe}_2\text{C}_8\text{H}_{34}\text{N}_6\text{O}_{20}\text{S}_2$: C, 13.53; H, 4.83; N, 11.83%. Found: C, 13.49; H, 4.41; N, 11.84%. IR (KBr, cm^{-1}): 3451s, 3335s, 3255s, 1645m, 1602w, 1540m, 1444m, 1216w, 1107s, 1074s, 1021m, 982w, 825w, 655m. UV-vis (diffuse reflectance, cm^{-1}): 29000, 24500sh, 11700.

[Co(H₂O)₄(ampyz)₂][Fe(H₂O)₆](SO₄)₂(H₂O)₂ (IV-3) was synthesized in a similar manner to that of compound **IV-1** by using $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (0.25 mmol, 70 mg) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.25 mmol, 70 mg) instead. After four days, yellowish orange crystals of **IV-3** were obtained. Yield 72 mg (20%) based on metal salt. Anal. Calcd for $\text{CoFeC}_8\text{H}_{34}\text{N}_6\text{O}_{20}\text{S}_2$: C, 13.47; H, 4.80; N, 11.78%. Found: C, 13.48; H, 4.28; N, 11.80%. IR (KBr, cm^{-1}): 3450s, 3337s, 3257s, 1644m, 1540m, 1444w, 1216w, 1109s, 1075s, 1022m, 982w, 824w, 655m. UV-vis (diffuse reflectance, cm^{-1}): 31600, 24300sh, 19200sh, 11100br.

[Cd(ampyz)(H₂O)₂(SO₄)_n(H₂O)_n (IV-4) was synthesized in a similar manner to that of compound **IV-1** by using $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ (0.5 mmol, 385 mg) instead. After four days, colorless crystals of **IV-4** were obtained. Yield 90 mg (53%) based on metal salt. Anal. Calcd for $\text{CdC}_4\text{H}_{10}\text{N}_3\text{O}_6\text{S}$: C, 14.10; H, 2.96; N,

12.34%. Found: C, 14.09; H, 2.34; N, 12.33%. IR (KBr, cm^{-1}): 3426m, 3328m, 3223m, 1634m, 1542m, 1474w, 1444m, 1360w, 1327w, 1218m, 1114s, 1075m, 1017m, 814w, 617s. UV-vis (diffuse reflectance, cm^{-1}): 27700.

2.3 Co(II) 3,5-Pyridinedicarboxylate Frameworks

[Co(pydc)(H₂O)₂]_n (IV-5)

A methanol solution (1 mL) of Co(NO₃)₆·6H₂O (0.2 mmol, 58 mg) was carefully layered on a mixed DMF/H₂O solution (2 mL) of H₂pydc (0.1 mmol, 17 mg) and KOH (0.4 mmol, 23 mg) in a glass tube. This tube was sealed and allowed to stand undisturbed at room temperature. After three weeks, deep pink rod-shaped crystals of **1** were obtained. Yield: 76 mg (77%) based on cobalt salt. Anal. Calcd for CoC₇H₇NO₆: C, 32.33; H, 2.71; N, 5.39%. Found: C, 32.24; H, 2.42; N, 5.78 %. IR (KBr, cm^{-1}): 3316m, 3110m, 1615m, 1557s, 1456m, 1439m, 1401w, 1128w, 1034w, 852w, 763m, 753m, 589m. UV-vis (diffuse reflectance, cm^{-1}): 34 100, 19 220, 16 610sh, 11 780, less than 9 000.

[Co(pydc)(H₂O)₄]_n(H₂O)_n (IV-6)

An aqueous solution (5 mL) of Co(NO₃)₆·6H₂O (1 mmol, 291 mg) was carefully layered on a DMF solution (5 mL) of H₂pydc (0.5 mmol, 84 mg) in a glass vial (15 mL). This vial was sealed and allowed to stand undisturbed at room temperature. After two weeks, orange crystals of **2** were obtained. Yield: 318 mg (85%) based on cobalt salt. Anal. Calcd for CoC₇H₁₃NO₉: C, 26.77; H, 4.17; N, 4.46%. Found: C, 26.78; H, 4.01; N, 4.52%. IR (KBr, cm^{-1}): 3346m, 3203m, 1606s, 1557s, 1445w, 1403m, 1381m, 1125w, 832w, 772m, 737m, 619w. UV-vis (diffuse reflectance, cm^{-1}): 33 910, 20 270, less than 9 000.

2.3. Series of azido cobalt(II) hybrid frameworks (Compounds V-1-4)

[Co₃(N₃)₆(OH₂)₂(2,2'-bpe)₂]_n(2,2'-bpe)_n (V-1) and [Co(N₃)₂(2,2'-bpe)]_n (V-2). A solution containing CoCl₂·6H₂O (0.5 mmol, 119 mg) and 2,2'-bpe (0.5 mmol, 91mg) in a mixture of water (2 mL) and ethanol (2 mL) was carefully layered on an aqueous solution (2 mL) of NaN₃ (1 mmol, 65 mg) in 18 mL of glass vial. The vial was sealed and allowed to stand undisturbed at room temperature. After five days, long blue rod-shaped crystals of **V-1** and small pink square-shaped crystals of **V-2** were obtained. These crystals were manually separated, washed with water, and dried in air. Yield for **V-1**: 26 mg (5%) based on metal salt. Anal. Calcd for Co₃C₃₆H₃₄N₂₄O₂: C, 42.74; H, 3.39; N, 33.23%. Found: C, 42.49; H, 3.10; N, 32.98%. IR (KBr, cm^{-1}): 3200br, 2089vs, 2050m, 1592m, 1479m, 1296m, 1158w, 974m, 780m. UV-vis (diffuse reflectance, cm^{-1}): 18500sh, 16500, 12500sh, 9800. Yield for **V-2**: 56 mg (34%) based on metal salt. Anal. Calcd for CoC₁₂H₁₀N₈: C, 44.32; H, 3.10; N, 34.46%. Found: C, 44.04; H, 2.98; N, 34.51%. IR (KBr, cm^{-1}): 3397w, 3091w, 2097vs, 2072vs, 1599m, 1480m, 1298w, 1160m, 970m, 779m, 743m, 542w. UV-vis (diffuse reflectance, cm^{-1}): 18000, 16500, less than 9000. The single-crystals of **V-2** were prepared in a U-shaped tube. An aqueous solution (2 mL) of NaN₃ (1 mmol) was filled into the one branch of U-tube that contains distilled water 1 mL. Another branch was filled with a solution containing

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and 2,2'-bpe (0.5 mmol) in a mixture of water (1 mL) and ethanol (2 mL). After one week, the suitable single-crystals of **V-2** for X-ray diffraction study were obtained.

2D layer of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (V-3). A mixture solution of water (1 mL) and ethanol (2 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 145 mg) was carefully layered on an aqueous solution (3 mL) of NaN_3 (1 mmol, 65 mg) in a glass vial (20 mL). Then an ethanolic solution (3 mL) of ampyz (1 mmol, 95 mg) was layered on this mixture. The vial was sealed and allowed to stand undisturbed at room temperature. After one week, orange rectangular crystals of **V-3** were obtained and then washed with water and filtered. Yield 36 mg (30%) based on metal salt. Anal. Calcd for $\text{CoC}_4\text{H}_5\text{N}_9$: C, 20.18; H, 2.12; N, 52.95%. Found: C, 20.62; H, 2.05; N, 53.27%. IR (KBr, cm^{-1}): 3407m, 3326m, 2100vs, 2080vs, 1629m, 1541m, 1443m, 1354w, 1298w, 1220m, 1079w, 1025m, 804m. UV-vis (diffuse reflectance, cm^{-1}): 18400, less than 9000. The single-crystals of **V-3** were prepared in a U-shaped tube. An ethanolic solution (1 mL) of ampyz (1 mmol) was filled into the one branch of U-tube that contains distilled water (1 mL). Another branch was filled with an aqueous solution (1 mL) containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and NaN_3 (1 mmol). After one week, the suitable single-crystals of **V-3** for X-ray diffraction study were obtained.

3D framework of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (V-4). A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 145 mg), NaN_3 (1 mmol, 65 mg) and ampyz (1 mmol, 95 mg) in water (2 mL) and ethanol (2 mL) was sealed in a Pyrex tube (7 mL), then heated to 90 °C (temperature increase rate of 18°C/min), allowed to stay for 24 h, and cooled to 30°C (temperature decrease rate of 0.04°C/min). The red-orange polygonal crystals of **V-4** were obtained in a major phase together with unidentified purple powder phase. The crystals were washed with water and filtered to give pure crystals of **V-4**. Yield 53 mg (45%) based on metal salt. Anal. Calcd for $\text{CoC}_4\text{H}_5\text{N}_9$: C, 20.18; H, 2.12; N, 52.95%. Found: C, 19.80; H, 2.15; N, 52.00%. IR (KBr, cm^{-1}): 3415m, 3307m, 2105vs, 2068vs, 1624m, 1540m, 1438m, 1322w, 1298w, 1218m, 1026w, 821w. UV-vis (diffuse reflectance, cm^{-1}): 18400, 9300.

3. Results and Discussion

3.1 Structural diversity and magnetic properties of copper(II) coordination polymers containing aminopyrazine and different carboxylato bridges

The field of coordination polymers has been extensively investigated over the past few decades with a focus on functional material research and crystal engineering. In material research, the coordination networks with interesting properties in areas such as molecular adsorption, catalysis, photoluminescence, magnetism and so on, are constructed for fine-tuning the properties and creating new functional materials.^[1-7] On the other hand, crystal engineering is attracting interest from both the synthetic routes and the art of structural design.^[8-14] One of the challenges in this field is to forecast the crystal structure from the building units. It is well-known that the chemistry of metal carboxylates shows various structural diversities beginning from a simple mononuclear complex to 3D frameworks with functional properties.^[15-18] This

diversity results from the fact that the carboxylate groups can coordinate metal centers in various ways, such as monodentate, chelate, monatomic bridge, bridging bi- and tridentate, and also less common multiple bridges.^[18-21] Therefore, the combination of metal carboxylates and other coligands, either bridging or terminal coligands, has a large potential to construct novel coordination networks. Consequently, this field has become a popular research area in recent decades.^[15, 22-24]

The short rigid rodlike spacer pyrazine (pyz) is a *N,N'*-ditopic diimine which is widely used for constructing many metal-organic frameworks.^[8, 25-27] It is well known that the pyz spacer is a good electron transfer agent in the superexchange pathways between connected metal centers showing antiferromagnetic routes. Several compounds with mixed pyz spacer ligands and metal carboxylates exhibiting various structural topologies together with interesting magnetic phenomena have been extensively investigated.^[28-33] With Cu^{II} ion, both pyz and carboxylates play a key role for building Cu^{II} coordination polymers, and interesting compounds have been observed. For instance, the 2D layered structure of [Cu(HCO₂)(NO₃)(pyz)]_n presents a long-range magnetic ordering below 3.7 K,^[28] while [Cu₂(pyz)(O₄C₃H₂)₂]_n(H₂O)_{2n} (in which H₂C₃O₄²⁻ is the malonate anion) shows a unique 3D framework displaying metamagnetism.^[29, 30]

The ligand 2-aminopyrazine (ampyz) is a substituted pyz containing an electron withdrawing amine group attached at the pyz ring and it also effectively acts as an organic spacer in many metal-organic frameworks.^[34-37] However, no compounds containing both the ampyz spacer and bridging carboxylate groups have been reported as yet. Consequently, the present work demonstrates the use of ampyz as a rigid ditopic spacer in combination with either mono- or dicarboxylate anions. Formate (HCO₂⁻), acetate (CH₃CO₂⁻), propionate (C₂H₅CO₂⁻), malonate (CH₂C₂O₄²⁻), and succinate (C₂H₄C₂O₄²⁻) anions have been used to construct a variety of Cu^{II} coordination polymers.

3.1.1 General observations and spectroscopic characterizations

In the present work, reaction of copper(II) and carboxylate anion with ampyz in a mixture of ethanol and aqueous media gives various copper(II) coordination polymers containing ampyz spacer together with carboxylato bridges. The different types of carboxylates can lead to structural diversities due to their coordination modes, steric effect, and flexibility. For the simplest carboxylate with the smallest steric effect, formate anion gives a 2D wavy sheet structure, whereas the larger sterically crowded carboxylates, acetate and propionate anions, give a polymeric chain, constructed from paddle-wheel CuNO₄ chromophores. On the other hand, the dicarboxylates can provide more opportunity to bind with metal centers in particular the flexible dicarboxylates, such as malonate and succinate anions mostly constructing unpredictable crystal frameworks.^[29, 38-41] For this study, a 2D layer which contains the double-stranded chain of paddle-wheel units is built from succinate anions as well as 2D stairlike layer built from malonate anions. The description of the structures **III-1-5** is discussed in the following topics, together with the

comparison with the bridging pyrazine spacer in the similar Cu^{II} systems with their spectroscopic and magnetic properties.

The solid-state IR spectra of **III-1-5** in the region $4000\text{--}450\text{ cm}^{-1}$ exhibit characteristic bands for carboxylates and ampyz ligand (Figure 1). Compounds **III-1-3** show two narrow weak bands in the region $3400\text{--}3300\text{ cm}^{-1}$ and $3100\text{--}3200\text{ cm}^{-1}$, which can be assigned to asymmetric and symmetric stretching of the primary amine in the ampyz ligand. Compounds **III-4** and **III-5** show broadbands in the region $3100\text{--}3400\text{ cm}^{-1}$ due to the bands overlapping of the $\nu(\text{O--H})$ of water molecule. The NH_2 scissoring mode shows medium bands around $1640\text{--}1660\text{ cm}^{-1}$ which overlap with the $\nu_{\text{as}}(\text{OCO})$ of carboxylate appearing strong bands in the range of $1620\text{--}1570\text{ cm}^{-1}$. The $\nu_{\text{s}}(\text{OCO})$ shows medium bands in the region $1320\text{--}1430\text{ cm}^{-1}$. The weak, sharp band around $1070\text{--}1080\text{ cm}^{-1}$ can be assigned to the $\nu(\text{C--N})$ of ampyz. The solid-state UV-visible diffuse reflectance spectra (Figure 2) show a single broadband around $14,270\text{--}14,450\text{ cm}^{-1}$ for compounds **III-2-4**, which are in agreement with those of common Cu^{II} paddle-wheel complexes with a square-pyramidal geometry ($d_{xy}, d_{xz}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$ transition).^[42]

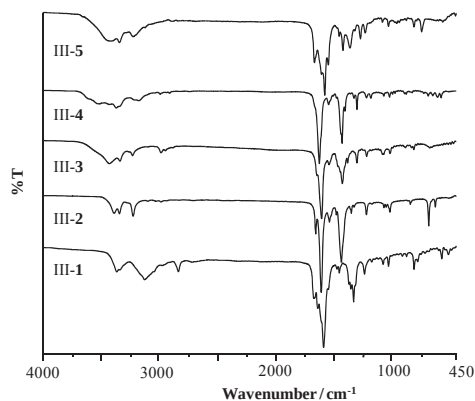


Figure 1 Infrared spectra for compounds **III-1-5**.

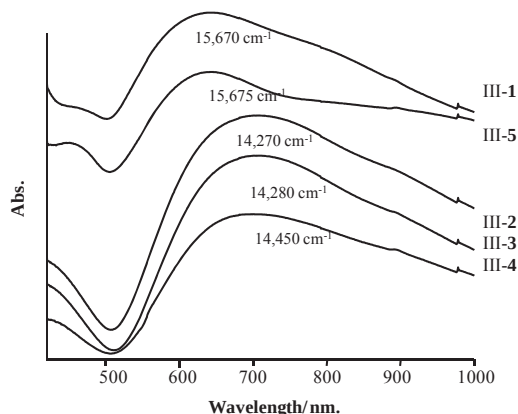


Figure 2 Solid-state UV-visible diffuse reflectance spectra for compounds **III-1-5**.

Compounds **III-1** and **III-5** show a single broadband at a higher energy, *i.e.* around 15,670 cm⁻¹, corresponding to the further structural distortion toward an elongated octahedral geometry with the sixth off-the-axis weakly interacting to Cu^{II} center. In fact these values of the transition energy (14,270 to 15,670 cm⁻¹) are all in the range usually found for the distorted square-pyramidal geometry of Cu^{II} centers ($d_{xy}, d_{xz}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$ transition).^[43]

3.1.2 Description of crystal structures

[Cu(ampyz)(O₂CH)₂]_n (**III-1**)

The coordination environment of the Cu^{II} center is shown in Figure 3. Each Cu^{II} ion is five-coordinated showing a distorted square-pyramidal CuN₂O₃ chromophore with a τ value of 0.011 ($\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramid).^[44] The equatorial plane around the copper atom is composed of two formate oxygen atoms (O1 and O3A) with the average Cu–O distance of 1.965(5) Å and two ampyz-nitrogen atoms with the Cu–N distances of 2.039(4) Å. The apical position is occupied by an oxygen from a formate bridge (Cu–O2' = 2.300(5) Å). The CuN₂O₂ square base is not perfectly planar with tetrahedral twists between the O1–Cu–N1 and O3A–Cu–N1' planes of 13.57°. The copper atoms are slightly shifted by 0.007 Å from the mean basal plane toward the apical position. This value is too small for the typically found square-pyramidal geometry which is attributed to the semicoordinated O2 atom of formate group weakly interacting to Cu center in off-the-axis position of an elongated octahedral geometry with the longest Cu–O2 distance of 2.718(5) Å.

The formate bridges exhibit a *syn,anti*- $\eta^1:\eta^1:\mu_2$ coordinative mode bridging between adjacent Cu^{II} centers along the *a* axis with Cu...Cu separations of 4.7807(10) Å resulting a wavy polymeric chain structure as shown in Figure 4(a). The ditopic ampyz spacers link the Cu–HCO₂–Cu wavy chains parallel to the *b* axis with Cu...Cu separation of 6.8558(6) Å *via* ampyz.

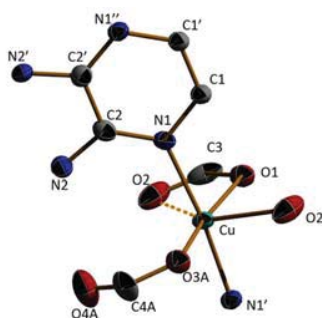


Figure 3 Asymmetric unit and atom labeling scheme of **III-1**. The ellipsoids are shown at 35% probability level, and the disordered O3B, C4B, O4B and hydrogen atoms are omitted for clarity. Both disordered positions of N2 are shown. The dashed line represents weak interaction in the off-the-axis position.

The N1–Cu–N1' angle slightly deviates from linearity (9.5°). Consequently, the wavy 2D network is constructed from μ_2 -HCO₂[−] and μ_2 -ampyz with the square grid dimension of ca. 4.781×6.856 Å in the *ab* plane (Figure 4(b)). In addition, the layer of **III-1** is stabilized by hydrogen bonding and π - π stacking interactions within the layer. The intralayer hydrogen bonds are built from the amine hydrogen of ampyz and two formate oxygen atoms forming a rhomboid hydrogen bonding array throughout the layer [N2H...O4Aⁱ = 2.25 Å (124°), N2...O4Aⁱ = 2.824(9) Å, (i) = *x*, 3/2−*y*, *z*; N2H...O3Aⁱ = 2.32 Å (134°), N2...O3Aⁱ = 2.979(9) Å, (i) = −1+*x*, *y*, *z*]. The lattice is further stabilized by π - π stacking between adjacent ampyz ligands merely overlaying at the edges of the rings with the separation of 3.632(3) Å.^[45]

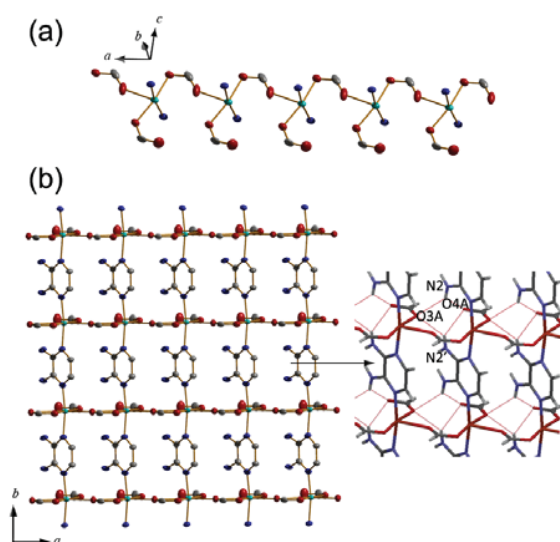


Figure 4 Segment of a wavy polymeric chain in **III-1** constructed from *syn-anti* formate bridges along *a* axis. Ampyz rings are omitted for the sake of clarity (a). Two-dimensional sheet structure of **III-1** in the *ab* plane; the inset presents the intralayered hydrogen bonds. Both disordered positions of amino group are shown. Cu atoms are represented in green, N in blue, O in red, and C in gray (b).

Interestingly, the crystal packing of these wavy sheets reveals the alternated ampyz arrangement in the *bc* plane (Figure 5), because of the 2₁-fold screw axis lined between the layers and the steric nature of ampyz ligands. Moreover, the interlayer hydrogen bonding between the hydrogen atoms of ampyz and the terminal formate oxygen atoms of the adjacent layer [N2H...O4Aⁱ = 2.06 Å (152°), N2...O4Aⁱ = 2.848(10) Å, (i) = −*x*, 1−*y*, −*z*] stabilizes the double sheet of **III-1** with the closest interlayer Cu...Cu separation of 6.7695(9) Å (inset of Figure 5).

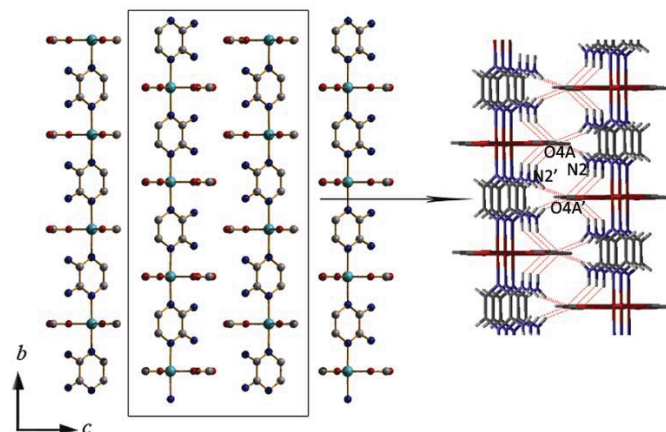


Figure 5 Packing diagram of the sheets in **III-1** showing the alternating ampyz ring arrangements in the *bc* plane. The inset shows hydrogen bonds stabilizing the double sheets of **III-1**. Both disordered positions of amino group are shown.

In comparison with mixed bridging pyrazine and formate in Cu^{II} complexes, the structure of compound **III-1** is close to the 2D sheet of $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$,^[28] which crystallizes in the orthorhombic space group (*Pnma*) with the coordinated nitrate (Figure 6), whereas **III-1** crystallizes in the monoclinic space group (*P2₁/m*) with a monodentate formate instead of a nitrate group. In contrast $[\text{Cu}(\text{HCO}_2)_2(\text{pyz})]_n$ ^[31] reveals a 3D framework which consists of tetragonally elongated CuN_2O_4 octahedra made up of four bridging formate anions and two neutral pyz ligands (Figure 7).

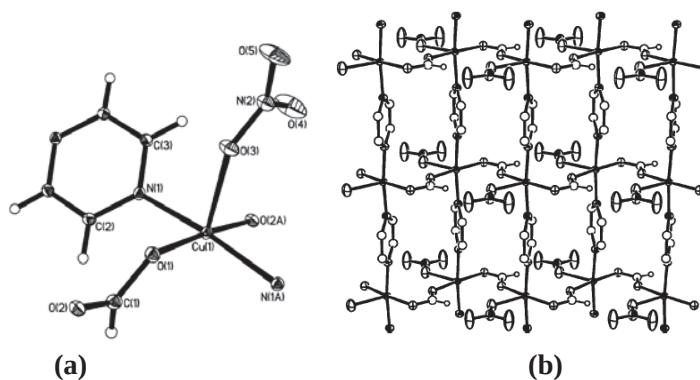


Figure 6 Crystal structure (a) and 2D corrugated layer of $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$ (b).^[28]

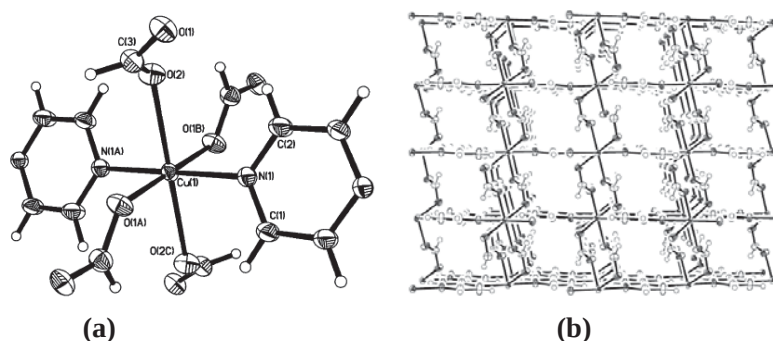


Figure 7 Crystal structure (a) and 3D scaffold structure of $[\text{Cu}(\text{HCO}_2)_2(\text{pyz})]_n$ (b).^[31]

$[\text{Cu}_2(\text{ampyz})(\text{O}_2\text{C}_2\text{H}_3)_4]_n$ (III-2) and $[\text{Cu}_2(\text{ampyz})(\text{O}_2\text{C}_3\text{H}_5)_4]_n$ (III-3)

Both compounds **III-2** and **III-3** consist of a polymeric chain structure built up from bridging ampyz spacers connecting the paddle-wheel units of $[\text{Cu}_2(\mu_2\text{-O}_2\text{C}_2\text{H}_3)_4]$ or $[\text{Cu}_2(\mu_2\text{-O}_2\text{C}_3\text{H}_5)_4]$ for **III-2** and **III-3**, respectively. Their structures with atom numbering scheme are shown in Figure 8. Each Cu^{II} ion is five-coordinate showing a distorted square pyramidal CuNO_4 chromophore with $\tau = 0.002$ (for **III-2**) and 0.004 (for **III-3**). The basal position of the square pyramid is occupied by four oxygen atoms from four different carboxylate groups with mean distance of 1.967(2) and 1.966(3) Å for **III-2** and **III-3**, respectively. The apical position is occupied by a nitrogen atom from ampyz with $\text{Cu-N} = 2.229(2)$ and 2.230(2) Å for **III-2** and **III-3**, respectively. The basal plane is nonplanar with tetrahedral twist of 16.59° for **III-2** and 16.89° for **III-3**. The copper atom lies 0.202 Å (for **III-2**) and 0.207 Å (for **III-3**) above the mean basal plane toward the axial site.

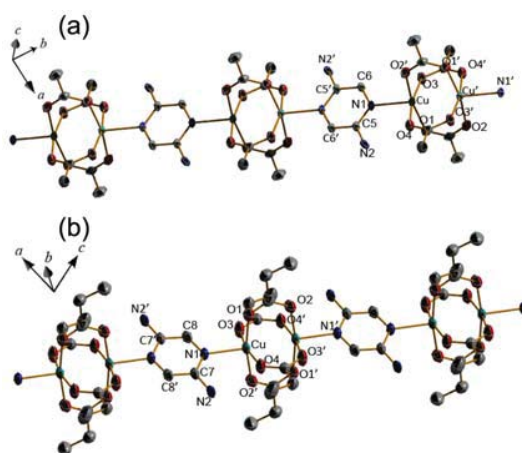


Figure 8 Part of a 1D chain structure of **III-2** (a) and **III-3** (b) with used atom labeling. The ellipsoids are shown at 35% probability level, and hydrogen atoms are omitted for clarity. Both disordered positions of N2 are shown.

Both acetate and propionate anion acts as a bidentate bridge in $\text{syn,syn-}\eta^1:\eta^1:\mu_2$ coordinative mode bridging between Cu^{II} centers forming a paddle-wheel secondary building unit (SBU). The Cu...Cu separation in each dinuclear unit is 2.6286(4) Å for **III-2** and 2.6322(7) Å for **III-3**, which indicates a metal-metal interaction, and it agrees well with those reported for Cu^{II} paddle-wheel complexes of acetate and propionate.^[42, 46, 47] The paddle-wheel SBUs are connected by μ_2 -ampyz giving rise to the polymeric chain structure with Cu...Cu separation *via* ampyz of 7.2377(3) and 7.2498(5) Å for **III-2** and **III-3**, respectively. In the packing motif (Figure 9), both 1D chains of **III-2** and **III-3** are assembled alternatively *via* hydrogen bonding between amine hydrogen of ampyz and a carboxylato oxygen [for **III-2**: $\text{N2H}\cdots\text{O4} = 1.96$ Å (159°), $\text{N2}\cdots\text{O4} = 2.774(4)$ Å; $\text{N2H}\cdots\text{O1}^i = 2.13$ Å (166°), $\text{N2}\cdots\text{O1}^i = 2.973(5)$ Å, (i) = $-x, 2 -y, 1 -z$; for **III-3**: $\text{N2H}\cdots\text{O4} = 2.12$ Å (146°), $\text{N2}\cdots\text{O4} = 2.875(6)$ Å; $\text{N2H}\cdots\text{O2}^i = 2.46$ Å (160°), $\text{N2}\cdots\text{O2}^i = 3.285(7)$ Å, (i) = $x, y, -1+z$] to construct the 2D sheets with the closest Cu...Cu interchain distance of 6.3693(4) Å for **III-2** and 6.9001(7) Å for **III-3** corresponding to the steric size of carboxylate groups. These assembled sheets of **III-2** or **III-3** are alternately arranged in a zigzag jigsaw-like motif to complete the overall solid-state structure, as shown in Figure 10.

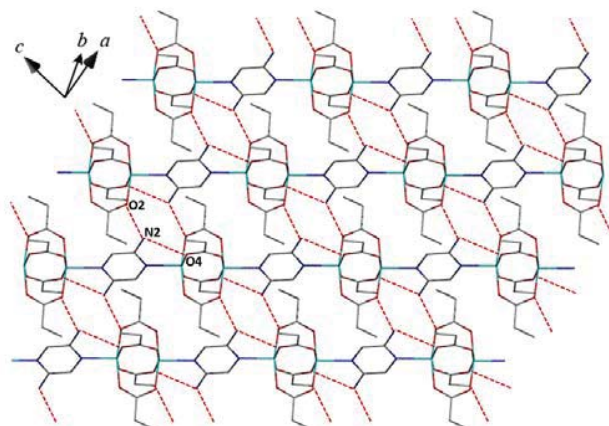


Figure 9 The 2D sheet formed by hydrogen bonding between the chains of **III-3**.

The copper paddle-wheel complexes have been investigated for a long time. The first 1D chain for the present system with a paddle-wheel SBU is $[\text{Cu}_2(\text{pyz})(\text{O}_2\text{C}_2\text{H}_3)_4]_n$ ^[46] and was reported in 2006.^[47] The polymeric chain of **III-2** is almost the same as the previously reported structure (Figure 11). However, their crystal systems, space groups and packing motifs are dissimilar due to the amine groups appending on pyz moieties leading to the different arrangement in the solid-state structure. Contrary to **III-3**, the first mixed pyz and propionate in $[\text{Cu}_4(\text{pro})_4(\text{CH}_3\text{O})_4(\text{pyz})]_n$ ^[48] gives rise to a 2D network as depicted in Figure 12. The distinctive structure is probably due to the higher steric effect of ampyz as compared to pyz. Therefore the paddle-wheel unit is possibly dominant leading to the 1D chain of **III-3**.

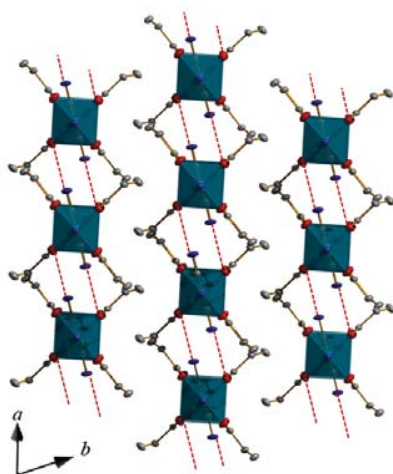


Figure 10 Packing diagram of the 2D sheets in **III-3** showing zigzag arrangement of layers in *ab* plane. The hydrogen bonding between H-donors and H-acceptors are shown in red broken lines, and the blue pyramids represent CuNO_4 chromophores. Both disordered positions of amino group are shown.

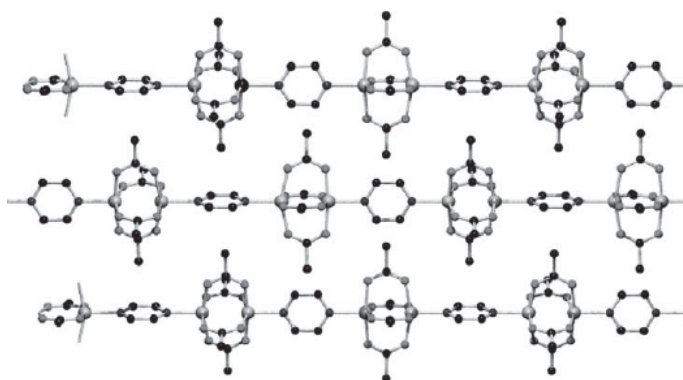
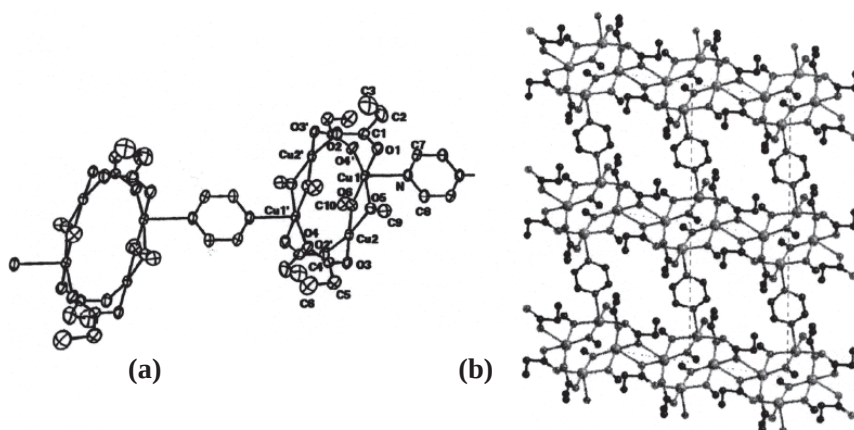


Figure 11 Packing diagram of reported $[\text{Cu}_2(\text{pyz})(\text{O}_2\text{C}_2\text{H}_3)_4]_n$.^[47]



[Cu₂(ampyz)(O₄C₄H₄)₂]_n(H₂O)_n (III-4)

The structure of **III-4** with its atom labeling scheme is shown in Figure 13. Each Cu^{II} ion is five-coordinate showing distorted square pyramidal CuNO₄ chromophore with $\tau = 0.003$. The basal position of the square pyramid is occupied by four oxygen atoms from four different bridging succinate groups with average distance of 1.964(3) Å. The nitrogen of ampyz occupies the axial position of the square pyramid with a Cu–N distance of 2.206(3) Å. The basal plane is nonplanar with tetrahedral twist of 17.40°. The copper atom lies 0.212 Å above the mean basal plane toward the apical position. Four succinate anions are bridging between the Cu^{II} centers in a *syn,syn*- $\eta^1:\eta^1:\mu_2$ coordinative mode of carboxylate forming a Cu^{II} paddle-wheel SBU. The Cu...Cu separation in each dinuclear unit is 2.6457(10) Å showing metal-metal bonding which is in good agreement with those reported for Cu^{II} paddle-wheel complexes of succinate.^[49] The succinate anion is a dicarboxylate containing two aliphatic carbons in the backbone. For **III-4**, the succinate acts as a tetradentate ligand connecting four adjacent Cu centers of the paddle-wheel SBU to form a double-stranded chain of a paddle-wheel unit, which reveals the repeating 14-membered ring of {Cu₂(C₂O₄)₂} with the cavity's dimension of ca. 6.594 × 5.880 Å. The closest Cu...Cu separation among the paddle wheel SBUs is 6.5942(9) Å. The conformation

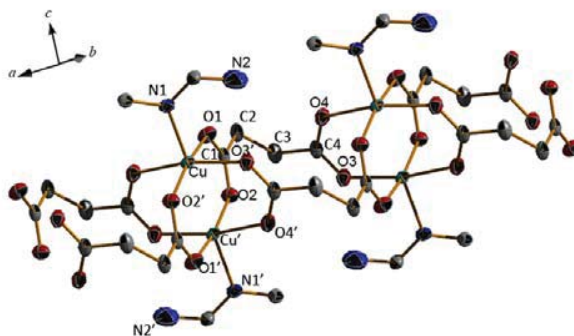


Figure 13 The double-stranded array of a paddle-wheel unit formed by four *syn-syn* succinate bridges of **III-4** with atom labels. The ellipsoids are shown at 35% probability level. The uncoordinated water molecule and the hydrogen atoms are omitted for clarity.

of the succinate group in **III-4** exhibits the *syn-anti* mode^[32] with a torsion angle of 69.88°, and the orientation of carboxylate moiety with respect to the carbon aliphatic backbone line generates angles of ca. 67.50° and 62.25°. Furthermore, these double-stranded chains are connected by ampyz spacers on an apical site of each paddle-wheel SBU with a Cu...Cu separation of 7.1951(6) Å *via* ampyz, giving rise to the 2D network together with uncoordinated water molecules filling on the upper and lower sites of the cavities (Figure 14(a)). The dimension of this cavity is about 6.594 × 7.195 Å.

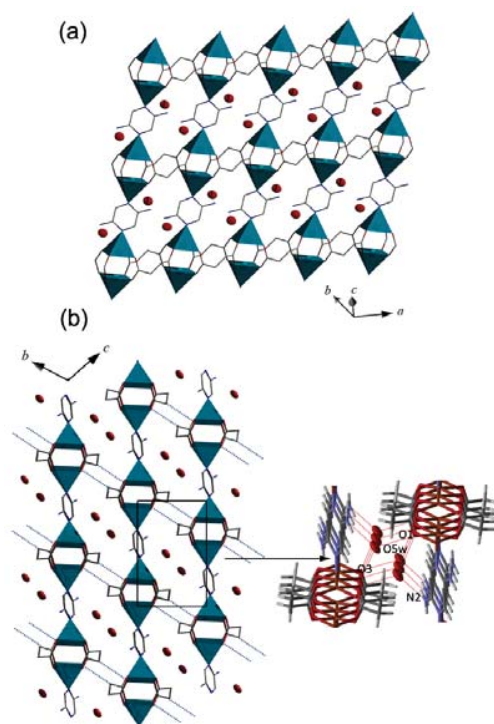


Figure 14 2D layer with uncoordinated water molecules filling up the windows of the sheet of **III-4**. (a) 3D packing structure of **III-4** formed by weak hydrogen bonding (blue dotted lines) between layers. The inset shows water molecules stabilizing the supramolecular network *via* hydrogen bonds. The blue pyramids are the CuNO₄ chromophores. Both disordered positions of amino group are shown (b).

In the molecular packing motif, each 2D layer of **III-4** is assembled *via* intermolecular weak hydrogen bonding between an aliphatic hydrogen of succinate and a bridging succinato oxygen of the adjacent layer [$\text{C3H}\cdots\text{O3}^i = 2.57 \text{ \AA}$ (147°), $\text{C3}\cdots\text{O3}^i = 3.431(6) \text{ \AA}$, ($i = -x, -1-y, -z$)] as shown in Figure 14(b). Moreover, the uncoordinated water molecules play an important role to stabilize the whole packing structure *via* hydrogen bonding between amine hydrogen of ampyz and water oxygen [$\text{N2H}\cdots\text{O5w}^i = 1.94 \text{ \AA}$ (150°), $\text{N2}\cdots\text{O5w}^i = 2.715(15) \text{ \AA}$, ($i = 1+x, y, z$)] and supposing *via* hydrogen bonding between succinato oxygen and water hydrogen with the $\text{O1}\cdots\text{O5w}$ and $\text{O3}\cdots\text{O5w}$ distances of $2.854(9) \text{ \AA}$ and $2.974(12) \text{ \AA}$, respectively. The neighboring $\text{O5w}\cdots\text{O5w}'$ distances are $2.972(16) \text{ \AA}$ indicative of normal hydrogen bonds. The closest $\text{Cu}\cdots\text{Cu}$ interlayer distance is $7.9690(8) \text{ \AA}$.

The comparison was made with known mixed bridging succinate-pyz complexes, like $[\text{Cd}_2(\text{O}_4\text{C}_4\text{H}_4)_2(\text{pyz})(\text{H}_2\text{O})]_n$ [32] which reveals a 2D infinite grid sheet containing a pentagonal bipyramidal chromophore. For the Cu^{II} system, the compound $[\text{Cu}_2(\text{O}_4\text{C}_4\text{H}_4)_2(\text{H}_2\text{O})_2]_n(\text{H}_2\text{O})_{2n}$ was obtained, being the

first example of double-stranded chain motif (Figure 15).^[49] The pyz only acts as the molecular template which is uncoordinated with Cu centers. In contrast, ampyz can incorporate in the network of **III-4** due to the maintenance of interlayer hydrogen bonding as well as the intralayer hydrogen bonding [$\text{N2H}\cdots\text{O3}^i = 2.00 \text{ \AA}$ (144°), $\text{N2}\cdots\text{O3}^i = 2.741(10) \text{ \AA}$, (i) = $1-x, -y, -z$] stabilizing the 2D network of **III-4**.

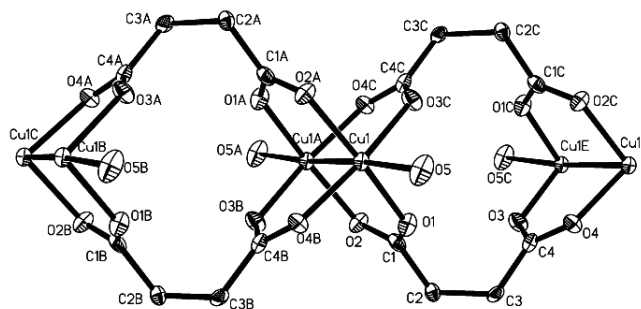


Figure 15 Infinite double-stranded chain structure of $[\text{Cu}_2(\text{O}_4\text{C}_3\text{H}_2)_2(\text{H}_2\text{O})_2]_n(\text{H}_2\text{O})_{2n}$.^[49] Hydrogen atoms have been omitted for clarity.

$[\text{Cu}(\text{ampyz})(\text{O}_4\text{C}_3\text{H}_2)]_n(\text{H}_2\text{O})_{2n}$ (III-5**)**

The coordination environment of the Cu^{II} center is shown in Figure 16. Each Cu^{II} ion is five-coordinated, showing a distorted square pyramidal CuN_2O_3 chromophore with $\tau = 0.1058$. Two oxygen (O2 and O3) atoms from two different malonate groups and two ampyz nitrogen atoms occupy the equatorial plane of the square pyramidal geometry with average Cu–O and Cu–N distances of 1.945(3) and 2.049(2) $\text{\AA}$, respectively. The axial position is occupied by a malonate oxygen atom with Cu–O1 distance of 2.179(2) $\text{\AA}$. The copper atom is shifted by 0.130 $\text{\AA}$ from the mean basal plane toward the apical position. Each malonate anion acts as tridentate ligand bridging two adjacent Cu^{II} centers by use of a bidentate chelating mode through O2 and O1 toward Cu, forming a six-membered ring with the subtended angle at the copper atom being 92.08° . The bidentate triatomic bridge through O1 and O3' toward the adjacent Cu' resulting in a 1D zigzag chain along crystallographic a axis in *syn-anti* coordinative mode of malonate yields a Cu $\cdots$ Cu separation of 4.9881(6) $\text{\AA}$. The dihedral angle between the basal planes of two adjacent copper atoms is 24.32° . The values of the bond lengths and angles of malonate ligand are comparable to those previously reported for malonate bridged Cu^{II} complexes.^[38]

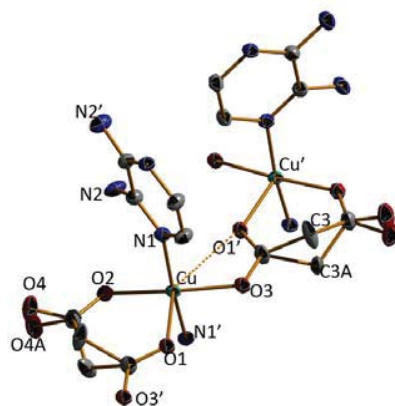


Figure 16 Asymmetric unit and the atom labeling scheme of **III-5** with 35% probability level. The two uncoordinated water molecules and the hydrogen atoms are omitted for clarity. Both disordered positions of N2 are shown. The dashed line represents weak interaction in the off-the-axis position.

Furthermore, these 1D zigzag chains are connected by ditopic ampyz spacer along the *b* axis leading to 2D layered structure with the unbound water molecules filling up the windows (Figure 17(a)). The Cu...Cu separation *via* ampyz is 6.8579(3) Å. Interestingly, the layers of **III-5** contain two sets of guest water molecules, as shown in Figure 17(b). The former set is filled in the cavities of the layer in zigzag fashion spreading along the *ab* plane where the hydrogen bonding stabilizes this water set *via* uncoordinated malonate oxygen of adjacent layer with O4'...O6w separations of 2.913(11) Å. The dimension of the grid cavity is about 6.858×4.988 Å. Another set of water molecules is filled among the layers which is stabilized by hydrogen bonding between the amine hydrogen of ampyz spacer and the water oxygen atom [N2H_a...O5w = 1.98 Å (137°), N2...O5w = 2.671(6) Å] and also by a hydrogen bond from the bridging malonate oxygen of the adjacent layer with O3'...O5w separations of 2.850(6) Å. The filling of the different positions of water

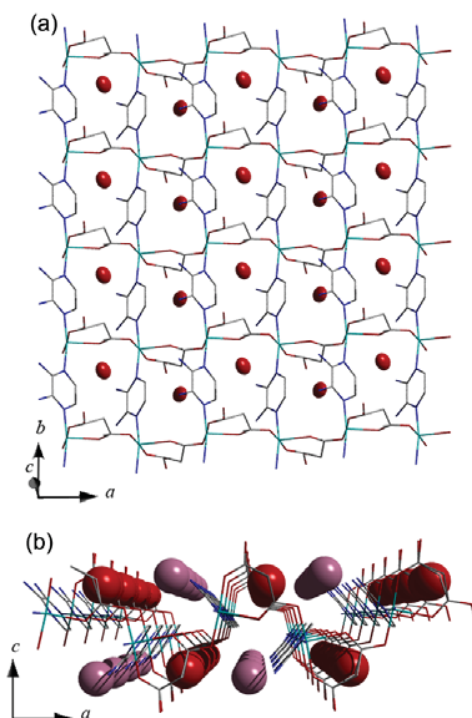


Figure 17 View of the 2D layer of **III-5** containing nearly perpendicular orientation of ampyz spacers and uncoordinated water molecules filling up the windows (a). Another view in the *ac* plane of a 2D stairlike layer showing the arrangement of two different groups of uncoordinated water molecules (b). The two sets of water molecules are represented in different colors in the space-filling model. Both disordered positions of amino group are shown.

molecules causes the arrangement of ampyz rings in the layers of **III-5** that are twisted nearly perpendicular one another with the dihedral angle between adjacent ampyz aromatic rings being 73.52° (Figure 17(a)). This structural feature contributes to the stairlike layered structure (Figure 18). In the packing motif, each 2D stairlike layer of **III-5** is assembled *via* hydrogen bonding between amine hydrogen and malonate oxygen atom [$\text{N2H}_b \cdots \text{O2}^i = 2.45 \text{ \AA}$ (160°), $\text{N2} \cdots \text{O2}^i = 3.274(5) \text{ \AA}$, ($i = 1-x, -1/2+y, -z$ and $\text{N2H}_b \cdots \text{O4}^i = 2.11 \text{ \AA}$ (135°), $\text{N2} \cdots \text{O4}^i = 2.783(7) \text{ \AA}$, ($i = -x, -y, 1-z$)] together with the uncoordinated water molecules stabilizing the layers which completely results to the overall 3D structure of **III-5** as shown in the inset of Figure 3.18.

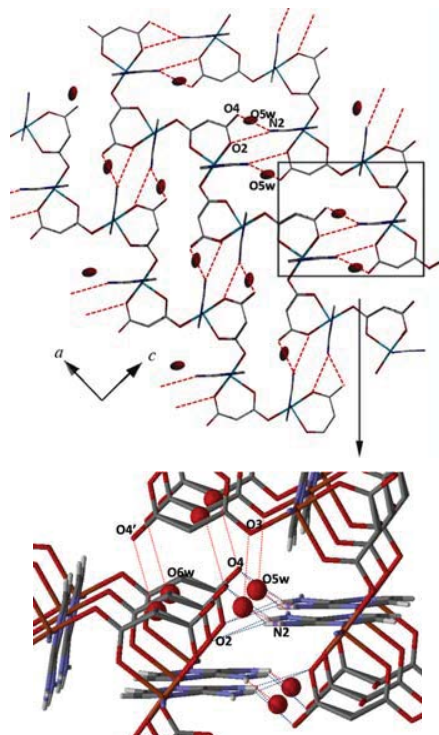


Figure 18 The 3D packing structure of **III-5** viewed along the *b* axis formed by the hydrogen bonding between stairlike layers. The inset presents the hydrogen bonds from uncoordinated water molecules stabilizing the supramolecular assembly.

A comparison was made with the mixed bridging malonate-pyz Cu^{II} complexes, like $[\text{Cu}_2(\text{pyz})(\text{O}_4\text{C}_3\text{H}_2)_2]_n(\text{H}_2\text{O})_{2n}$ [29] which was reported to exhibit a unique 3D network constructed from bridging tetradentate malonate groups and μ_2 -pyz (Figure 19). Compound **III-5** reveals a 2D stairlike network that may be attributed from the higher steric effect of ampyz spacer which causes malonate only acting as a tridentate connector with a terminal oxygen atom.

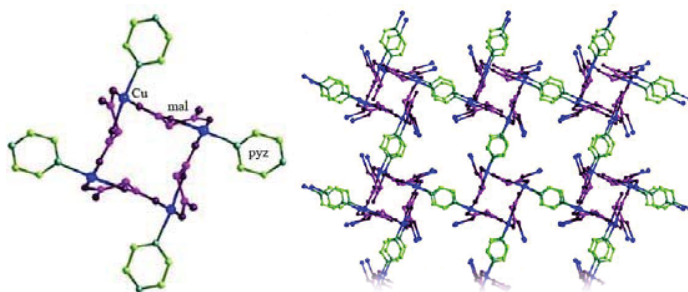


Figure 19 Asymmetric unit and 3D network of $[\text{Cu}_2(\text{pyz})(\text{O}_4\text{C}_3\text{H}_2)_2]_n(\text{H}_2\text{O})_{2n}$. [29]

3.1.3 EPR and magnetic measurements

EPR spectra

The X-band EPR was measured on polycrystalline samples at room temperature (RT) and 77 K for all five compounds. Compounds **III-2** and **III-4** showed in principle the same spectrum at 77 K, while at RT the intensities of particular features differed somewhat between them (Figure 20-22). In particular, at 77 K, where the triplet ($S = 1$) state is the only significantly populated excited state, two peaks are visible at around 250 and 4700 G, which are assigned to the turning points in the triplet powder pattern with $H_{//}$ and $H_{\perp}$, respectively. Other expected parallel turning points ($H_{//2}$) are either outside the available magnetic field range (>6000 G), or not observable in X-band because the value of D approaches that of the microwave quantum. The recorded spectra are indeed typical for a triplet state with a sizable zero-field splitting, such as that well-known for the classical paddle-wheel type dicopper tetracarboxylates.^[50-54] In compound **III-3**, an additional feature is the hyperfine structure appearing on the parallel turning point of the spectrum at 77 K, due to hyperfine interaction of the unpaired electron with two equivalent Cu^{II} nuclei ($I = 3/2$) within the dinuclear unit. The occurrence of the several additional peaks in the 700-4000 G range in the RT-EPR spectra of compounds **III-2-4** are in all likelihood caused by higher excited states ($S = 2$) being populated at elevated temperatures.^[55] The peak at around 3200 G is an $S = 1/2$ signal of a mononuclear Cu^{II} impurity and is ignored in the analysis. The EPR spectra of the classical paddle-wheel type dicopper tetracarboxylates may be described by the spin Hamiltonian:^[55]

$$\hat{H} = DS_z^2 + E(S_x^2 - S_y^2) + g_z H_z S_z + g_x H_x S_x + g_y H_y S_y \quad (1)$$

D and E values are the tetragonal and rhombic zero-field splitting parameters and $S = 1$. The x , y and z are the principal coordinate axes, where z -axis is taken parallel to the Cu–Cu direction inside the dimer. The other symbols have their usual meaning. The spin Hamiltonian parameters optimized to simulate the experimental triplet EPR spectra at 77 K are $S = 1$, $g_{//} = g_z = 2.00$, $g_{\perp} = (g_x + g_y)/2 = 2.05$, $E = 0 \text{ cm}^{-1}$ and $|D| = 0.336 \text{ cm}^{-1}$ for **III-2** and **III-4**. Compound **III-3** is characterized by an almost identical set of parameters, with the addition of two copper ($I = 3/2$) nuclei interacting with the $S = 1$ electron spin, with the $A_{//}$ component of the hyperfine tensor equal to $4 \times 10^{-3} \text{ cm}^{-1}$ (120 MHz), and $A_{\perp}$ unresolved. The appearance of triplet EPR spectra in compounds **III-2-4** is in accordance with the magnetic susceptibility observations and the fact that these three compounds all have very short Cu...Cu distances. Compounds **III-1** and **III-5**, which have different structures and both have a very long Cu...Cu distance, only show a broad isotropic $S = 1/2$ signal with $g = 2.12$ both at 77 K and RT (Figure 23), giving no information regarding the electronic ground state.

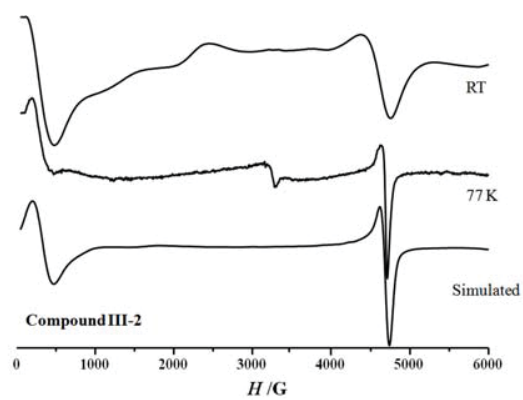


Figure 20 EPR spectra of **III-2** at RT and 77 K and the simulation for dinuclear Cu^{II} at 77 K.

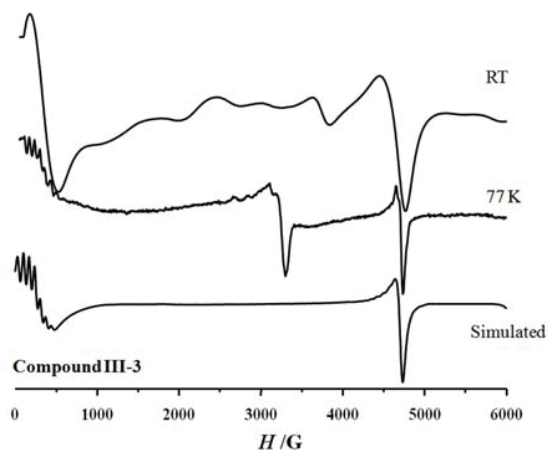


Figure 21 EPR spectra of **III-3** at RT and 77 K showing Cu hyperfine splitting at 77K around 200 G and the simulation for dinuclear Cu^{II} at 77 K.

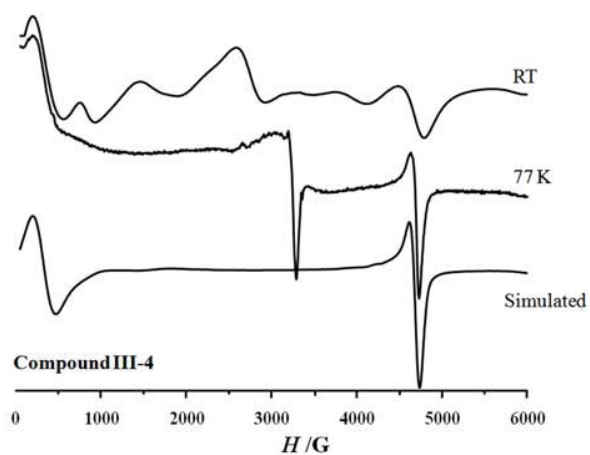


Figure 22 EPR spectra of **III-4** at RT and 77 K and the simulation for dinuclear Cu^{II} at 77 K.

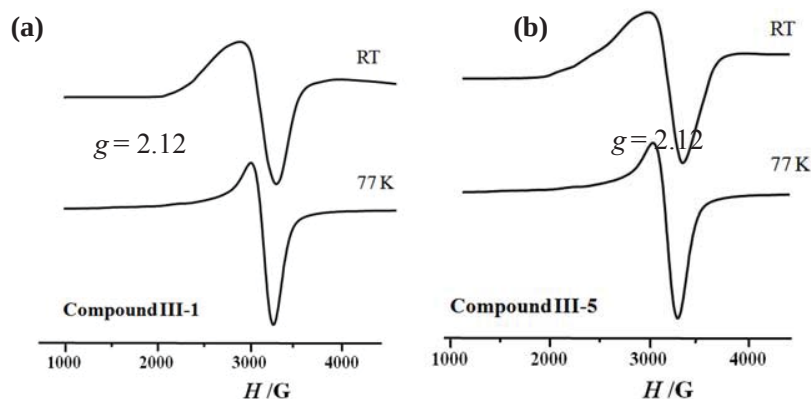


Figure 23 EPR spectra of **III-1** (a) and **III-5** (b) at RT and 77 K.

Magnetic measurements

The magnetic susceptibility of powdered sample of all five compounds was measured from 2-300 K under a constant magnetic field of 0.1 T. The magnetic properties of **III-1** and **III-5** are mutually the same because they are 2D layers that contain the similar μ_2 -*syn-anti* carboxylato in axial-equatorial configuration and μ_2 -ampyz spacer bridging between Cu^{II} centers. The magnetic susceptibilities of **III-1** and **III-5** are depicted in Figures 24 and 25. The $\chi_{\text{m}}T$ value of ca. $0.40 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K is slightly larger than value expected for uncorrelated Cu^{II} ion ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$ for $g = 2$), owing to the g -tensor anisotropy. Upon cooling from 300 K, $\chi_{\text{m}}T$ slowly increases, reaching a broad maximum around 50 K ($0.45 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-1** and $0.46 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-5**), which indicates the dominance of ferromagnetic interactions *via* orthogonally μ_2 -*syn-anti*-formato in **III-1** and μ_2 -*syn-anti*-malonato in **III-5** bridging between Cu^{II} ions.^[56-58] Below this, $\chi_{\text{m}}T$ decreases rapidly to $0.15 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-1** and $0.17 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-5**, due to the build-up of significant antiferromagnetic interactions *via* μ_2 -ampyz spacer. There is no evidence for a transition to long-range ordering. The χ_{m}^{-1} values above 100 K were fitted with the Curie-Weiss law $\chi = C/(T-\theta)$ with a Curie constant $C = 0.43 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-1** and $0.45 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-5**, yielding $g = 2.14$ for **III-1** and 2.19 for **III-5**. Weiss constants θ are $+17.4 \text{ K}$ for **III-1** and $+19.1 \text{ K}$ for **III-5** indicating dominant ferromagnetic coupling *via* μ_2 -*syn-anti*-carboxylate bridges above 100 K. Both g and θ values agree very well to those values of $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$,^[28] ($g = 2.17$ and $\theta = +17.4 \text{ K}$) which contains the same μ_2 -*syn-anti* formato and μ_2 -pyz spacer bridging between Cu^{II} centers (Figure 6).

As discussed previously, the adjacent Cu^{II} ions of **III-1** and **III-5** are linked by ferromagnetically μ_2 -*syn-anti* carboxylato and antiferromagnetically μ_2 -ampyz which are the same as the reported rectangular 2D spin lattice of $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$. The analysis of the magnetic susceptibility for **III-1** and **III-5**, therefore 2D spin lattice is treated as chains, in which the intrachain spin exchange, J_{intra} , is negative and

the interchain spin exchange, J_{inter} , is positive. The effective susceptibility, χ_{eff} given by Hamiltonian $\hat{H} = -\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, is expressed in terms of the intrachain susceptibility, χ_{intra} and the interchain susceptibility, χ_{inter} , as^[28]

$$\frac{1}{\chi_{\text{eff}}} = \frac{1}{\chi_{\text{inter}}} + \frac{1}{\chi_{\text{intra}}} \quad (2)$$

The interchain susceptibility is given by

$$\chi_{\text{inter}} = - \frac{Ng^2 \beta^2}{J_{\text{inter}}} \quad (3)$$

The intrachain susceptibility is given by

$$\chi_{\text{intra}} = \frac{Ng^2 \beta^2}{kT} \frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 0.68854x^3} \quad (4)$$

when

$$x = \frac{|J_{\text{intra}}|}{kT}$$

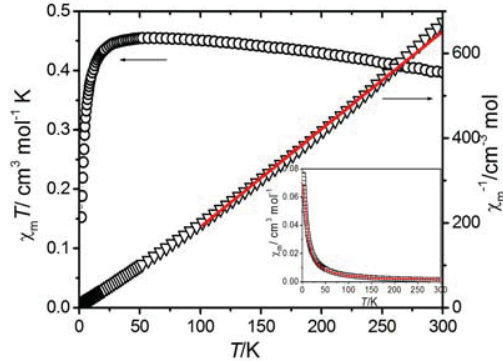


Figure 24 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **III-1** from 2 to 300 K. Inset: plot of χ_m vs. T for **III-1**. The solid lines correspond to the best fit (see the text).

The least-square fitting analysis (inset of Figures 24 and 25) leads to the values of $g = 2.17$, $J_{\text{inter}}/k = +6.9$ K and $J_{\text{intra}}/k = -2.3$ K, $R = 2.2 \times 10^{-3}$ for **III-1** and $g = 2.18$, $J_{\text{inter}}/k = +7.4$ K and $J_{\text{intra}}/k = -2.2$ K, $R = 2.4 \times 10^{-3}$ for **III-5** (R is the agreement factor defined as $R = \sum [\chi_{m, \text{calc}} - \chi_{m, \text{exp}}]^2 / (\chi_{m, \text{exp}})^2$). These g values practically close to the g values obtained from the Curie-Weiss law in the high temperature range and EPR spectra. The values of J_{inter} and J_{intra} show the same magnitude as those reported ($J_{\text{inter}}/k = +8.2$ K and $J_{\text{intra}}/k = -5.4$ K) for $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$ ^[28]. However, it should be mentioned that both J_{intra} are lower than that found for $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$ which could be attributed to the less electron transfer in

the superexchange pathways for ampyz, due to an electron withdrawing amine group attached at the pyz ring.

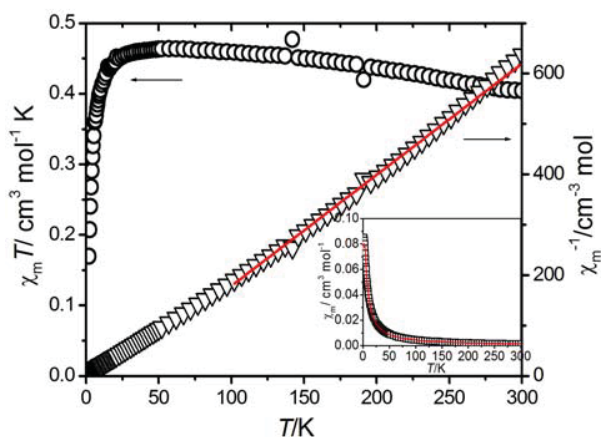


Figure 25 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **III-5** from 2 to 300 K. Inset: plot of χ_m vs. T for **III-5**. The solid lines correspond to the best fit (see the text).

The magnetic properties of compounds **III-2-4** are in accordance with the earlier EPR observations. The $\chi_m T$ vs. T plots for one Cu^{II} ion of **III-2-4** are shown in Figures 26 and 27. For **III-2**, The $\chi_m T$ value per one Cu^{II} ion of ca. $0.18 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K is much smaller than value expected for uncorrelated Cu^{II} ion ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$ for $g = 2$), owing to the very strong antiferromagnetic coupling *via* four μ_2 -syn-syn acetate bridging between Cu^{II} ions. Upon cooling from 300 K, $\chi_m T$ value smoothly decreases to $0.00 \text{ cm}^3 \text{ K mol}^{-1}$ at around 95 K, staying constant until 20 K. This magnetic behavior agrees with a very strong antiferromagnetic interaction which is well-known for the classical paddle-wheel type dicopper(II) tetracarboxylates ($J \sim -300$ to -400 cm^{-1}).^[47, 49-54]

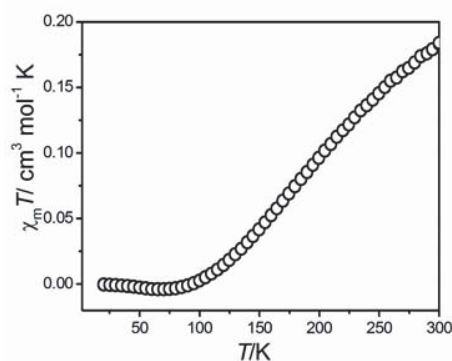


Figure 26 Temperature dependence of $\chi_m T$ of **III-2** from 20-300 K.

For **III-3** and **III-4**, At 300 K the $\chi_m T$ value per one Cu^{II} ion is almost diamagnetic and has a value at around $0.04 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-3** and $0.02 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-4**, which is much lower than the value expected for one uncorrelated Cu^{II} ion ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$), owing to the very strong antiferromagnetic coupling. Upon cooling the $\chi_m T$ products gradually decrease and reach a plateau giving the minimum of $-0.02 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-3** and $-0.03 \text{ cm}^3 \text{ K mol}^{-1}$ for **III-4** at around 100 K, then finally increase to $0.00 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This magnetic behavior agrees with a very strong antiferromagnetic interaction. It should be noted that the very much small $\chi_m T$ values of **III-3** and **III-4** should be attributed from an error in the SQUID system during the measurement which was not well working. The increase of $\chi_m T$ again at low temperature is due to the presence of a noncoupled Cu^{II} impurity which was clearly observed in EPR spectra at 77 K.^[59]

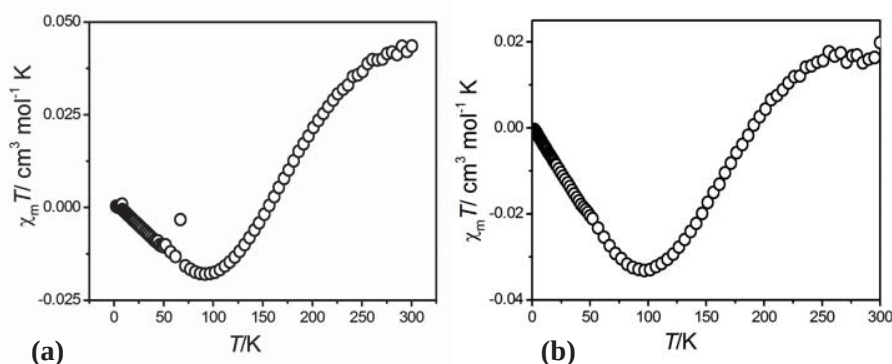


Figure 27 Temperature dependence of $\chi_m T$ of **III-3** (a) and **III-4** (b) from 2-300 K.

3.2 Reversible structural transformation with chromotropism in metal supramolecular frameworks containing aminopyrazine and sulfate anions

Flexible and dynamic molecular solids recently have received great attention because of their fascinating architectures with promising functional properties. Particularly, the guest removal and re-adsorption in metal-organic frameworks are of interest for many potential applications especially in the areas of gas storage and sensors.^[60-68] The guest-induced crystalline-to-amorphous transformation and the guest-induced backward transformation are characteristic of the 3rd generation compounds (Figure 1.16) which are typically found in the flexible coordination frameworks supported by weak molecular interactions, such as hydrogen bonds, π - π stacking, van der Waals forces and others.^[60, 61] Whereas, such reversible structural transformations in non-coordination supramolecular systems are not common^[69-78] since the structural destruction accompanying with the guest removal is too severe to recover the crystallinity after re-adsorption process, contrastive to the cases of the flexible coordination polymers which contain the bridging spacers maintaining the skeleton of whole structures. Within the field of

inorganic-organic supramolecular chemistry, the utilization of transition metal ions and organic spacers can form a number of extended frameworks through either coordination or weak intermolecular interactions.^[13, 14, 79-83] It is known that the metal sulfate is a good candidate for constructing the open-framework materials along with other organic spacers, especially *N,N'*-ditopic spacers, yielding various supramolecular architectures because sulfate anion (SO_4^{2-}) can behave as a versatile connector playing the role of monodentate ligand, bridging ligand, and good hydrogen acceptor.^[84-90] For examples, $[\text{Co}_2(\text{bipy})_3(\text{SO}_4)_2(\text{H}_2\text{O})_2](\text{bipy})(\text{CH}_3\text{OH})$ ^[85] and $[\text{Co}(\text{SO}_4)(\text{H}_2\text{O})_3(\text{bipy})](\text{H}_2\text{O})_2$ ^[86] (bipy = 4,4'-bipyridine) show distinctive structures supported by sulfate ions. Likewise, the structural diversity were also observed in Cu^{II} pyrazine complexes containing sulfato ligand.^[87, 88]

3.2.1 General observations and spectroscopic characterizations

The layering diffusion reaction of metal(II) sulfate with ampyz in 1:2 molar ratio in a mixture of ethanolic and aqueous media yielded high purity single-crystals of **IV-1-4**. The IR spectra of four compounds (Figure 28) show strong bands in the region $3400\text{--}3100\text{ cm}^{-1}$ which can be assigned to the stretching $\nu(\text{N-H})$ of the primary amine in the ampyz ligand overlapping with $\nu(\text{O-H})$ of water molecule. The NH_2 scissoring mode^[91] shows medium bands around $1660\text{--}1640\text{ cm}^{-1}$ and the strongest bands due to SO_4^{2-} stretching vibrations are observed around 1100 cm^{-1} .^[92]

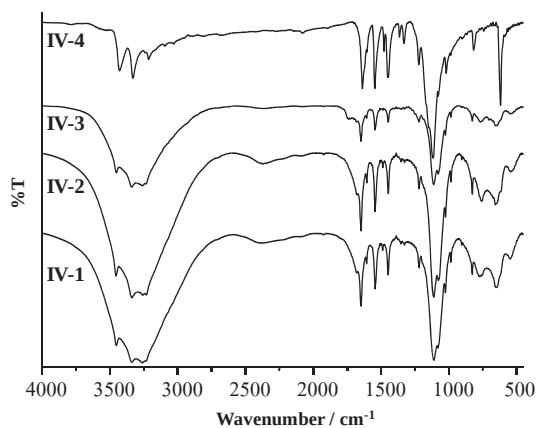


Figure 28 Infrared spectra for compounds **IV-1-4**.

The solid-state UV-vis diffuse reflectance spectra of **IV-1-4** are depicted in Figure 29. The spectrum of **IV-1** agrees with the typical *d-d* transition of high-spin Co^{II} in octahedral geometry with two observed bands at $22,000\text{--}19,500$ and less than $9,000\text{ cm}^{-1}$, which are assigned to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ transitions, respectively. For compound **IV-2**, the broad band around $11,700\text{ cm}^{-1}$ is attributed to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition for high-spin Fe^{II} in octahedral geometry.^[93] The bands which appear at higher than $24,000\text{ cm}^{-1}$ due to charge transfer transition and internal transition within ampyz. Whereas compound **IV-3** is a

heterometallic complex, so the spectrum of **IV-3** shows the overlaying transitions between Co^{II} and Fe^{II} in octahedral geometries, resulting yellowish orange in the color which is between orange crystal of **IV-1** and yellow crystal of **IV-2**. Besides the crystallographic data, the positions of Co^{II} and Fe^{II} chromophores in **IV-3** were further verified by far-IR spectra ($500\text{--}50\text{ cm}^{-1}$) which yield the information of M–O and M–N vibrations in compounds **IV-1-3** as shown in Figure 30.

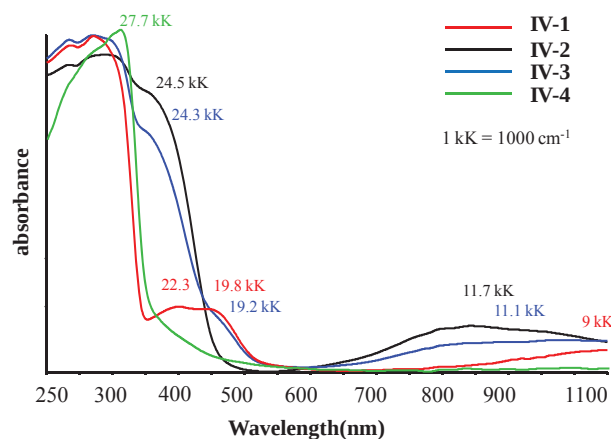


Figure 29 Solid-state UV-visible diffuse reflectance spectra for **IV-1-5**.

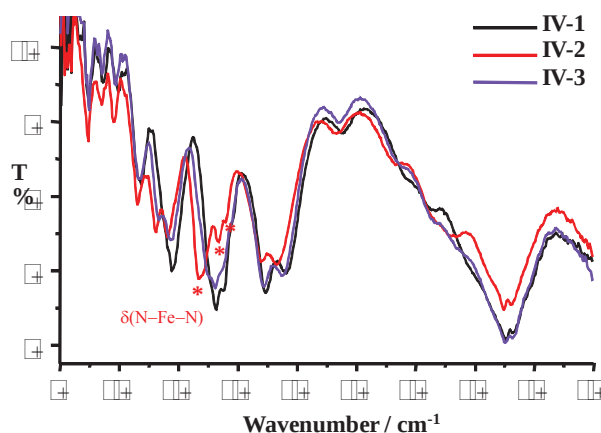


Figure 30 Far-IR spectra ($500\text{--}50\text{ cm}^{-1}$) of **IV-1-3**.

The far-IR spectrum of **IV-3** almost shows close resemblance to the spectrum of **IV-1**, especially in the range of $160\text{--}250\text{ cm}^{-1}$, where the deformations of N–M–N and the asymmetric stretching vibrations of M–N. These low-frequency modes are sensitive to metal-ion mass and provide a clue to metal-site preference. This result strongly suggests that the Co^{II} ion in **IV-3** is accommodated in $[\text{M}(\text{H}_2\text{O})_4(\text{ampyz})_2]^{2+}$ unit rather than $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ unit, and supports the X-ray structure of $[\text{Co}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ for **IV-3**.

3.2.2 Description of crystal structures

[Co(H₂O)₄(ampyz)₂][Co(H₂O)₆](SO₄)₂(H₂O)₂ (IV-1)

[Fe(H₂O)₄(ampyz)₂][Fe(H₂O)₆](SO₄)₂(H₂O)₂ (IV-2)

and [Co(H₂O)₄(ampyz)₂][Fe(H₂O)₆](SO₄)₂(H₂O)₂ (IV-3)

Single-crystal X-ray diffraction analyses revealed that compounds **IV-1–3** are not only isostructural frameworks, but also form a beautiful isomorphous series and the structure of **IV-1** is only described in detail here. Crystal structure of **IV-1** is shown in Figure 31.

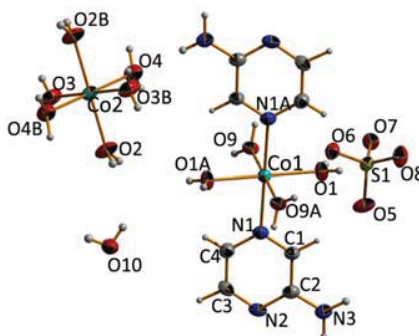


Figure 31 Crystal structure and atom labeling scheme of **IV-1**. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A” and “B” are symmetry-generated equivalents, (A) $-x, 1-y, 1-z$; (B) $-x, 2-y, -z$.

Compound **IV-1** contains two crystallographically independent Co^{II} ions (Co1 and Co2) in [Co(H₂O)₄(ampyz)₂]²⁺ and [Co(H₂O)₆]²⁺ cationic units. Both Co^{II} ions are 6-coordinated and lie on independent inversion centers. Co1 shows elongated octahedral geometry comprised of four oxygen atoms from water molecules at equatorial positions with the average Co1–O distance of 2.0702(13) Å, and two nitrogen atoms from ampyz ligands at axial sites with Co1–N1 distance of 2.2071(16) Å. Co2 shows slightly compressed octahedron, surrounded by six water molecules with the average Co2–O bond length at equatorial plane of 2.1072(15) Å and the Co2–O3 distance at apical position of 2.0691(14) Å. The bond angles around octahedron are in the range of 87.33–180°, which are close to ideal octahedral geometry.

[Co(H₂O)₄(ampyz)₂]²⁺ units are assembled by intermolecular hydrogen bonding between pyrazine nitrogen and hydrogen of coordination water along *b* axis [O9–H[⋯]N2ⁱ = 1.86 Å (173°), O9[⋯]N2ⁱ = 2.792(2) Å, (i) = $x, 1+y, z$] and π - π stacking interaction among adjacent ampyz moieties along *a* axis with the separation of 3.417–3.557 Å, giving rise to 2D layer substructure in *ab* plane with the closest intermolecular Co[⋯]Co separation of 6.5697(4) Å (Figure 32). Moreover, these layers are supported by electrostatic forces and the intermolecular hydrogen bonds involving sulfate anions (O5–O8), amine

moieties on ampyz (N3), coordination waters in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ unit (O2–O4), and lattice water molecules (O10), to provide an entire 3D supramolecular structure of **IV-1** as shown in Figure 33.

The crystal structures of isostructures **IV-2-3** are depicted in Figure 34.

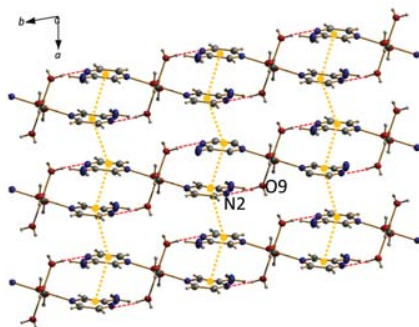


Figure 32 2D sheet structure of **IV-1** in the *ab* plane, assembled *via* the intermolecular π – π stacking and hydrogen bonding interaction which are represented in yellow and red broken lines, respectively.

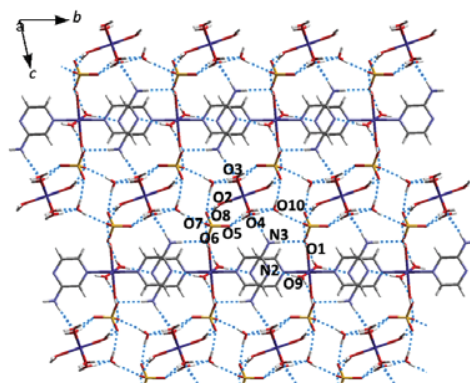


Figure 33 3D packing structure of **IV-1** in *bc* plane formed by intermolecular hydrogen bonding (blue dotted lines) among layers through ampyz, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ unit, SO_4^{2-} , lattice and coordination water molecules.

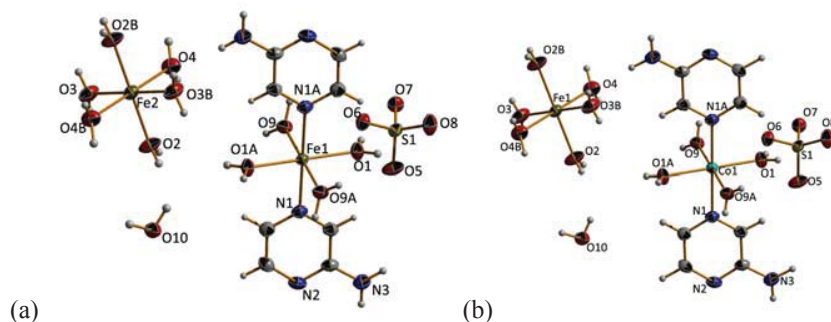


Figure 34 Crystal structure and atom labeling scheme of **IV-2** (a) and **IV-3** (b). The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A” and “B” are symmetry-generated equivalents, (A) $-x, 1-y, 1-z$; (B) $-x, 2-y, -z$.

[Cd(ampyz)(H₂O)₂(SO₄)_n(H₂O)_n (IV-4)

The coordination environment of the Cd^{II} center is shown in Figure 35. The Cd1 atom, sulfate atoms S1, O1, O2 and the water oxygen O4 all lie on a mirror plane in this structure. Each Cd^{II} ion is five-coordinated showing a distorted square-pyramidal CdN₂O₃ chromophore with $\tau = 0.04$.^[44] The basal plane around the cadmium atom is comprised of one oxygen atom from coordination water (O4) and one oxygen atom from a μ_2 -sulfato bridge (O2A) with the Cd–O distance of 2.303(6) and 2.297(5) Å, respectively and two ampyz-nitrogen atoms with the Cd–N distances of 2.315(4) Å. The apical position is occupied by a μ_2 -sulfato oxygen (O2) with Cd–O2 length of 2.587(5) Å. The bond angles between axial shared with a neighbouring square pyramid and square corners are remarkably deviated from 90° and rather distorted from regular square pyramidal geometry of Cd^{II}.^[94, 95] It is possibly attributed to three sulfato oxygen atoms excluded from μ_2 -bridges, weakly interacting with adjacent Cd^{II} centers with Cd...O3 and Cd...O1 distances of 2.754(6) and 2.765(6) Å, respectively, forming the semi-eight coordination. The weak secondary bonds of Cd...O are also reported in other Cd^{II} complexes.^[96-98]

The sulfato ligand acting as a monoatomic bridge connects Cd^{II} centers in *ac* plane, yielding the Cd^{II} dimer with the separation of 4.0359(5) Å. These Cd^{II} dimers are linked by the ditopic ampyz spacers along *b* axis leading to 1D ladder chain structure with Cd...Cd separation *via* ampyz of 7.3913(4) Å (see Figure 36). Moreover, when above-mentioned weak coordination bonds are considered, the inorganic double-stranded chain of metal sulfate^[84] is observed, which is comprised by CdN₂O₆ polyhedra and SO₄ tetrahedral units, as shown in Figure 36(a). The monoatomic sulfato bridge connects Cd^{II} ions, leading to edge-sharing CdN₂O₆ polyhedra that further share edges with tetradentate bridges of SO₄ tetrahedra to form a four-member ring ladder along *c*-axis. In addition this chain is linked by the ampyz spacers along *b* axis, giving rise to the 2D layer structure of **IV-4** as shown in Figure 36(b). The lattice water molecules (O5) are filled in between 2D sheets, which effectively provide the intermolecular hydrogen bonds with amine nitrogen of ampyz (N2), sulfato oxygen (O1, O3) and coordination water (O4), contributing to the stabilization of the overall 3D supramolecular structure as shown in Figure 37.

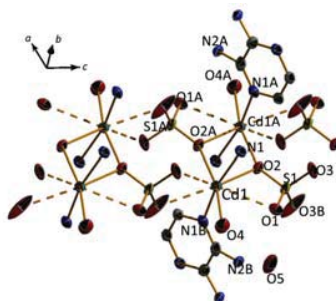


Figure 35 Expanded asymmetric unit and atom labeling scheme of **IV-4**.

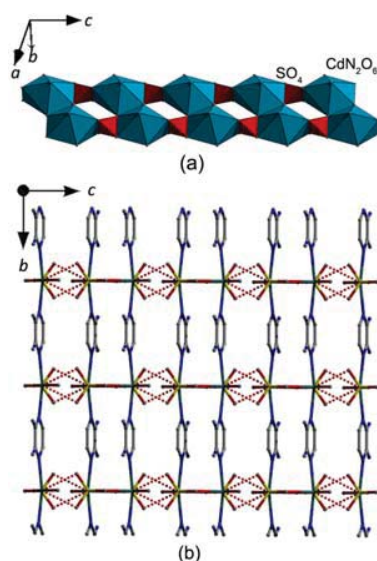


Figure 36 Double-stranded chain of $[\text{Cd}(\text{ampyz})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$ (a). View of the 2D layer of **IV-4** in bc plane. The red broken lines represent the weak coordinative bonds between sulfate oxygen atoms and $\text{Cd}(\text{II})$ ions (b).

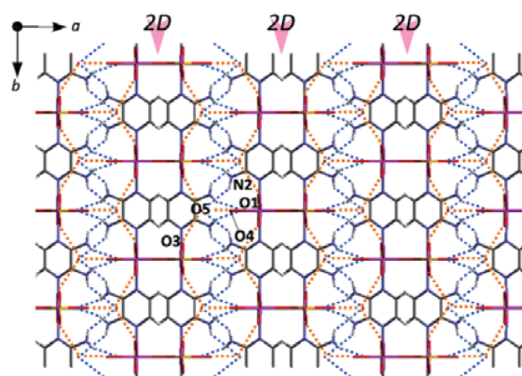


Figure 37 3D packing structure of **IV-4** in ab plane formed by intermolecular hydrogen bonding between layers and lattice water molecules. The blue and orange dotted lines represent the $\text{N2-H}\cdots\text{O}(1,5)$ and $\text{O5}\cdots\text{O}(4,3)$ intermolecular hydrogen bonds, respectively.

3.2.3 Reversible structural phase transformation with chromotropism

Thermogravimetric analyses

To examine the thermal stabilities of compounds **IV-1-4**, the TGA were performed in the temperature range $25\text{--}500^\circ\text{C}$, as shown in Figure 38.

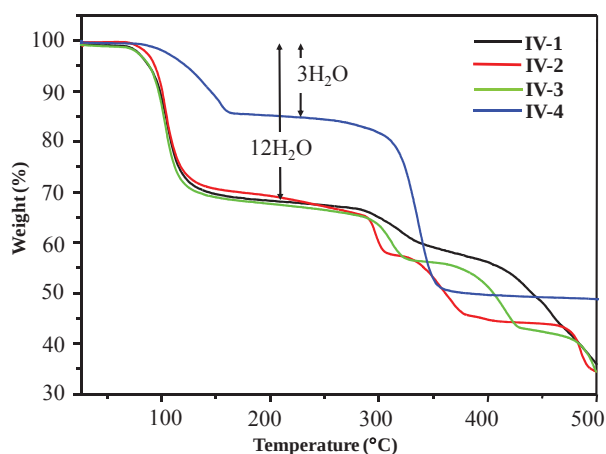


Figure 38 TGA curves of compounds **IV-1-4**.

The TGA profiles of **IV-1-3** indicate that the releases of all twelve water molecules including coordinated and lattice water molecules occur at the first step of weight loss in the temperature range 55–180°C (found, 31.46%; Anal. Calcd, 30.15% for **IV-1**; found, 29.44%; Anal. Calcd, 30.41% for **IV-2**; found, 31.48%; Anal. Calcd, 30.28% for **IV-3**), resulting to the dehydrated forms of $[M_2(\text{ampyz})_2(\text{SO}_4)_2]$ (**IV-1A-3A**), which are stable up to $\approx 240^\circ\text{C}$ and then the structures gradually decompose to the unidentified products. The TGA profile of **IV-4** shows two steps of weight loss. The first step (75–180°C) corresponds to the loss of all three water molecules (found, 15.20%; Anal. Calcd, 15.86%), resulting to the dehydrated forms of $[\text{Cd}(\text{ampyz})(\text{SO}_4)]$ (**IV-4A**), which are stable up to $\approx 250^\circ\text{C}$. The second step (250–420°C) gives a mixture of the CdO and CdS as main products.

3.2.4 Water-induced reversible structural phase transformation with chromotropism

Aforementioned all compounds contain both lattice and coordination water molecules and weak intermolecular interactions stabilize entire 3D molecular frameworks. In addition the stable dehydrated forms of **IV-1A-4A** were clarified by TGA profiles. The dynamic structural behaviors of **IV-1-4** relating to their dehydration and rehydration processes are thus studied by elemental analyses, XRPD, and spectroscopic techniques.

When the single-crystals of **IV-1-4** were heated to 220°C in air for 30 minutes (Figure 39), these crystals suddenly lose the crystallinity and the colors changed from orange to purple for **IV-1**; yellow to orange for **IV-2**; yellowish orange to brown for **IV-3**; and no color changes was observed in colorless compound **IV-4**. Then these non-crystalline solids were exposed to the laboratory air for 8 hours and the colors of solids **IV-1A-3A** returned to their original crystalline ones. Consequently, the bulk samples of **IV-1-4** were used to study in the detail. The dehydrated forms of **IV-1A-4A** were obtained by heating the bulk

samples at 220°C in air for 4 hours and the rehydrated forms of **IV-1'-4'** were obtained by exposing the dehydrated samples to water vapor for 2 days at room temperature without condensation.



Figure 39 The colors of the single-crystals of **IV-1-4**, dehydrated forms of **IV-1A-4A** and rehydrated forms of **IV-1'-4'**.

The XRPD pattern of **IV-1** is shown in Figure 40. The TGA, elemental analysis of **IV-1A** (Anal. Calcd: C, 19.21; H, 2.02; N, 16.80%. Found: C, 18.51; H, 2.10; N, 16.18%) and XRPD results indicate that the dehydrated $[\text{Co}_2(\text{ampyz})_2(\text{SO}_4)_2]$ (**IV-1A**) is in an amorphous phase which is formed by the collapse of supramolecular structure of **IV-1** accompanied with the destruction of hydrogen bonding networks when all water molecules are removed. The original crystalline phase $[\text{Co}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ (**IV-1'**) can be restored from the amorphous phase of **IV-1A** after rehydration process which confirmed by the elemental analysis (Anal. Calcd: C, 13.41; H, 4.78; N, 11.73%. Found: C, 13.39; H, 4.29; N, 11.72%) and the XRPD pattern. These results suggest the crystalline-to-amorphous and amorphous-to-crystalline transformations in supramolecular network of **IV-1** triggered by the hydration control. Furthermore, this structural change of bulk sample is accompanied with a remarkable color change as confirmed by the solid-state UV-vis diffuse reflectance spectra in Figure 41 for **IV-1**. The UV-vis spectra clearly show that the bands observed in **IV-1** and **IV-1'** correspond very well to the identical transitions causing the same color of bulk products, and evidence that **IV-1** and **IV-1'** have the same Co^{II} environments.

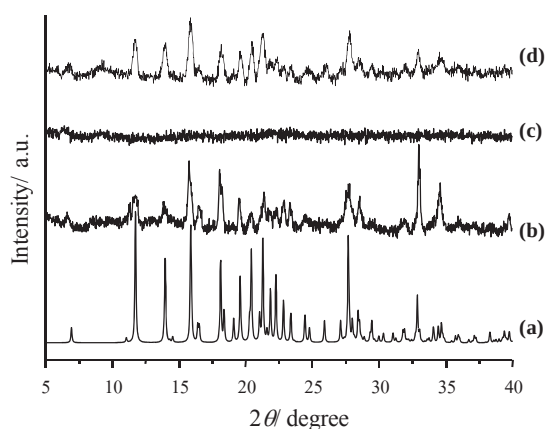


Figure 40 XRPD patterns: simulated from single-crystal X-ray data (a); as-synthesize **IV-1** (b); the dehydrated form **IV-1A** (c); the rehydrated form **IV-1'**(d).

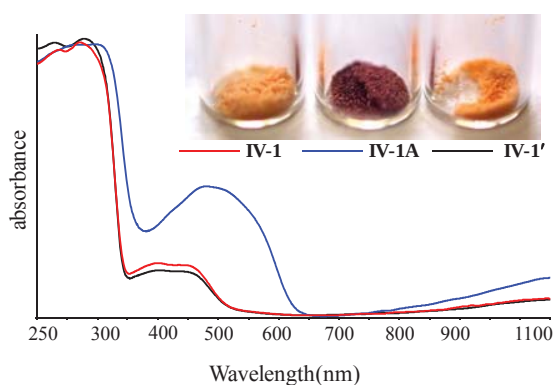


Figure 41 The UV-vis diffuse reflectance spectra of as-synthesize **IV-1** (red line), the dehydrated form **IV-1A** (blue line), and the rehydrated form **IV-1'** (black line), representing together with the chromatic changes in bulk samples.

Whereas the amorphous phase **IV-1A** shows the different *d-d* transition with a lower-energy broad band centered around 550 nm, giving the distinctive purple color. The chromotropic behaviors of **IV-1** are principally ascribed to the changes of the *d*-orbital energy level, induced by the drastic change in the coordination environments around metal center during dehydration and rehydration processes.^[85, 99-101] In addition, these results agree with the reversible change of the sulfate vibrational band in IR spectra (Figure 42) where the different splitting peaks at ~ 1100 (ν_3) and ~ 630 cm^{-1} (ν_4) are observed for the amorphous phase, indicating that site symmetry at sulfate ions is lowered.^[92] Reversely, these splits are removed in the IR spectra of the rehydrated form, which are identical to those of as-synthesized one. All of results confirm the water-induced reversible crystalline-to-amorphous phase transformation with chromotropism in supramolecular network of **IV-1**. This phenomenon is also observed in the isostructural **IV-2** and **IV-3**. The XRPD patterns, IR and UV-vis spectra of **IV-2-3** are given in Figure 43-48. The spectrum of **IV-3A** shows

the overlap bands between **IV-1A** and **IV-2A** indicating that **IV-3A** is also a hetero-metallic compound (Figure 47).

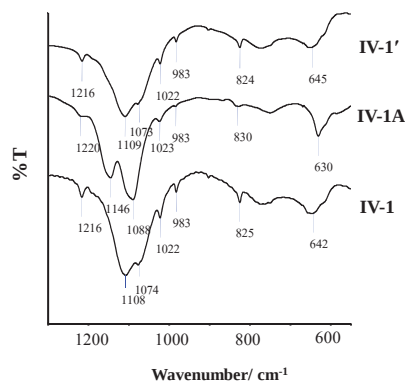


Figure 42 IR spectra ($1300\text{--}550\text{ cm}^{-1}$) for as-synthesize **IV-1**, the dehydrated form **IV-1A** and the rehydrated form **IV-1'**.

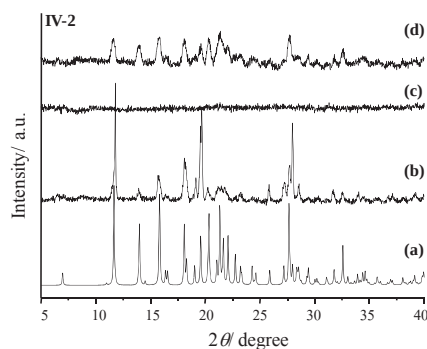


Figure 43 XRPD patterns: simulated from single-crystal X-ray data (a); as-synthesize **IV-2** (b); the dehydrated form **IV-2A** (c); the rehydrated form **IV-2'**(d).

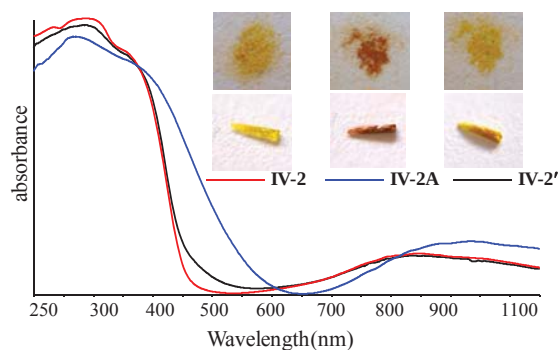


Figure 44 The UV-vis diffuse reflectance spectra of as-synthesize **IV-2** (red line), the dehydrated form **IV-2A** (blue line), and the rehydrated form **IV-2'** (black line), representing together with the chromatic changes in bulk samples.

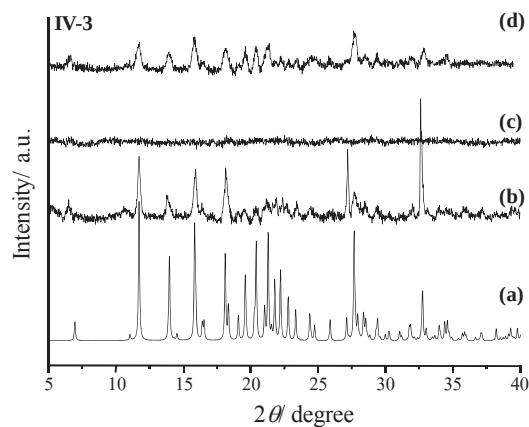


Figure 45 XRPD patterns: simulated from single-crystal X-ray data (a); as-synthesize **IV-3** (b); the dehydrated form **IV-3A** (c); the rehydrated form **IV-3'**(d).

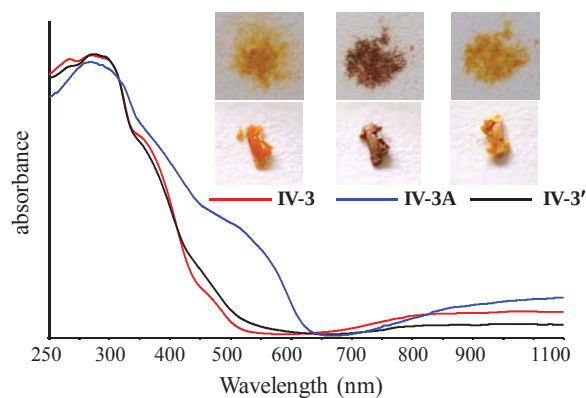


Figure 46 The UV-vis diffuse reflectance spectra of as-synthesize **IV-3** (red line), the dehydrated form **IV-3A** (blue line), and the rehydrated form **IV-3'** (black line), representing together with the chromatic changes in bulk samples.

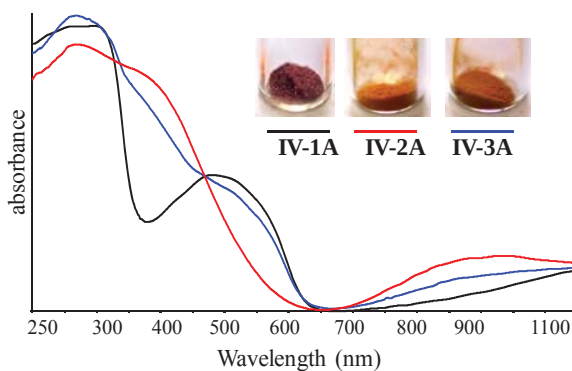


Figure 47 UV-vis diffuse reflectance spectra of the dehydrated compounds **IV-1A–3A**, represented together with the colors of their dehydrated samples. The spectrum of **IV-3A** shows the overlap bands between **IV-1A** and **IV-2A** indicating that **IV-3A** is also a hetero-metallic compound.

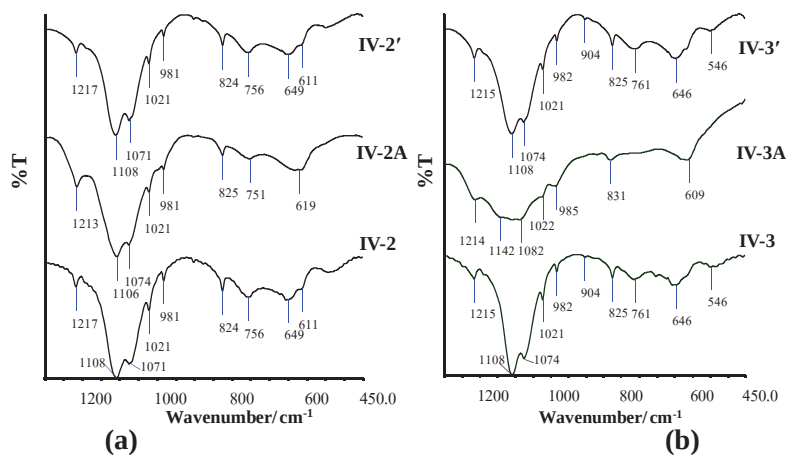


Figure 48 IR spectra (1300-450 cm^{-1}) for as-synthesize **IV-2**(a), **IV-3**(b), the dehydrated form **IV-2A** (a), **IV-3A** (b) and the rehydrated form **IV-2'** (a), **IV-3'**(b).

On the other hand, the coordination network **IV-4** exhibits the structural phase change in the dehydrated phase, $[\text{Cd}(\text{ampyz})(\text{SO}_4)]$ (**IV-4A**) which reveals the different XRPD pattern comparing with as-synthesized **IV-4** (Figure 49). Interestingly, this crystalline phase is converted to the same structure of original one (**IV-4'**) by rehydration process, which can be confirmed by the XRPD, IR-spectra (Figure 50), and elemental analysis. These results confirm the water-induced structural phase transformation in coordination network **IV-4**.

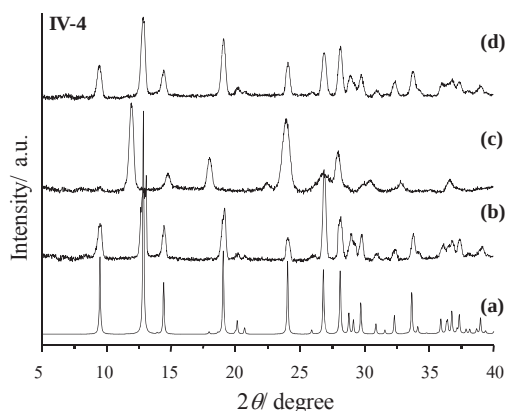


Figure 49 XRPD patterns: simulated from single-crystal X-ray data (a); as-synthesize **IV-4** (b); the dehydrated form **IV-4A** (c); the rehydrated form **IV-4'**(d).

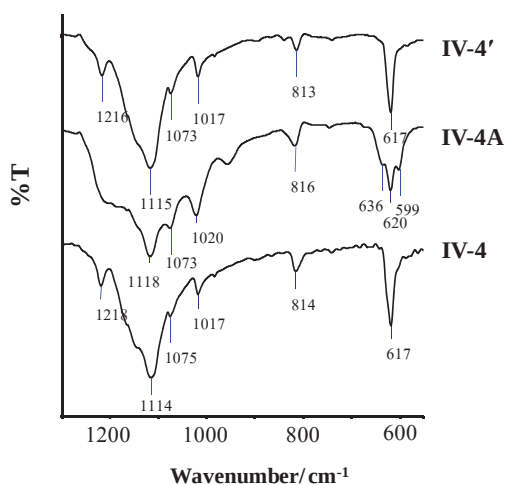


Figure 50 IR spectra (1300-550 cm^{-1}) for as-synthesize **IV-4**, the dehydrated form **IV-4A** and the rehydrated form **IV-4'**.

When the lattice and coordination water molecules are removed, the supramolecular networks **IV-1-3** collapse due to the destruction of the hydrogen bonding networks while the coordination polymer **IV-4** does not collapse but exhibits another crystalline phase. This result indicates that the coordination bridges *via* ampyz spacer and sulfato ligand play an important role for supporting the structural skeleton in **IV-4**. Remarkably, all compounds recover original crystalline phases after the exposure to water vapor, indicating that the significant role of hydrogen bonding through water molecules can trigger the reformation of other weak intermolecular interactions such as π - π stacking among ampyz moieties in **IV-1-3** and other hydrogen bonds through sulfate ions in **IV-1-4**.

3.2.5 Selective guest accommodation with chromotropism

One of the interesting aspects of cobalt in contrast to nickel, iron and manganese is the range of stable geometries, such as octahedral, tetrahedral, square pyramidal, trigonal bipyramid and square-planar together with a wide range of colors.^[102] Consequently, in order to investigation of the guest-induced structural transformation phenomena, the dehydrated $[\text{Co}_2(\text{ampyz})_2(\text{SO}_4)_2]$ (**IV-1A**) was used to study with various solvents, *i.e.* methanol, ethanol, propanol, butanol, acetone, acetonitrile, tetrahydrofuran and dichloromethane. The dehydrated **IV-1A** was exposed to solvent vapor for 2 days at room temperature in a closed vial. Remarkably the chromotropism is observed only in **IV-1A** which was exposed to methanol vapor (**IV-1A·MeOH**) and the colors change from purple (**IV-1A**) to red (**IV-1A·MeOH**). For other ones, the purple solids (**IV-1A**) still remain. IR spectra of all compounds including **IV-1A·MeOH** show the vibrational bands as same as those of dehydrated **IV-1A** (Figure 51) indicating the similar environments of

functional groups that are observed in amorphous phase **IV-1A**. The dynamic structural behaviors of **IV-1A** relating to the accommodation of methanol are studied in details by TGA, XRPD and spectroscopic techniques. The red solid **IV-1A·MeOH** which was obtained by exposing the purple dehydrated **IV-1A** to methanol vapor shows the amorphous phase as confirmed by XRPD patterns (Figure 52). However, the **IV-1A·MeOH** easily loses methanol molecules after exposing in laboratory air within 2 hrs and the colors change from red (**IV-1A·MeOH**) to the original orange crystalline sample (**IV-1''**), as depicted in Figure 53. Furthermore after heating **IV-1A·MeOH** at $\approx 200^\circ\text{C}$ for 10 min the color changes from red (**IV-1A·MeOH**) to the previous purple sample (**IV-1A**) which denotes the reversible process of methanol accommodation in **IV-1A** with chromotropism. These results agree with the thermal analysis of **IV-1A·MeOH** in the temperature range $25\text{--}500^\circ\text{C}$ as depicted in Figure 54. The TGA profile indicates that the release of four methanol molecules from $[\text{Co}_2(\text{ampyz})_2(\text{SO}_4)_2](\text{MeOH})_4$ (**IV-1A·MeOH**) occurs at room temperature to $\approx 220^\circ\text{C}$ (found, 80.85%; Anal. Calcd, 80.15%) resulting to the dehydrated forms of $[\text{Co}_2(\text{ampyz})_2(\text{SO}_4)_2]$ (**IV-1A**), which are stable up to $\approx 240^\circ\text{C}$ and then the structures gradually decompose to the unidentified products. The XRPD and IR spectrum of **IV-1''** which was obtained by the evaporation of methanol from **IV-1A·MeOH** in laboratory air, reveal the identical XRPD positions and IR bands to the original crystalline **IV-1** (Figures 51 and 52). These results are indication of high selective recognition of **IV-1A** to water molecules. The selective methanol accommodation with chromotropism in dehydrated **IV-1A** when comparing with many solvents excluding water could be attributed to proper size of methanol molecule and weak host-guest interactions. The remarkable color change was also confirmed by the solid-state UV-vis diffuse reflectance spectrum in Figure 55. The spectrum of **IV-1A·MeOH** agrees with the typical *d-d* transition of high-spin Co^{II} in octahedral geometry with two observed bands at 21,200–19,300 and less than $9,000\text{ cm}^{-1}$, which are assigned to the $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$ and $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ transitions, respectively. These bands are slightly shifted to a lower energy when evaluating with the bands of **IV-1**, resulting the distinctive red color. As found in nature, cobalt-containing MOFs can have a wide range of colors which makes it easy, in many cases, to identify different phases. The most common colors are a very light pink for octahedral coordinated ones and an intense blue for tetrahedral coordination. For distorted octahedra, the pink color can intensify to orange, dark red, purple and violet depending on the ligand and the type of distortions.^[102] The selective guest accommodation with chromotropism of **IV-1** is summarized in Figure 56.

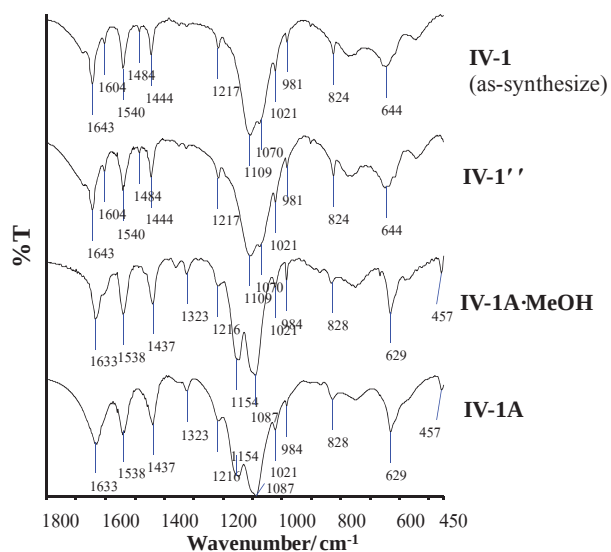


Figure 51 IR spectra for the dehydrated form **IV-1A**, the methanolic form **IV-1A·MeOH**, the rehydrated form **IV-1''** and as-synthesize **IV-1**.

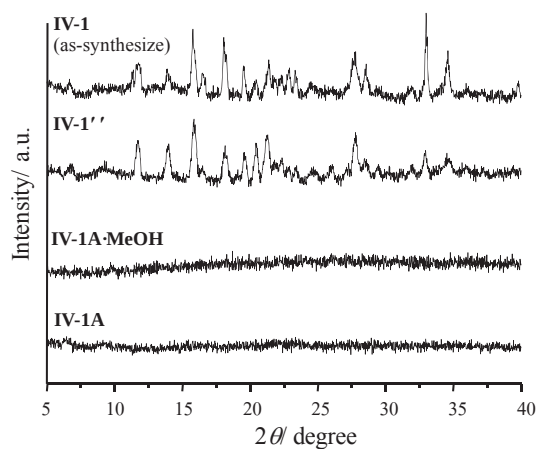


Figure 52 XRPD patterns for the dehydrated form **IV-1A**, the methanolic form **IV-1A·MeOH**, the rehydrated form **IV-1''** and as-synthesize **IV-1**.

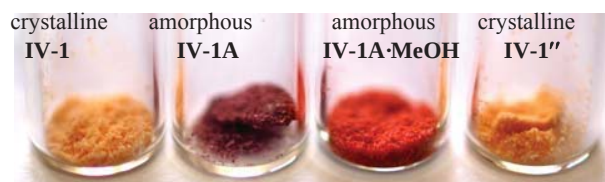


Figure 53 The chromatic changes in bulk samples.

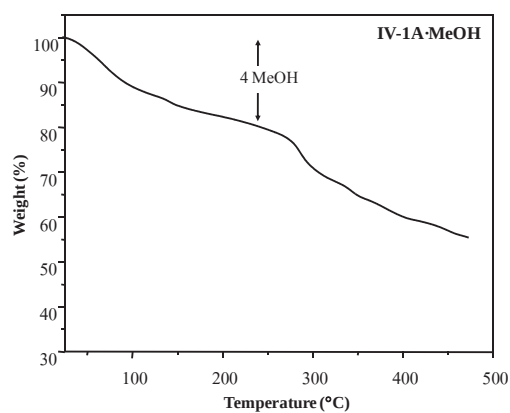


Figure 54 TGA curve of IV-1A·MeOH.

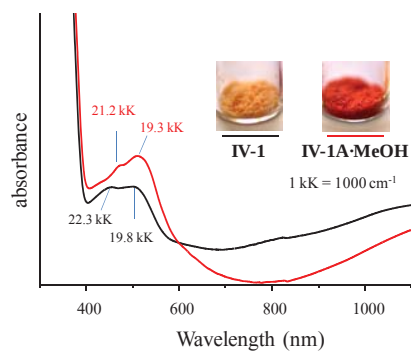


Figure 55 UV-vis diffuse reflectance spectra of as-synthesize IV-1 (black line) and IV-1A·MeOH (red line).

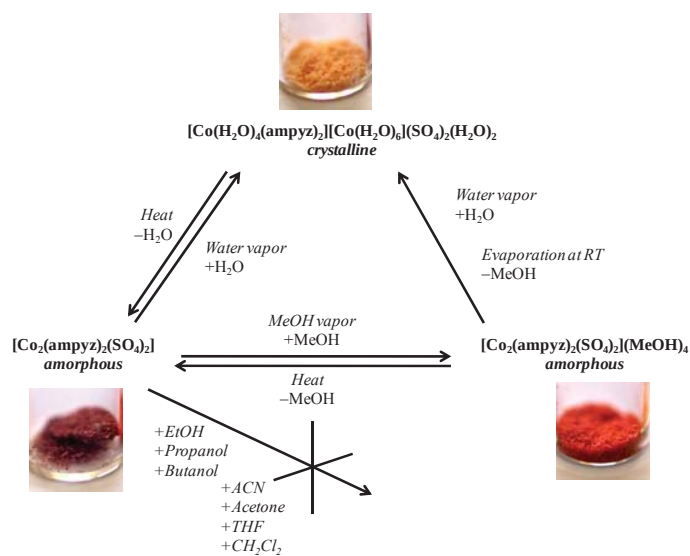


Figure 56 Selective guest accommodation with chromotropism of IV-1.

3.3 2D-1D Structural Phase Transformation of Co(II) 3,5-Pyridinedicarboxylate Frameworks with Chromotropism

3.3.1 Syntheses

Compound $[\text{Co}(\text{pydc})(\text{H}_2\text{O})_2]_n$ (**IV-5**) as well-shaped, high purity, and high quality single crystals suitable for X-ray diffraction was obtained by the direct reaction of the cobalt(II) nitrate hexahydrate with 3,5-pyridinedicarboxylic acid (H_2pydc) and potassium hydroxide in mixture of methanol, *N,N'*-dimethylformamide and aqueous media. Whereas the layering diffusion of aqueous solution of cobalt(II) nitrate hexahydrate into a *N,N'*-dimethylformamide solution of 3,5-pyridinedicarboxylic acid resulted in the single crystal formation of compound $[\text{Co}(\text{pydc})(\text{H}_2\text{O})_4]_n(\text{H}_2\text{O})_n$ (**IV-6**). These crystalline solids are stable in air and insoluble in water or common organic solvents such as methanol and ethanol. The 2D and 1D cobalt(II) coordination polymers containing two different coordination modes of 3,5-pyridinedicarboxylate bridges were obtained. The structures of **IV-5** and **IV-6** are described in the details here.

3.3.2 Description of crystal structures

$[\text{Co}(\text{pydc})(\text{H}_2\text{O})_2]_n$ (**IV-5**)

The coordination environment of the Co(II) center is shown in [Figure 57a](#). The Co^{2+} ions, with a CoNO_4 chromophore, have an intermediate geometry with a τ value of 0.57. The Co^{2+} ions is five-coordinated with a basal plane consisting of two oxygen atoms from coordination water molecule (O3 and O3A) with the Co–O distance of 2.075(1) Å and two oxygen atom from pydc bridges (O2 and O2A) with the Co–O distance of 2.149(1) Å. The apical position is occupied by nitrogen atom from pydc bridge (N1B) with the Co–O length of 2.188(2) Å. In addition, weak interactions are formed by two pydc-oxygen atoms (O1 and O1A) with the $\text{Co}\cdots\text{O}$ distance of 2.431(2) Å, forming seven-coordination. These secondary $\text{Co}\cdots\text{O}$ bonds are also reported in other Co complexes, for example, $[\text{Co}(4,4'\text{-bipy})_{1.5}(\text{NO}_3)_2]$, $[\text{Co}(1,2\text{-bis}(4\text{-pyridyl})\text{ethane})_{1.5}(\text{NO}_3)_2]_n$, $[\text{Co}(1,2\text{-bis}(4\text{-pyridyl})\text{ ethyne})_{1.5}(\text{NO}_3)_2](\text{MeOH})$ and $[\text{Co}(1,4\text{-bis}(3\text{-pyridyl})\text{-}2,3\text{-diaz-1,3-butadiene})_{1.5}(\text{NO}_3)_2(\text{H}_2\text{O})]_n$.²² However, the $\text{Co}\cdots\text{O}$ bond distances that found in compound **IV-5** are significantly longer than those in the reported compounds; therefore, it can be considered as semi-coordination.

The pydc^{2-} anion is not planar since the dihedral angles between the carboxylate group and the pyridyl ring is 13.62°. Each pydc act as tridentate ligand bridging three adjacent Co(II) centers. Two carboxylate groups are all deprotonate and coordinate to two cobalt atoms in a monodentate fashion, and pydc-nitrogen atom coordinates to the third cobalt atom, forming an infinite 2D layer structure in *ab* plane as shown in [Figure 57b](#). The three metal centers are in an isosceles triangle with the edge lengths (Co $\cdots$ Co separations) of 9.887(1) and 7.759(1) Å. Such unit repeats along the *ab* plane to generate an infinite 2D honeycomb network, which contains edge-sharing hexagons, with the metal ion and the

geometrical center of the pyridyl ring of pydc ligand being the vertex alternately and each arm of pydc ligand being the edge (Figure 58a). The layers are stacked together in an ABAB-sequence with the distance between layers of 3.566 Å, resulting in novel layer structures, eschewing interpenetration.

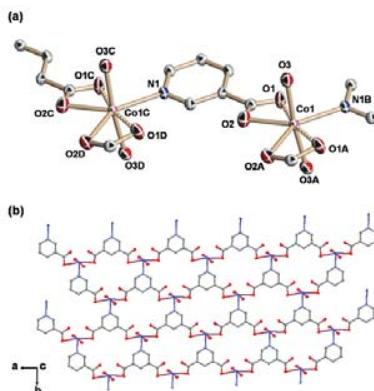


Figure 57 (a) Expanded asymmetric unit and atom labeling scheme of **IV-5**. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation A, B, C and D are symmetry-generated equivalents, (A) $-x, y, 1/2-z$; (B) $-1/2+x, 1/2+y, z$; (C) $1/2+x, -1/2+y, z$; (D) $1/2-x, -1/2+y, 1/2-z$. The dash lines present the weak coordinative bonds between pydc oxygen atoms and Co(II) ions and hydrogen atoms are omitted for the clarity. (b) 2D layer structure of **IV-5** in the *ab* plane.

These adjacent 2D sheets are mutually interlinked via the π - π interactions between the pyridyl rings of pydc in adjacent layers with a distance of 3.813 Å. (Figure 58a) and the 3D supramolecular architecture is further reinforced by strong interlayer hydrogen bonding among the carboxylate groups of pydc²⁻ ligands and coordinated water molecules (O(3)-H(1)⋯O(2) and O(3)-H(2)⋯O(1)) with O⋯O distances of 2.795(1) and 2.771(1) Å as shown in Figure 59.

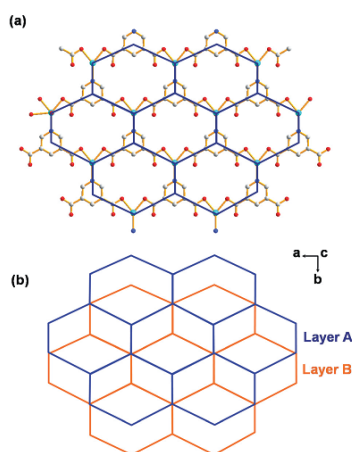


Figure 58 (a) Perspective view of the 2D layer with the honeycomb structure (blue line). (b) Schematic view of the two layers showing the honeycomb structure stacking viewed along *c*-axis.

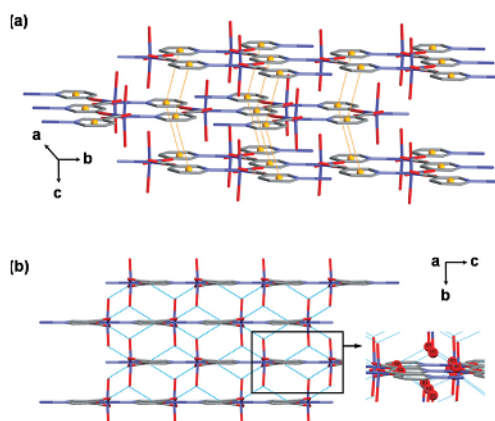


Figure 59 (a) The 3D framework formed by the intermolecular π - π interactions between the layers of **IV-5**. (b) Packing diagram of 3D network showing zig-zag arrangement of layers viewed along a -axis. The hydrogen bonding between the layers are shown in blue broken lines. The inset presents the hydrogen bonds from coordinated water molecules and carboxylate oxygen of pydc ligands.

[Co(pydc)(H₂O)₄]_n(H₂O)_n (IV-6)

Asymmetric unit of compound **IV-6** consists of two crystallographically independent Co²⁺ ions which are sited at the crystallographic symmetry center with half site occupancy, one pydc²⁻ anion, four coordinated and one uncoordinated water molecules as shown in [Figure 60](#). Co1 shows elongated octahedral geometry comprised of four oxygen atoms from water molecules at equatorial positions with the average Co1–O distance of 2.0850(10) Å, and two nitrogen atoms from pydc ligands at axial sites with Co1–N1 distance of 2.1698(12) Å. Co2 also shows an elongated octahedral geometry, surrounded by four water molecules at equatorial plane with the average Co2–O bond length of 2.0840(11) Å and two pydc-oxygen atoms at apical positions with the Co2–O6 distance of 2.0980(9) Å. The O/N–M–O/N bond angles are in the range of 84.63(5)–180.00(7)°, which are close to the ideal octahedral geometry.

The pydc acts as a didentate ligand connecting two Co, leading to a 1D zig-zag chain running along c axis with the Co...Co separation of 7.372(1) Å as shown in [Figure 61a](#). These adjacent 1D chains are mutually interlinked via the hydrogen bonds between the carboxylate groups of pydc²⁻ ligands, uncoordinated and coordinated water molecules, forming a 2D hydrogen-bonded layer as shown in [Figure 61b](#). Additionally, these 2D layers are arrayed orderly in a staggered ABAB... packing pattern viewing along the crystallographic b -axis with a distance of 3.675 Å between the pyridyl rings of the adjacent layers and then extended to a 3D network, via the π - π interactions between the pyridyl rings of pydc²⁻ ligands as shown in [Figure 62a](#), forming 1D channels along the crystallographic b axis with guest water molecules inside as shown in [Figure 62b](#). The 3D supramolecular architecture is further reinforced by the O–H...O

hydrogen bonding among the coordinated water molecules and pydc^{2-} ligands with the $\text{O}\cdots\text{O}$ distances in the range of 2.651(1)-2.831(1) Å.

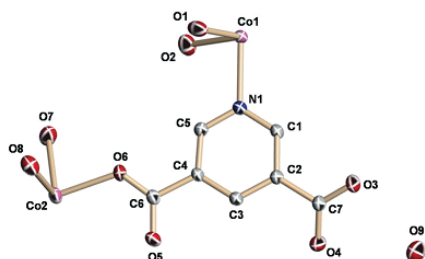


Figure 60 Asymmetric unit and atom labeling scheme of **IV-6**. The ellipsoids are shown at 50% probability level. All hydrogen atoms are omitted for the clarity.

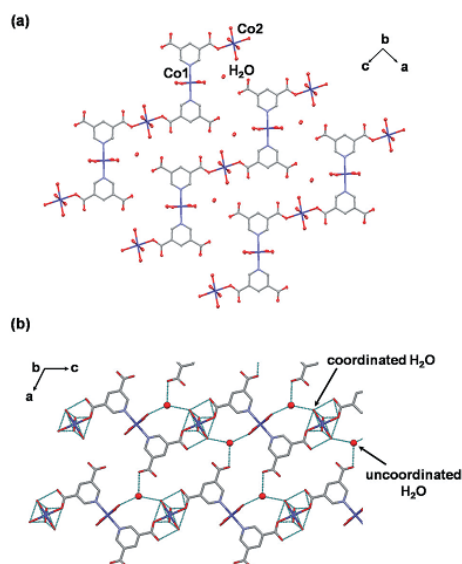


Figure 61 (a) 1D zig-zag chain of **IV-6** in the ac plane formed by the Co(II) and pydc^{2-} ligand. Water molecule filled in the cavity between chains. (b) The 2D hydrogen-bonded layered network via hydrogen bonds between pydc^{2-} ligands, coordinated- and uncoordinated water molecules among the 1D zig-zag chains (blue dash lines). All hydrogen atoms are omitted for the clarity.

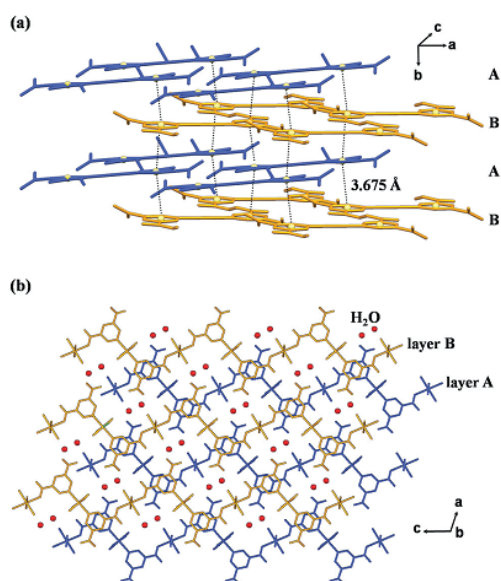


Figure 62 (a) Formation of the 3D framework in **IV-6** by face-to-face $\pi\cdots\pi$ interactions between staggered ABAB sheets (black dash lines). Uncoordinated H_2O are omitted for the clarity. (b) Packing diagram of **2** viewed along b -axis, showing 1D channels with guest water molecule inside.

3.3.3 Thermogravimetric Analysis

To assess the thermal stability, the thermal gravimetric (TGA) was recorded for the single-phase polycrystalline samples in the temperature range 30–800 °C. During the heating process, the TGA profile of **IV-5** (indicates that the releases of two coordinated water molecules occur at the first step of weight loss in the temperature range 80–190 °C (found, 13.71%; Anal. Calcd, 13.84%), resulting to the dehydrated form of $[\text{Co}(\text{pydc})]$ (**IV-5A**), which are stable up to ≈ 340 °C and then the structure rapidly decomposes at higher temperatures. For compound **IV-6**, TGA curve revealed that compound **IV-6** underwent a two-step weight loss. One solvated and four coordinated water molecules were loss below 190 °C with the weight loss of 26.19% (calcd. 28.68%), resulting to the dehydrated form of $[\text{Co}(\text{pydc})]$ (**IV-6A**). This dehydrated form **IV-6A** is stable up to ≈ 340 °C and then rapidly decomposes to the unidentified products.

3.3.4 Structural Phase Transformation by Thermal De/Rehydration Processes.

To verify the dynamic structural behavior of compounds **IV-5** and **IV-6**, the ad/desorption of coordinated and uncoordinated water molecules in both compounds have been studied relating to their dehydration and rehydration processes by elemental analyses, TGA, XRPD and spectroscopic techniques. Interestingly, the water molecules can be adsorbed fully by exposing the

evacuated samples to water vapor at room temperature. The heating and exposing procedures were repeated for four times to demonstrate the reversibility of the de- and rehydration processes.

The most promising feature of the crystals of **IV-5** is that it undergoes the water induced irreversible crystal-to-amorphous transformation with chromotropism driven by thermal dehydration and rehydration. When the single crystals of **IV-5** was heated to 200 °C in air for 30 min, these crystals suddenly lose the crystallinity and the colors changed from deep pink (**IV-5**) to purple (**IV-5A**). Then this non-crystalline solid was exposed to the water vapor for 12 h and the color of solid **IV-5A** was not return to that of the original crystalline one but change to pale orange (**IV-5B**). Therefore, the bulk sample of **1** was used to study in detail. The dehydrated form **IV-5A** was obtained by heating the bulk samples at 200 °C in air for 2 h and the rehydrated form **IV-5B** was obtained by exposing the dehydrated sample to water vapor for 24 h at room temperature without condensation. The XRPD pattern and TGA curve of **IV-5** are shown in Figures 63 and 64. The elemental analysis of **IV-5A** for [Co(pydc)] (Anal. Calcd: C, 37.53; H, 1.35; N, 6.25%. Found: C, 37.37; H, 1.41; N, 6.28%), and XRPD results indicate that the dehydrated form **IV-5A** is in an amorphous phase which is formed by the collapse of framework structure of **IV-5** accompanied with the destruction of hydrogen bonding networks when all water molecules are removed. The original crystalline phase **IV-5** cannot be restored from the amorphous phase of **IV-5A** after rehydration process but it is readily converted into the second crystalline phase **IV-5B** with the chemical composition of [Co(pydc)(H₂O)₄](H₂O) (Anal. Calcd: C, 26.77; H, 4.17; N, 4.46%. Found: C, 26.73; H, 3.76; N, 4.54%) and the XRPD pattern as shown in Figure 63 and the de/rehydrated processes between **IV-5A** and **IV-5B** take place reversibly. These results suggest the crystalline-to-amorphous and reversible amorphous-to-crystalline transformations in the framework of **IV-5** induced by the hydration control. However, XRPD pattern of **IV-5B** shows broad and low intensities diffraction peaks indicating that the crystallinity was incompletely recovered after rehydration processes.

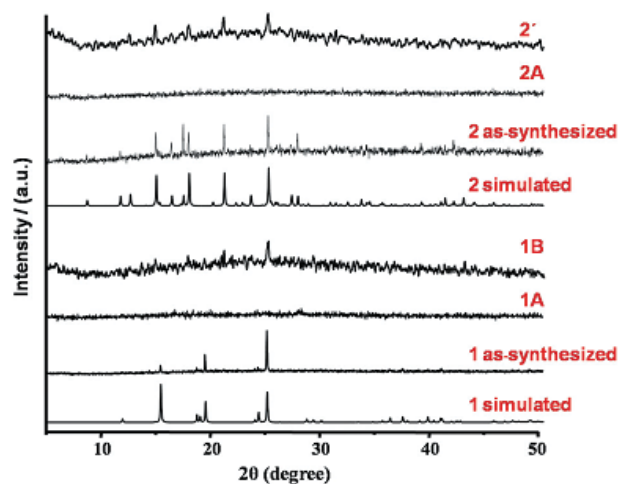


Figure 63 XRPD patterns of compounds **IV-5** (**1**) and **IV-6** (**2**).

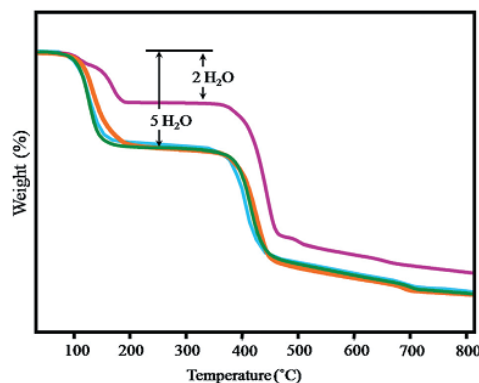


Figure 64 TGA curves of as-synthesized **IV-5** (pink line), the rehydrated form **IV-5B** (orange line), as-synthesized **IV-6** (green line) and the rehydrated form **IV-6'** (blue line).

For compound **IV-6**, after the as-synthesized compound **IV-6** was heated with the same condition to that of **IV-5**, a purple powder (**IV-6A**) was obtained. The elemental analysis and XRPD pattern results indicate that the chemical composition of the powder is $[\text{Co}(\text{pydc})]$ (**IV-6A**) in an amorphous phase (Anal. Calcd: C, 37.53; H, 1.35; N, 6.25%. Found: C, 37.25; H, 1.42; N, 6.31%). Interestingly, this amorphous phase **IV-6 A** can be restored to the original crystalline phase of **IV-6'** in which the color returns to that of the original one after being soaked in water vapor for 24 h, as indicated by the elemental analysis with the chemical composition of $[\text{Co}(\text{pydc})(\text{H}_2\text{O})_4](\text{H}_2\text{O})$ (Anal. Calcd: C, 26.77; H, 4.17; N, 4.46%. Found: C, 26.77; H, 3.98; N, 4.65) and the XRPD measurement results. The restored solid has the same XRPD pattern as the simulated one from single-crystal X-ray diffraction data of **IV-6** as shown in Figure 4.37, indicating that **IV-6'** and **IV-6** are the same compound. Therefore, **IV-6** could be a new absorbing agent for water molecules. In fact, **IV-6** has a dynamic structure resulting from the water adsorption behavior of its evacuated solid which is typical for a first-generation porous solid following the Kitagawa classification with the “guest-induced crystal-to-amorphous transformation (CAT)” framework. When the water molecules (guest and coordinated) are removed, the framework collapses due to the destruction of the hydrogen bond system. The framework of **IV-6** is restored with the reintroduction of water molecules between chains and the reformation of the hydrogen-binding system. The analogous situation was reported on the 1D linear chains of $[\{\text{Cu}(\text{BF}_4)_2(4,4'\text{-bipy})(\text{H}_2\text{O})_2\}4,4'\text{-bipy}]_n$, which are linked by hydrogen bonds between metal-free 4,4'-bipy molecules and coordinated H_2O molecules to form 2D non-interpenetrated sheets.

Furthermore, the IR spectra were present to confirm the structural phase transformation behavior in **IV-5** and **IV-6** where the decreasing intensity peak at ~ 1560 ($\nu_s \text{ COO}^-$) and the different splitting peaks at ~ 1440 cm^{-1} ($\nu_s \text{ COO}^-$) are observed for the amorphous phase (Figure 65). These indicate that the

coordination mode of carboxylate bridging ligand was lost of symmetry. In contrast, these features are removed in the IR spectra of the rehydrated form, which are unidentical to those of the as-synthesized one for **IV-5** but being identical to those of the fresh one for **IV-6**. All of these results confirm the water-induced crystalline-to-amorphous phase transformation with chromotropism in the supramolecular network of **IV-5** and **IV-6** with irreversible and reversible processes, respectively. In addition, the reversibility of the water adsorption and the change in the coordination environment can be visualized by the change in color of the compounds. This change of color can be attributed to the change of the crystal field splitting of the central Co^{2+} ions during the adsorption and removal of molecules. The change of the color of the Co compounds prompted us to study the changes in the electronic transitions in the samples. For this, the solid-state UV-vis diffuse reflectance spectra as shown in Figure 66 clearly show that the bands observed in **IV-6** and **IV-6'** correspond very well to the identical transitions causing the same color of bulk products, and evidence that **IV-6** and **IV-6'** have the same Co^{2+} environments. While **IV-5** and **IV-5B** exhibit the different spectra indicating that the geometry of Co^{2+} center rearranged when the water molecules are adsorbed. In addition, the spectrum of **IV-5B** is found to be identical to that of **IV-6** and **IV-6'**, indicating the same Co^{2+} environments and the same orange color. Whereas the amorphous phases **IV-5A** and **IV-6A** show the identical spectra with a lower-energy broad band centered around 550 nm, but different from those of other samples, giving the distinctive purple color. The chromotropic behaviors of both compounds are principally ascribed to the changes of the d-orbital energy level, induced by the drastic change in the coordination environments around metal center during dehydration and rehydration processes. All of these results confirm the water-induced structural phase transformation in coordination networks **IV-5** and **IV-6**.

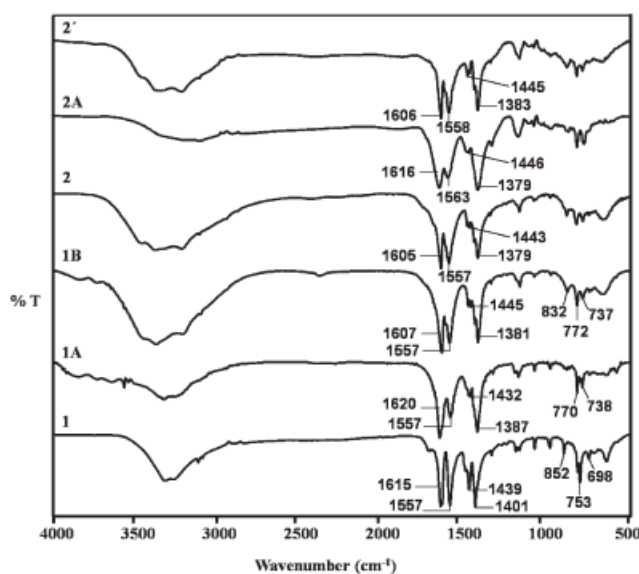


Figure 65 IR spectra of compounds **IV-5** and **IV-6**.

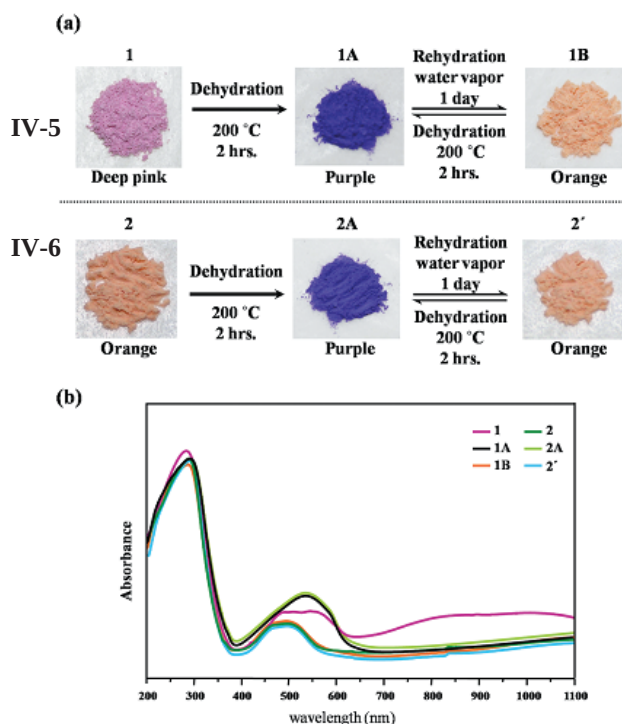


Figure 66 (a) Change in color during de- and rehydration in bulk samples of **IV-5** and **IV-6**. (b) The UV-vis diffuse reflectance spectra of as-synthesized **IV-5** (pink line), the dehydrated form **IV-5A** (black line), the rehydrated form **IV-5B** (orange line), as-synthesized **IV-6** (deep green line), the dehydrated form **IV-6A** (pale green line) and the rehydrated form **IV-6'** (blue line).

However, the rehydrated form **IV-5B** and **IV-6'** were heated and cooled for four times to repeat the reversibility of the de- and rehydration processes. The results exhibit the color shuttle change between pale orange (**IV-5B** and **IV-6'**) and purple (**IV-5A** and **IV-6A**), suggesting the water induced reversible crystal-to-amorphous transformation phenomenon. The IR spectra, UV-vis diffuse reflectance spectra, XRPD spectra, elemental analysis and TGA curve of **IV-5B** and **IV-6'** correspond very well to the identical results, these indicate that the structure of **IV-5** completely transforms to the structure of **IV-6** through the dehydration and rehydration processes as the schematic representation of this structural phase transformation shown in Figure 67.



Figure 67 Schematic diagram illustrates the structural conversion of 2D layer to 1D chain structures by thermal dehydration and rehydration processes.

In order to elucidate the important role of the crystal structure (via the intermolecular interactions) on the dynamic behavior of the frameworks we have compiled our previously published data of the mononuclear compounds $[M(H_2O)_4(ampyz)_2][M(H_2O)_6](SO_4)_2(H_2O)_2$ and the present data of 2D and 1D frameworks. Both compound systems exhibit crystal-to-amorphous phase transformation with chromotropism but with different dynamic behaviors. The previous compounds contain numerous hydrogen donors and hydrogen acceptors from coordinated and uncoordinated water molecules, amino and sulfate groups to generate the intermolecular hydrogen bond interactions as well as π - π stacking. Thus, they have more accessible intermolecular hydrogen bonding that able to trigger the reversible crystal-to-amorphous phase transformation after de/readsoption processes. While in the present compound **IV-5** after the water readsoption process, the 2D framework of **IV-5** was not recovered but change to another crystalline phase of 1D framework (compound **2**). This new phase is more stable and responsible for the reversible crystal-to-amorphous phase transformation with chromotophism. This may be due to the less intermolecular interactions which are not enough to trigger the phase transformation to the original 2D framework as compared to that of **IV-6**.

3.4 Structural diversity and magnetic studies in 1D, 2D and 3D azido-bridged cobalt(II) hybrid frameworks

3.4.1 Structural diversity and magnetic properties in 1D and 2D azido-bridged cobalt(II) complexes with 1,2-bis(2-pyridyl)ethylene

Molecule-based magnetic materials involving azido bridges have incessantly attracted much attention because of their diverse architectures with interesting physical properties, such as single molecule magnet, single chain magnet and long-range magnetic ordering behaviours.^[2, 102-105] The crystal engineering of molecular magnetism aims to control the spins in molecules and molecular assemblies.^[59, 106] As an excellent ligand, containing several pairs of electrons, azido can readily bridge two or more spin

carriers (Figure 5.1) and effectively mediate either ferromagnetic or antiferromagnetic coupling, normally through EO and EE modes, respectively.^[2, 102-105] It is known that one of the interesting structural aspects of working with the cobalt ion is the wide range of stable geometries.^[102] Consequently, when the azide ion and coligands are coupled with cobalt(II) ions, which accommodate four-, five- and six-coordination depending on the situation, various low-dimensional structures are expected along with interesting magnetism.^[107-112] The versatile *N,N'*-ditopic bridging spacer 1,2-bis(4-pyridyl)ethylene and its derivatives have been used as coligands widely in organic-inorganic hybrid materials including azido complexes and they usually give unexpected structures with interesting magnetic orders.^[113-116] However, the *trans*-1,2-bis(2-pyridyl)ethylene (2,2'-bpe) (Figure 68) has not yet been reported in any azido complexes. Herein this chapter shows that 2,2'-bpe can act as both terminal (*endo*) and bridging (*exo*) co-ligands in a Co^{II} azido system, which effectively support either blocking the metal's coordination sites or extending the structural dimensions.

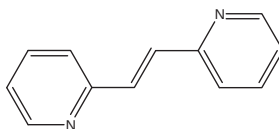


Figure 68 *trans*-1,2-bis(2-pyridyl)ethylene (2,2'-bpe)

3.4.1.1 General observations and spectroscopic characterizations

The layered diffusion reaction of CoCl₂·6H₂O, 2,2'-bpe and NaN₃ in a 1:1:2 molar ratio in water and ethanol media yielded the mixture of blue rod-shaped crystals of **V-1** and pink square-shaped crystals of **V-2**. The crystals were manually separated because of their visible differences in colors and shapes of the crystals. Then the physical purities of crystalline phase of bulk products were confirmed by XRPD technique comparing with their simulated XRD patterns from the single-crystal data (Figure A6, Appendix A). An attempt has been made to find the optimal condition for preparing a single phase of **V-1** or **V-2**, based on molar ratios and solvents without success. The IR spectrum (Figure 69) of **V-1** with end-on mode of azide shows a very strong band at 2089 cm⁻¹ $\nu_{as}(\text{N}_3^-)$ with a shoulder peak and medium band at 1296 cm⁻¹ $\nu_s(\text{N}_3^-)$. Compound **V-2** containing both μ_2 -1,1 and μ_2 -1,3 bridging azides shows two very strong bands due to $\nu_{as}(\text{N}_3^-)$ mode at 2097 and 2072 cm⁻¹ and medium band at 1296 cm⁻¹ $\nu_s(\text{N}_3^-)$. The electronic spectra show the overlapped bands of the *d-d* transitions arising from penta-coordination and octahedral geometries of high-spin Co^{II} ions for **V-1** and exhibit the typical *d-d* transitions of octahedral geometry for **V-2** (Figure 70).

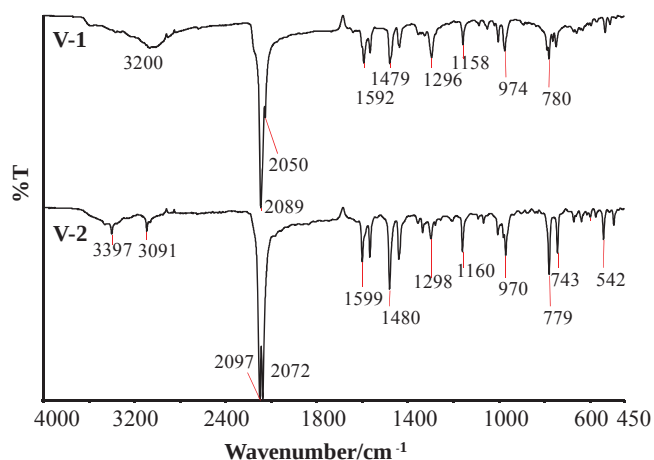


Figure 69 Infrared spectra of **V-1** and **V-2**.

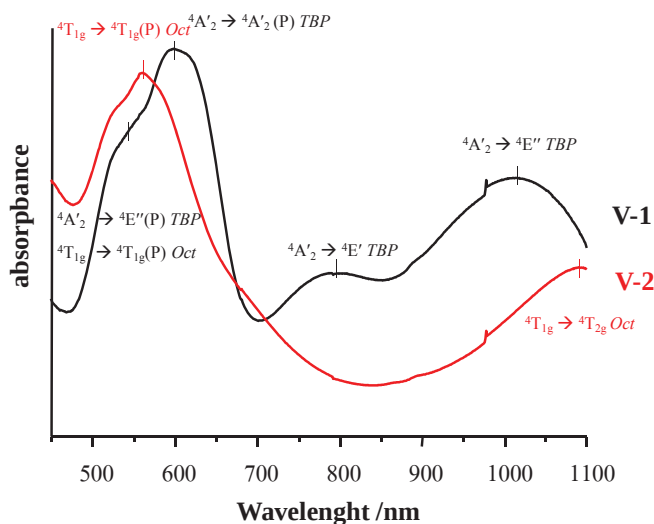


Figure 70 UV-Vis diffuse reflectance spectra of **V-1** and **V-2** with the *d-d* transitions labeled.^[93]

3.4.1.2 Description of crystal structures

$[\text{Co}_3(\text{N}_3)_6(\text{OH}_2)_2(2,2'\text{-bpe})_2]_n(2,2'\text{-bpe})_n$ (**V-1**)

X-ray analysis revealed that compound **V-1** contains two crystallographic independent Co1 and Co2 ions bridged by three independent EO azido ligands as shown in Figure 71(a). Co1 is placed in an intermediate 5-coordination geometry, slightly distorted toward trigonal bipyramid with a τ value^[44] of 0.55, where the metal atom is coordinated by four N atoms from four EO azide anions and a N atom from a monodentate 2,2'-bpe. Co2 has a CoN_4O_2 compressed octahedral geometry, which is located on the crystallographic inversion centre and it is coordinated by four N atoms from EO azido ligands in the equatorial positions and two water molecules in the axial sites.

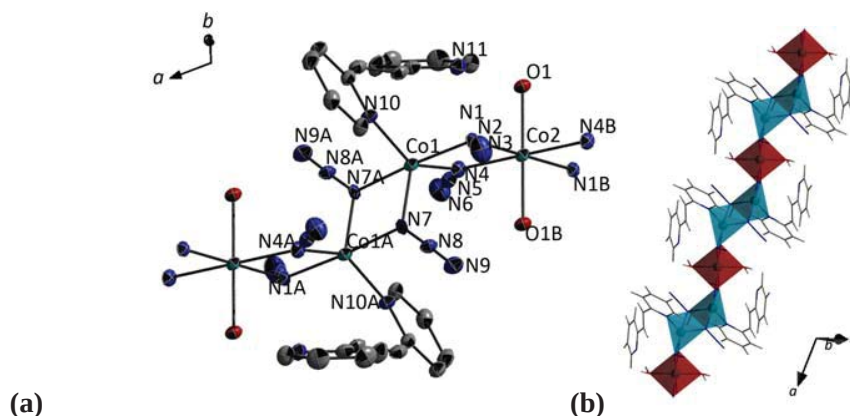


Figure 71 Crystal structure and atom labeling scheme of **V-1**. The ellipsoids are shown at 50% probability level (a). Atoms labeled with the notation “A” and “B” are symmetry-generated equivalents, (A) $1-x, -y, 1-z$; (B) $-x, -y, 1-z$. The 1D chain of **V-1** is running along a axis with octahedra and hexahedra of Co^{II} ions (b). The free 2,2'-bpe and H atoms are omitted for clarity.

The adjacent Co^{II} centres are connected by an azide in the double-EO mode along the a axis associated with the inversion centre, to build a 1D zigzag chain with the rare $[-5-5-6-]$, sequence of cobalt(II) coordination numbers (Figure 71(b)). The bond angles of $\text{Co}-\text{N}-\text{Co}$ are in the range between $97.09(12)^\circ$ and $100.37(12)^\circ$ and the intrachain $\text{Co}\cdots\text{Co}$ separations through double EO azido bridges are $3.174(1) \text{ \AA}$ for $\text{Co1}\cdots\text{Co1}^i$ ($i = 1-x, -y, 1-z$), and $3.207(1) \text{ \AA}$ for $\text{Co1}\cdots\text{Co2}$, as usually observed for this kind of bridging in cobalt(II) azido compounds.^[107] The coordination 2,2'-bpe acts as terminal coligand because the intrachain hydrogen bonding between N atom on terminal pyridine of coordination 2,2'-bpe and H atom of coordination water [$\text{O1H}\cdots\text{N11} = 1.89 \text{ \AA}$ (172°), $\text{O1}\cdots\text{N11} = 2.811(4) \text{ \AA}$] causes the arrangement of 2,2'-bpe in *cis* position with the dihedral angle between two pyridine rings of $55.65(1)^\circ$. In addition, the chains are assembled *via* $\text{C}-\text{H}\cdots\pi$ interactions and the intermolecular hydrogen bonds between uncoordinated 2,2'-bpe and coordination water along b axis [$\text{O1H}\cdots\text{N12} = 1.80 \text{ \AA}$ (172°), $\text{O1}\cdots\text{N12}^i = 2.750(4) \text{ \AA}$], yielding 2D structure of **V-1** as shown in Figure 72. The interchain $\text{C}-\text{H}\cdots\pi$ interactions involve $\text{C4}-\text{H}$ interacting to the centroid of terminal pyridine ring of adjacent coordination 2,2'-bpe with the distance of $2.876(4) \text{ \AA}$ and a $\text{C4}-\text{H}\cdots\pi$ angle of 133° .

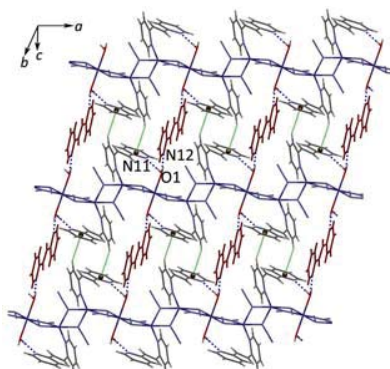


Figure 72 Formation of 2D sheet of **V-1** in *ab* plane formed by C–H... π interactions and hydrogen bonds between the neighbouring chains. The dotted lines represent the intramolecular O1–H...N11 hydrogen bond and the intermolecular O1–H...N12 hydrogen bond and C–H... π interaction.

[Co(N₃)₂(2,2'-bpe)]_n (V-2**)**

The crystal structure of **V-2** is depicted in Figure 73. Compound **V-2** has a 2D wavy layer structure which consists of an azido-Co^{II} neutral chain with alternating double EE and double EO azido bridges along *a* axis and ditopic 2,2'-bpe bridging Co^{II} ions along *b* axis. There is only one crystallographically independent Co^{II} ion, which has elongated octahedron comprised of two N atoms from bridging 2,2'-bpe in the axial sites and four N atoms from two EE and two EO azide ions located in the equatorial positions. The adjacent Co^{II} ions in a chain are related by inversion centers and linked alternately by double EE and double EO azido bridges with the Co...Co distances of 5.052(2) Å and 3.314(1) Å, respectively. These bridging modes of azide are widely found in the polymeric chain complexes containing additional chelating ligands.^[115, 117-123]

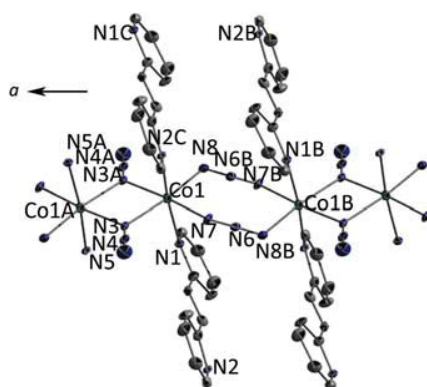


Figure 73 Expanded asymmetric unit and atom labeling scheme of **V-2**. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A”, “B” and “C” are symmetry-generated equivalents, (A) 1–*x*, 1–*y*, 1–*z*; (B) –*x*, 1–*y*, 1–*z*; (C) *x*, 1+*y*, *z*.

In double EO bridged $\text{Co}(\text{N}_3)_2\text{Co}$ moiety, the Co1-N3-Co1A-N3A ring is strictly planar due to the existence of the inversion center with the Co1-N3-Co1A angle of $102.25(14)^\circ$. For double EE mode, the EE bridges adopt a chair conformation for the $\text{Co}-(\text{N}_3)_2\text{-Co}$ unit with the dihedral angle between N7N6N8BN8N6BN7B plane and CoN8N7 plane of $33.8(1)^\circ$. The 2,2'-bpe acts as ditopic connector in *trans* position bridging the cobalt(II) azido neutral chains along *b* axis, building 2D wavy sheet of **V-2** (Figure 74). The $\text{Co}\cdots\text{Co}$ separation *via* 2,2'-bpe spacer is $8.322(2)$ Å.

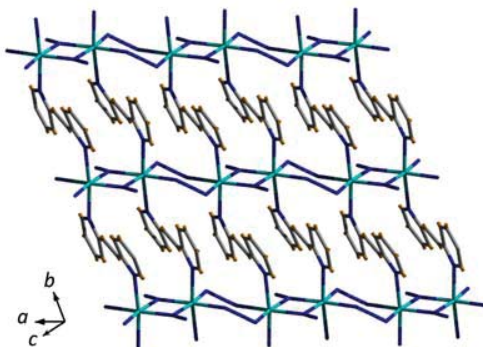


Figure 74 2D wavy coordination network of **V-2**.

3.4.1.3 Long-range magnetic ordering behaviors

The magnetic susceptibility of a polycrystalline sample of **V-1** at 2-310 K is shown in Figure 75. At 310 K, the $\chi_m T$ value is $11.16 \text{ cm}^3 \text{ K mol}^{-1}$ per Co_3 unit, which is significantly higher than the spin-only value of $5.62 \text{ cm}^3 \text{ K mol}^{-1}$ expected for uncoupled three $S = 3/2$ ions, owing to ferromagnetic interactions and the significant orbital contribution of high-spin Co^{II} in an octahedral surrounding. $\chi_m T$ value increases gradually upon cooling to *ca.* 50 K. Below this temperature, $\chi_m T$ increases abruptly to a maximum value of $48.75 \text{ cm}^3 \text{ K mol}^{-1}$ at 15 K because of rapidly increasing ferromagnetic coupling between adjacent spin carriers. Upon cooling to 2 K, $\chi_m T$ decreases quickly to $8.32 \text{ cm}^3 \text{ K mol}^{-1}$ because of magnetization saturation and possible interchain antiferromagnetic interactions. The similar behavior has been observed in other related complexes containing 1D double EO azido bridge such as $[\text{Co}(2,2'\text{-bithiazoline})(\text{N}_3)_2]_n$ ^[107], $[\text{Mn}(\text{N}_3)_2(\text{pyz})]_n$ ^[124] (*pyz* = pyrazine) and $[\text{Ni}(\text{en})(\text{N}_3)_2]_n$ ^[125] (*en* = ethylenediamine). The χ_m^{-1} values above 100 K were fitted with the Curie-Weiss law $\chi = C/(T-\theta)$ with a Curie constant $C = 9.59(3) \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = +43.7(5) \text{ K}$ indicating dominant ferromagnetic coupling between Co^{II} ions *via* double EO azido bridges. Owing to lack of theoretical model for the complicated chain composed by octahedral Co^{II} and non-octahedral Co^{II} ions, the exchange parameters could not be estimated.

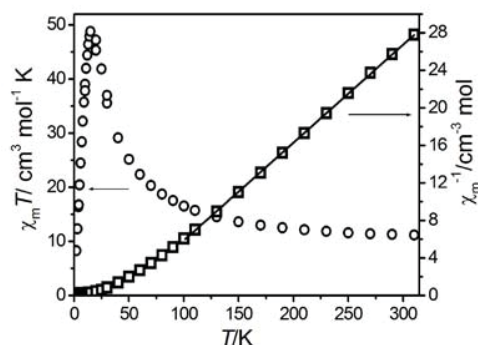


Figure 75 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **V-1** at $H = 10$ kOe from 2 to 310 K. The solid line represents the best fit to the Curie-Weiss law.

In addition, the dominant ferromagnetic coupling was confirmed by magnetization measurements performed at 1.8 K in an external field 0–5 T, as shown in Figure 76. The molar magnetization curve exhibits a rapid increase, reaching about 80% of M_s at 1 kOe which appears to be a soft ferromagnet because coercivity was not observed. At higher field, the saturation magnetization, $M_s = 8.81 N\beta$ agrees with three ferromagnetically coupled Co^{II} ions with an expectation value of $M_s = 6\text{--}9 N\beta$.^[126, 127] A comparison with the Brillouin function for three isolated $S = 3/2$ spins stresses the remarkable cooperativity in this system, consistent with the ferromagnetic interaction.

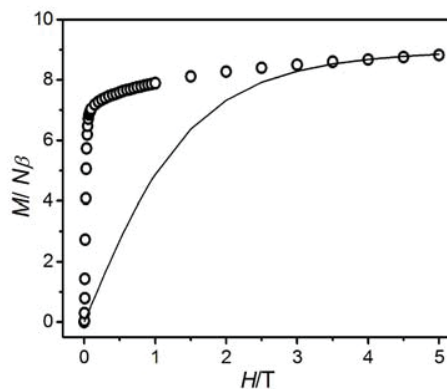


Figure 76 Field dependence of magnetization of **V-1** at 1.8 K. The continuous line corresponds to the Brillouin function for three Co^{II} ions $S = 3/2$ with $g = 2.0$.

All evidence points to the long-range magnetic ordering, likely due to interchain coupling through the extensive hydrogen bonds and $\text{C-H}\cdots\pi$ contacts. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization plot under a field of 50 Oe (Figure 77, inset) showed a disagreement below 6 K and presented a swell at around 6 K, suggesting the onset of long-range antiferromagnetic ordering

among the ferromagnetic chains. However, the ZFC-FC plot under a field of 1000 Oe shows no maximum and trends to saturate at lower temperature and does not show the irreversibility, thus indicating that the weak interchain antiferromagnetic interaction is overcome by the external field. These features are indicative of a metamagnet built of ferromagnetic chains. The temperature dependence of *ac* susceptibility was also measured at zero *dc* field (Figure 78). The χ' signal shows a peak at 6 K confirming the occurrence of phase transition, and the nonzero χ'' signal below 6 K is consistent with the ferromagnetic order. No frequency dependence of the *ac* signals was observed among 25-997 Hz. The metamagnetic behavior was further confirmed by the hysteresis loop measurements, as given in Figure 77, which revealed that **V-1** is a metamagnet with a typical crossover magnetic hysteresis in the slightly sigmoid shape of the *M(H)* curve.^[128-130] The critical field H_c is ≈ 70 Oe, estimated as the field at which a maximum $\delta M/\delta H$ value is reached.

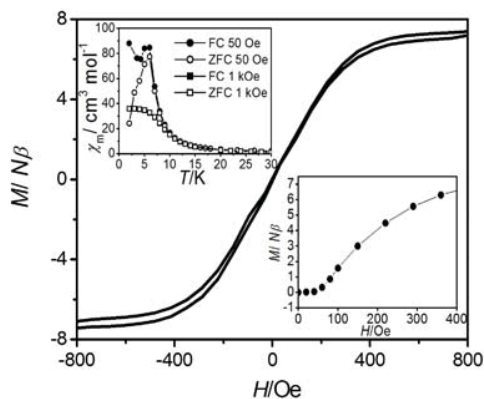


Figure 77 Hysteresis curve for **V-1** at 1.8 K. The insets show the initial plot in a low field (right) and the ZFC-FC plots of **V-1** at 50 Oe and 1 kOe (left).

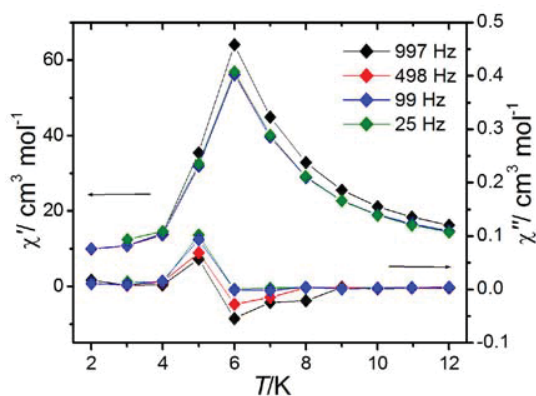


Figure 78 Temperature dependence of the *ac* susceptibility for **V-1** at $H_{dc} = 0$ Oe, $H_{ac} = 3$ Oe, with frequencies of 25 – 997 Hz.

This metamagnetic-like transition results from the presence of weak interchain antiferromagnetic interactions among the strong ferromagnetic chains. At low temperature, the antiferromagnetic coupling of the ferromagnetic chains leads to an antiferromagnetic ground state. With an increase in the external magnetic field ($H_c > 70$ Oe), the ferromagnetic chains tend to parallel align, resulting in ferromagnetic ordering. This behavior is characteristic of a metamagnet built of ferromagnetic chains.^[26, 125, 128-135] However, because of the strong spin-orbit coupling of Co^{II} ions, the magnetic interaction might be more complicated.^[102, 129] This similar metamagnetic-like transition was also observed in other polymeric chain systems containing ferromagnetically 1D double EO azido bridge with weak interchain antiferromagnetic interactions.^[26, 125, 128, 130] For instance, the previous related compound $[\text{Mn}(\text{tptz})(\text{N}_3)_2]_n$ ^[130] (tptz=2,4,6-tris(2-pyridyl)-1,3,5-triazine) (Figure 79) which contains similar double EO azide-bridged 1D chains assembling by face-to-face π - π and C-H $\cdots\pi$ interactions, revealed overall metamagnetic behavior below 2.7 K with very small H_c of approximately 80 Oe. This reported value of H_c is very close to that of this work.

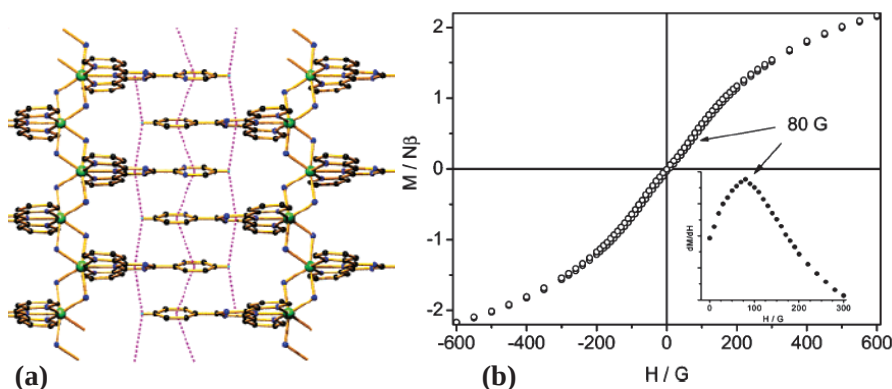


Figure 79 Formation of a 2D sheet of $[\text{Mn}(\text{tptz})(\text{N}_3)_2]_n$ (a) and the hysteresis curve with inset of $\delta M/\delta H$ at low field (b).^[130]

The magnetic susceptibility of **V-2** is depicted in Figure 80. The $\chi_m T$ value of ca. $3.01 \text{ cm}^3 \text{ K mol}^{-1}$ at 310 K is much higher than the spin-only value of high-spin d^7 ion ($1.87 \text{ cm}^3 \text{ K mol}^{-1}$), owing to ferromagnetic interactions *via* μ_2 -1,1 N_3^- bridges and the significant orbital contributions of the octahedral Co^{II} ions. Upon cooling, the $\chi_m T$ decreases gradually down to $0.04 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K, indicating dominant antiferromagnetic coupling *via* μ_2 -1,3 N_3^- bridges. The plot of χ_m versus T (Figure 5.16, inset) exhibits an abrupt increase below about 17 K to a maximum value of $0.02 \text{ cm}^3 \text{ mol}^{-1}$ at 2 K, which is probably attributed to paramagnetic impurity or possible spin canting. The data above 150 K obey the Curie-Weiss law with a Curie constant $C = 3.58(3) \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = -58(2) \text{ K}$. The

negative θ suggests the antiferromagnetic coupling between Co^{II} ions and spin-orbital coupling of Co^{II} ions in an octahedral field.

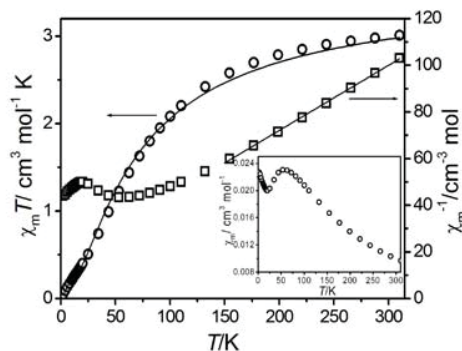


Figure 80 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **V-2** from 2 to 310 K. The solid lines correspond to the best fit (see the text). Inset: plot of χ_m vs. T for **V-2**.

Because of the spin-orbit coupling contribution of Co^{II} ions, it is difficult to find an accurate analytical expression to describe the temperature dependence of the magnetic susceptibility for the polymeric chains of the Co^{II} ions. However, Rueff et al.,^[136-138] have proposed a very successful phenomenological approach for a low-dimensional antiferromagnetic Co^{II} system that allows an estimation of the strength of the antiferromagnetic exchange interactions and also the effects of spin-orbit coupling. They postulate the phenomenological equation:

$$\chi_m T = A \exp(-E_1/kT) + B \exp(-E_2/kT) \quad (5)$$

$A + B$ equals the Curie constant ($\approx 2.8\text{-}3.4 \text{ cm}^3 \text{ K mol}^{-1}$ for octahedral Co^{II}) and E_1 and E_2 represent the activation energies corresponding to the spin-orbit coupling parameter and the antiferromagnetic exchange interaction, respectively where E_2 is related to the magnetic coupling constant J according to the Ising chain approximation, $\chi_m T \propto \exp(+J/2kT)$. This equation adequately describes the spin-orbit coupling, which results in a splitting between discrete levels and the exponential low-temperature divergence of the susceptibility. The reasonable values for magnetic coupling and spin-orbit interaction have been reported in several studies of 1D and 2D Co^{II} networks.^[136-141] The fitted parameters are $A + B = 3.58 \text{ cm}^3 \text{ K mol}^{-1}$, equivalent to the Curie constant obtained from the Curie-Weiss law in the high temperature range; $E_1/k = +61(2) \text{ K}$ which is consistent with those reported for 1D and 2D cobalt(II) systems.^[126, 136, 137, 140] For the value found for the antiferromagnetic exchange interaction, E_2/k equals to $+4.1(2) \text{ K}$, corresponding to $J = -8.2 \text{ K}$, according to the Ising chain approximation, $\chi_m T \propto \exp(+J/2kT)$.

It can be seen from the abrupt increase of the plot of χ_m vs. T below about 17 K and from the other reported complexes containing chains of alternating double *EO* and double *EE* bridging modes of azides that these complexes frequently exhibit weak ferromagnetism due to spin canting,^{[117, 119-}

^{122]} thus the magnetic behaviors of **V-2** were further clarified. The temperature dependencies of the ZFC and the FC magnetization were measured at a low field of 20 Oe, as shown in Figure 81(inset). The obvious divergence of the ZFC and FC plots below 12 K indicates hysteretic long-range magnetic order, which is compatible with the maxima in χ' and the nonzero χ'' signal around 12 K in *ac* susceptibility at 997 Hz (Figure 82). The isothermal magnetization with a field up to 5 T at 1.8 K is depicted in Figure 81. The initial increase of magnetization shows a slight positive curvature and is not linear with the field up to 7 kOe, and then it becomes almost linear up to 0.146 $N\beta$ at 5 T, far from the theoretical saturation magnetization of Co^{II} ion, suggesting the overall antiferromagnetic coupling between Co^{II} ions. A hysteresis loop of **V-2** is clearly observed when the field is less than 10 kOe, giving a coercive field of ≈ 300 Oe and remanent magnetization (M_r) of $\approx 0.002 N\beta$. These results indicate that the spin-canting effect between overall antiferromagnetically coupled Co^{II} ions leads to residual spins. The canting angle (α) is estimated to be about 0.05° based on the equation 1.17, $\alpha = \sin^{-1}M_r/M_s$ (theoretical saturation magnetization (M_s) = $g'SN\beta = 2.16 N\beta$, $S' = 1/2$, $g' = 4.33$ for octahedral Co^{II} at 1.8 K).^[59, 106]

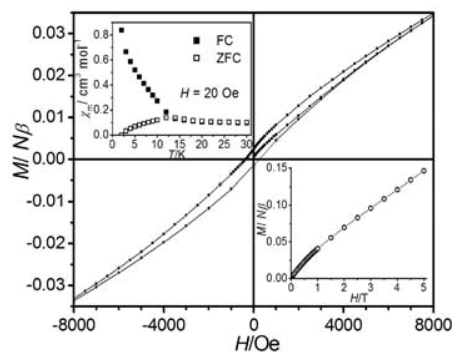


Figure 81 The hysteresis loop of **V-2** at 1.8 K. The insets show the ZFC and FC magnetization at $H = 20$ Oe from 2 to 30 K. (left) and the field dependence of magnetization at 1.8 K (right).

Compound **V-2** exhibits hard ferromagnetism whereas **V-1** is soft ferromagnetism, which may be attributed to the difference between parallel anisotropy axes in **V-2** and almost orthogonal trigonal bipyramidal and octahedral axes in **V-1**. It is well known that two mechanisms lead to spin canting (equation 1.16): (i) magnetic anisotropy and (ii) antisymmetric exchange.^[59, 106] However, the spin canted structure is not compatible with the crystal structure of **V-2** because of the presence of an inversion center between the bridged Co^{II} sites, which forbids the occurrence of antisymmetric interactions. The observation of the spin canting in **V-2** should be attributed to the great single-ion anisotropy of octahedral cobalt(II) ions or a possible structure phase transition at low temperature.^[117, 119-122] The weak ferromagnetism due to spin canting in the presence of an inversion center between metal sites were also observed in other complexes containing the same bridging mode of azide,

such as $[\text{Co}(\text{dpa})(\text{N}_3)_2]_n$ ^[121] (dpa = 2,2'-dipyridylamine), $[\text{Mn}(\text{dpq})(\text{N}_3)_2]_n$ ^[120] (dpq = dipyrdo-(3,2-*d*:2',3'-*f*)quinoxaline) and $[\text{Mn}(\text{TaiEt})(\text{N}_3)_2]_n$ ^[117] (TaiEt = 1-ethy-2-(*p*-tolylazo)imidazole). The spin canting of **V-2** will be discussed and compared with compounds **V-3**, **V-4** and the related azido complex systems next topic.

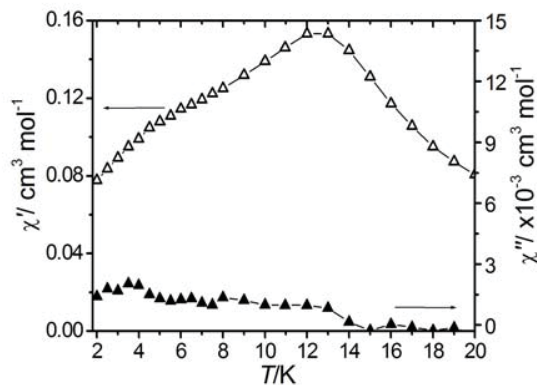


Figure 82 Temperature dependence of the *ac* susceptibility for **V-2** at $H_{\text{dc}} = 0$ Oe, $H_{\text{ac}} = 3$ Oe, with frequency of 997 Hz.

3.4.2 Spin canting and metamagnetism in 2D and 3D cobalt(II) coordination networks with alternating double end-on and double end-to-end azido bridges

The crystal engineering and magnetism of molecule-based coordination frameworks with low- or high dimensional structures have been of great interest in recent years with the intention of understanding the fundamental magneto-structural correlations within the structure and controlling the spins in molecules and molecular assemblies for conceiving practical functional molecule-based materials.^[59, 102, 142-144] To rational design of magnetic molecular assemblies, it is important to select the appropriate bridging ligands that effectively transmit the exchange interactions between the spin carriers together with the aspects of diverse topologies. An excellent azido ligand is the one of the extensively used bridging ligands in the construction of magnetic molecular materials because it can provide a short bridge with the extremely versatile coordination modes and effectively mediates either ferromagnetic or antiferromagnetic coupling generally through μ_2 -1,1 (end-on, EO) and μ_2 -1,3 (end-to-end, EE) modes, respectively. In addition the different combinations of EO and EE azido bridging modes may exist in the same structure, leading to several topologies as well as competing magnetic interactions in sign according to a certain EO and EE azido bridging sequence.^[103, 118, 122, 145-148] Consequently, the fascinating magnetic phenomena have been recognized in many azido-bridged coordination polymers which have been an active research area so far.^[2, 103, 105, 149] Likewise, the organic coligands are very significant to the formation of some particular architecture and to the structural modification. It is well-known that the *N,N'*-ditopic diimine spacer, pyrazine (pyz) is a long bridge for magnetic systems and effectively transfers electron in

the antiferromagnetic superexchange pathways between metal centers. With pyz and derivative of pyz ligands, the azido complexes usually exhibit various structural topologies together with interesting magnetic properties.^[26, 124, 150-152] For instances, 2D layer of $[\text{Fe}(\text{N}_3)_2(\text{pyz})]_n$ (Figure 83) showed metamagnetism arising from the competition of ferromagnetically coupled EO azido chain and 2D antiferromagnetically coupling *via* pyz.^[26] In contrast with the lack of local anisotropic ions, this metamagnetic feature for the Mn^{II} and Cu^{II} analogues was not observed.^[124, 152]

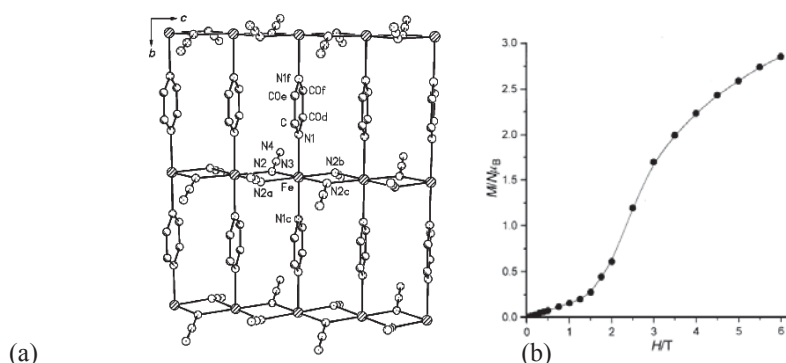


Figure 83 2D layer structure of $[\text{Fe}(\text{N}_3)_2(\text{pyz})]_n$ (a) and isothermal magnetization plot at 1.8 K.^[26]

This topic focused on the versatile 2-aminopyrazine (ampyz) spacer as organic coligand in magnetic azido complex system. Ampyz spacer contains many interaction sites; coordination sites at N atoms on pyrazine ring, hydrogen donor site at amino group, and the intermolecular π - π stacking site through aromatic moieties, which has been used for constructing many coordination polymers.^[34, 36, 37, 153, 154] Without the spin carriers, the structural diversity of zinc(II) azido complexes with ampyz has been recently obtained depending on the molar ratio of the starting components.^[36] With this in mind, herein this topic shows that ampyz spacer well accommodates in the magnetic anisotropic Co^{II} azido system. Remarkably, new 2D layer $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (**V-3**) and 3D framework $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (**V-4**) of azido-bridged Co^{II} coordination networks with the identical molar ratio were well prepared in different preparative techniques and characterized structurally and magnetically. In addition both compounds similarly contain the 1D chain of alternately double EO and double EE azido-bridged Co^{II} ions, whereas the ampyz spacers in **V-3** and **V-4** are in dissimilar arrangements, *trans*- and *cis*-positions in octahedral Co^{II} ions for **V-3** and **V-4**, respectively. As it is known, only two azido Co^{II} chains with alternating double EE and double EO bridges have been reported in the literature.^[121, 155] Although **V-3** and **V-4** are similar in local coordination environments but somewhat different in structural symmetries, dimensionalities and bridging parameters, consequently, their magnetic behaviors at low temperature reveal the significant disparities. The magnetic investigation of **V-3** shows the coexistence of big spin canting angle and metamagnetism having magnetic ordering at 10 K, whereas the magnetic behavior of **V-4** simply exhibits

spin-canted antiferromagnetism below T_N of 16 K. These behaviors allow us to perform the magnetic investigation and discussion.

3.4.2.1 General observations and spectroscopic characterizations

The different preparative methods of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, azide anion and ampyz in a 1:2:2 molar ratio in a mixture of ethanol and aqueous media yielded two cobalt(II) coordination polymers containing ampyz spacer together with the alternating double EO and double EE azido bridging mode which show the different dimensionalities. The layered diffusion reaction in ambient temperature gave the orange rectangular crystals of **V-3** showing the high symmetric 2D square-grid structure of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ whereas the hydrothermal reaction at 90 °C for 1 day yielded the red-orange polygonal crystals of **V-4** showing 3D framework of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$. These experiments do not only demonstrate the significant role of the primary units, the excellent azido bridges and versatile ampyz spacer for building both structures, but also demonstrate the important influence of reaction's conditions on the structural topologies and dimensionalities. The physical purities of crystalline phase of bulk products were confirmed by XRPD technique comparing with their simulated XRD patterns from the single-crystal data.

The IR spectra of both compounds are quite similar (Figure 84). Compounds **V-3** and **V-4** containing both μ_2 -1,1 and μ_2 -1,3 bridging azides, show two very strong bands due to $\nu_{\text{as}}(\text{N}_3^-)$ modes at 2100 and 2080 cm^{-1} for **V-3** and 2105 and 2068 cm^{-1} for **V-4** indicating the presence of two different azido groups. The weak band at $\approx 1320 \text{ cm}^{-1}$ is $\nu_{\text{s}}(\text{N}_3^-)$ for the EO bridge. This band is not active for the symmetrical EE bridge.^[118] Two narrow weak bands in the regions 3400–3300 cm^{-1} can be assigned to $\nu(\text{N-H})$ of the primary amine in the ampyz ligand.

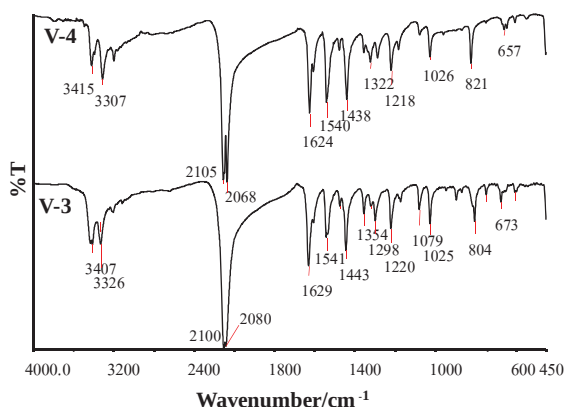


Figure 84 IR spectra of **V-3** and **V-4**.

The solid-state UV-vis diffuse reflectance spectra of both compounds (Figure 85) agree with the typical $d-d$ transition of high-spin Co^{II} in octahedral geometry with two observed bands at 20000–18000 and less than 9500 cm^{-1} , which are assigned to the ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ and ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$

transitions, respectively. The weak band at *ca.* 15000 cm⁻¹ which is assigned to the $^4T_{1g} \rightarrow ^4A_{2g}$ transition is not well resolved. The growing bands which appear higher than 22000 cm⁻¹ are due to charge transfer transition and internal transition within ampyz.^[93]

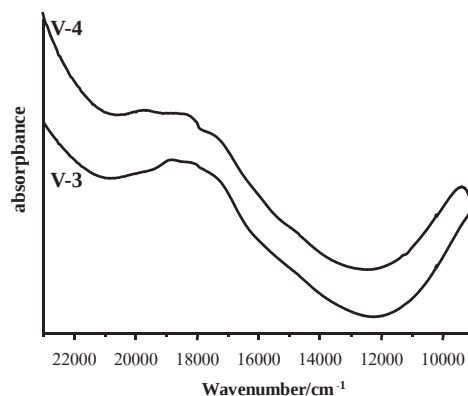


Figure 85 UV-Vis diffuse reflectance spectra of **V-3** and **V-4**.

3.4.2.2 Description of crystal structures

2D layer of [Co(N₃)₂(ampyz)]_n (**V-3**)

Compound **V-3** was crystallized in orthorhombic crystal system with high centrosymmetric space group, *Immm*. The coordination environment of the Co^{II} center is shown in Figure 86. The Co1 atom, EE azido atoms N6, N7 and EO azido N3 atom all lie on a crystallographically *ac* mirror plane. In addition there are three other vertical mirror planes. The first *bc* mirror plane lies on EO azido N3, N4 and N5 atoms. Second is another *bc* mirror plane lying on EE azido atom N7 and the third is *ab* mirror plane lying on pyrazine N1 and Co1 atoms. There is only one crystallographically independent Co^{II} ion, which has slightly elongated octahedron comprised of two N atoms from bridging ampyz in the axial sites (2.193(4) Å) and four N atoms from two EE and two EO azide ions located in the equatorial positions (2.141(5)–2.116(4) Å).

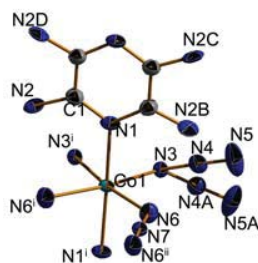
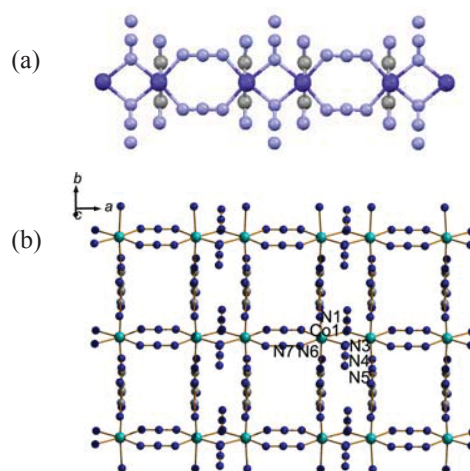


Figure 86 Crystal structure and atom labeling scheme of **V-3**, (i) $x, -y, 2-z$; (ii) $-x, -y, z$. The ellipsoids are shown at 50% probability level. All disordered positions of amino group and N atoms of EO-azide are shown.

The adjacent Co^{II} ions are related by those crystallographic mirror planes and inversion center and linked alternately by double EE and double EO azido bridges, giving rise to a neutral 1D perfect linear chain along a axis (Figure 87) with the $\text{Co}\cdots\text{Co}$ separations of 5.157(2) and 3.283(1) Å, respectively, where the sum of these values equals to the crystallographic a parameter of 8.440(2) Å. In double EO bridged $\text{Co}(\mu_2\text{-}1,1\text{ N}_3)_2\text{Co}$ moiety, the Co1-N3-Co1A-N3A ring is strictly planar due to the existence of the inversion center and mirror planes with the Co1-N3-Co1A angle of $101.7(3)^\circ$, as is usually observed for this kind of azido bridge.^[156] The disordered EO azido bridge, which is nearly linear ($\angle\text{N3-N4-N5} = 178.1^\circ$), slightly deviates (up and down) from that plane. For double EE mode, the $\text{Co}(\mu_2\text{-}1,3\text{ N}_3)_2\text{Co}$ moiety forms the perfect planarity because the crystallographic ac mirror plane is placed on this ring. As a result, a dihedral angle δ between the N6N7N6aN6cN7bN6b mean plane and the CoN6N6b plane is 0° , as shown in Figure 88. The symmetric $\text{Co1}\bar{\text{N6}}\text{N7}$ angle is $129.3(5)^\circ$. It is the uncommon observation of the complete planar for the $\text{M}(\mu_2\text{-}1,3\text{ N}_3)_2\text{M}$ moiety in the alternating chain of double EE and double EO azido bridges, where the chair conformation is usually observed.^[117, 123] As it is known, the lowest δ value is 1.82° which is found in $[\text{Mn}(\text{TaiEt})(\text{N}_3)_2]_n$ ($\text{TaiEt} = 1\text{-ethyl-2-}(\rho\text{-tolylazo})\text{imidazole}$).^[117]



The ampyz acts as a N,N' -ditopic connector in *trans* position, bridging this neutral azido cobalt(II) chain along b axis and building the 2D square-grid sheet of **V-3**, as shown in Figure 87. The intralayer π - π stacking interactions among ampyz spacers stabilize the layer of **V-3** with the separations of 3.502(4) and 4.938(4) Å. The Co...Co separation *via* ampyz spacer equals to the crystallographic b parameter of 7.1808(12) Å. Moreover, the adjacent 2D sheets of **V-3** are assembled by interlayer hydrogen bonding between the amine H of ampyz and N6 atom of EE azido bridge [$N2H\cdots N6^i = 2.39$ Å (157°), $N2\cdots N6^i = 3.205(14)$ Å, (i) = $1/2-x, 1/2-y, 1/2+z$], yielding a 3D framework of **V-3** with the closest interlayer Co...Co separation of 7.8453(9) Å, as shown in Figure 89.

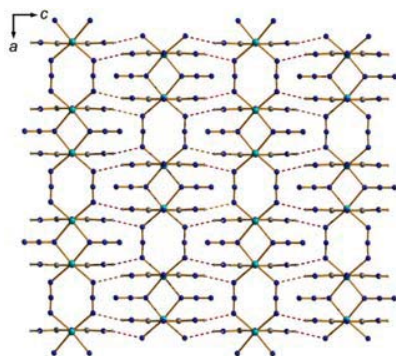


Figure 89 Formation of 3D framework of **V-3** in ac plane formed by hydrogen bonds between the neighboring layers. The dotted line represents the interlayer $N2-H2B\cdots N6$ hydrogen bond.

3D layer of $[Co(N_3)_2(ampyz)]_n$ (**V-4**)

The crystal structure of **V-4** is depicted in Figure 90. Compound **V-4** shows 3D framework which is isostructural to the reported zinc(II) compound $[Zn(N_3)_2(ampyz)]_n$.^[36] There is one crystallographically independent Co^{II} ion, which is octahedral CoN_6 chromophore comprised of two N atoms from two bridging ampyz ligands in *cis*-position and four N atoms from two EE and two EO bridging azido ions. 3D framework of **V-4** also consists of an azido cobalt(II) neutral zigzag chain with the alternating double EE and double EO azido bridges along a axis but N,N' -ditopic ampyz spacers link adjacent Co^{II} ions in *cis*-arrangement. The angle of Co...Co...Co in the zigzag chain is $116.62(8)^\circ$ and the Co...Co separation *via* ampyz spacers are 7.1119(14) and 7.6013(14) Å (Figure 91). The hydrogen bonds between the amine H of *cis*-ampyz spacers and N atoms of azido bridges additionally stabilize the entire framework [$N3H\cdots N4^i = 2.48$ Å (138°), $N3\cdots N4^i = 3.174(3)$ Å; $N3H\cdots N7^{ii} = 2.57$ Å (124°), $N3\cdots N4^{ii} = 3.130(3)$ Å; and $N3H\cdots N8^{iii} = 2.31$ Å (171°), $N3\cdots N8^{iii} = 3.165(3)$ Å, (i) = $1/2+x, 1/2-y, -1/2+z$, (ii) = $1/2-x, -1/2+y, 1/2-z$, (iii) = $-1/2+x, 1/2-y, 1/2+z$]. The adjacent Co^{II} ions in an azido chain are related by inversion centers and linked alternately by double EE and double EO azido bridges with the Co...Co

distances of 5.3279(10) Å and 3.2438(6) Å, respectively. In double EO bridging mode, the Co1–N4–Co1A–N4A ring is strictly planar due to the existence of the inversion center with the Co1–N4–Co1A angle of 98.90(7)°. The EO azido bridge is nearly linear ($\angle\text{N4–N5–N6} = 178.1(3)^\circ$) and deviate up and down 43.8° from the plane of Co_2N_2 . For double EE bridging mode, the EE bridges adopt a chair conformation for the $\text{Co}(\mu_2\text{--}1,3\text{ N}_3)_2\text{Co}$ unit with the dihedral angle δ of 12.57(6)°, as shown in Figure 5.24. The Co1N8N9 and Co1N7N9B angles are 124.3(2)° and 139.3(2)°, respectively.

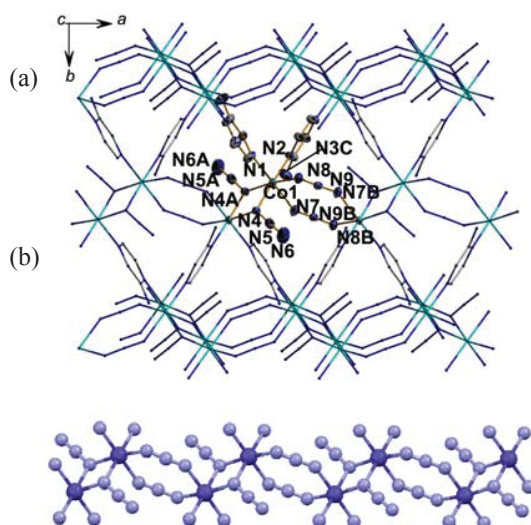


Figure 90 3D framework with atom labeling scheme of **V-4** in *ab* plane (a). The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A”, “B” and “C” are symmetry-generated equivalents, (A) $-x, 1-y, 1-z$; (B) $1-x, 1-y, 1-z$; (C) $1/2+x, 1/2-y, 1/2+z$. Azido Co^{II} neutral linear chain with the alternating double EE and double EO azido bridges along *a* axis (b).

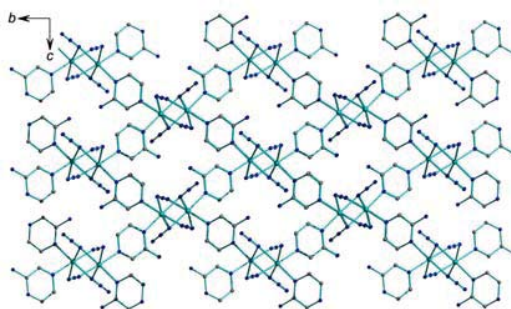


Figure 91 Another view of 3D structure of **V-4** in *bc* plane.

3.4.2.3 Long-range magnetic ordering behaviors

The magnetic susceptibility of a polycrystalline sample of **V-3** at 2-310 K is shown in Figure 92. At 310 K, the $\chi_m T$ value is $2.98 \text{ cm}^3 \text{ K mol}^{-1}$, which is significantly higher than the spin-only value of $1.87 \text{ cm}^3 \text{ K mol}^{-1}$ expected for $S = 3/2$ ion, owing to the significant orbital contribution of high-spin Co^{II} in an octahedral surrounding. Upon cooling, the $\chi_m T$ value decreases slowly, attains a minimum value of $2.21 \text{ cm}^3 \text{ K mol}^{-1}$ at 70 K and then shows an abrupt increase to a maximum value of $4.64 \text{ cm}^3 \text{ K mol}^{-1}$ at 18 K. This behavior indicates that a small spontaneous magnetization emerges in an antiferromagnetic system, owing to spin canting in which the predominantly antiferromagnetic coupled spins from different sublattices are not perfectly antiparallel, but canting to each other, and the resulting net moments are correlated in a weak ferromagnetic fashion.^[108, 111, 144] Upon further cooling to 2 K, $\chi_m T$ decreases gradually down to $0.70 \text{ cm}^3 \text{ K mol}^{-1}$, suggesting antiferromagnetic interactions among the neighboring azido Co^{II} chains or the magnetization saturation.

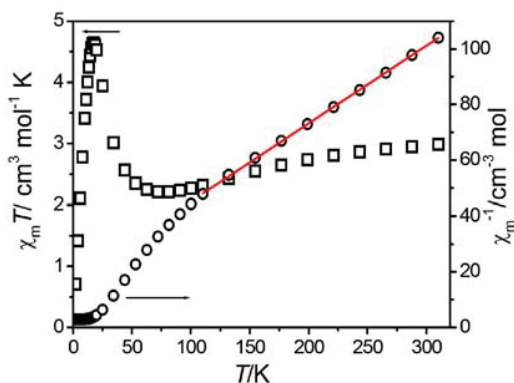


Figure 92 Temperature dependence of $\chi_m T$ (□) and χ_m^{-1} (○) of **V-3** from 2 to 310 K at $H = 10$ kOe. The solid lines correspond to the best fit to the Curie-Weiss law.

The χ_m^{-1} values above 100 K were fitted with the Curie-Weiss law $\chi = C/(T-\theta)$ with a Curie constant $C = 3.58(2) \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = -61.8(13) \text{ K}$. The C is in the usual range of octahedral high-spin Co^{II} ions.^[102, 111, 126] The negative θ value can be attributed to both significant spin-orbit coupling of the octahedral Co^{II} ions with a $^4\text{T}_{1g}$ ground term and the presence of antiferromagnetic coupling between the Co^{II} centers through the $\mu_{1,3}$ -azido bridging ligands. Owing to the lack of a theoretical model for the alternating chain of exchange interactions of octahedral Co^{II} with large spin-orbit coupling effects, the exchange parameters could not be estimated.

To characterize the low-temperature behaviors of **V-3**, the temperature dependencies of field-cooled (FC) and zero-field-cooled (ZFC) magnetization were performed under a field of 100 Oe upon warming from 2 K, as shown in Figure 93. The ZFC and FC plots present a cusp at around 11 K and show a disagreement below 10 K, suggesting the onset of long-range antiferromagnetic ordering

and hysteretic long-range magnetic order, respectively. The temperature dependence of the *ac* susceptibility measured in a field of 3 Oe shows the same features (Figure 94). The maximum of χ' observed at 11 K, in agreement with the above results, confirming the occurrence of phase transition. The absence of an out-of-phase signal (χ'') around this temperature points to a long-range antiferromagnetic order. However, the χ'' value shows nonzero signal below 10 K which is the signature of a magnetized state, thus indicating that a partly canted antiferromagnetic structure exists below this temperature.^[157-159]

The temperature dependence of the FC magnetization of **V-3** at various fields is depicted in Figure 93, inset. The application of different magnetic fields in the range of 100–3000 Oe showed a strong field dependence of the magnetic susceptibility below T_N . For applying fields below 500 Oe, the curves show a swell at around 11 K, indicating the antiferromagnetic ordered state. In lower temperature region, the magnetizations increase due to small spontaneous magnetization of canted antiferromagnetism. However, applying magnetic field above 800 Oe is sufficient to overcome these interactions. The cusp disappears and the magnetization tends to saturate at higher field. These trends suggest a field-induced magnetic phase transition from an antiferromagnetic to a ferromagnetic-like state.^[135, 160, 161]

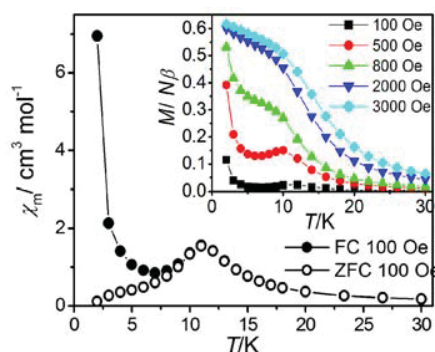


Figure 93 The ZFC and FC magnetization of **V-3** at $H = 100$ Oe from 2 to 30 K. The inset shows the FC magnetization plot of **V-3** below 30 K at various fields.

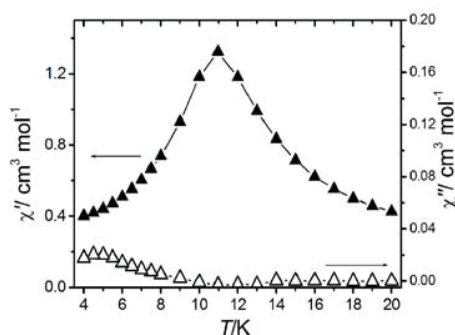


Figure 94 Temperature dependence of the *ac* susceptibility for **V-3** at $H_{dc} = 0$ Oe, $H_{ac} = 3$ Oe, with frequency of 997 Hz.

In addition, the spin canting and metamagnetic-like behaviors were confirmed by the hysteresis loop measurements at 2 K in an external field of 0–5 T, as given in Figure 95. The initial $M(H)$ plot shows a characteristic sigmoidal form (Figure 95, inset), which is a typical feature of a metamagnetic behavior.^[26, 135, 160, 161] The critical field H_c is ≈ 600 Oe, estimated as the field at which a maximum $\partial M/\partial H$ value is reached. At $H < 600$ Oe, a linear increase in $M(H)$ is associated with antiferromagnetic interactions, and then above the critical field, the magnetization is drastically increased to $H = 5$ T without saturation and exhibits a magnetization value of $0.79 N\beta$, that is far from the theoretical saturation magnetization of Co^{II} ion ($M_s = 2.16 N\beta$, $S' = 1/2$, $g' = 4.33$ for octahedral Co^{II} at 2 K),^[59, 106] suggesting the overall antiferromagnetic coupling between Co^{II} ions. Clearly, a higher field is required to reach saturation to a ferromagnetic phase. Upon decreasing the applied field, the magnetization curve decreases along a different route and exhibits a slightly sigmoid-shaped hysteresis loop with coercive field of ≈ 350 Oe and remanent magnetization M_r of $\approx 0.29 N\beta$. These behaviors confirm the occurrence of spontaneous magnetization of **V-3** which is in agreement with the observed coexistence of spin-canted antiferromagnetism and metamagnetism. The canting angle (α) is estimated to be about 7.7° based on the equation $\alpha = \sin^{-1} M_r/M_s$, where M_s the theoretical saturation magnetization of Co^{II} ion at 2 K.

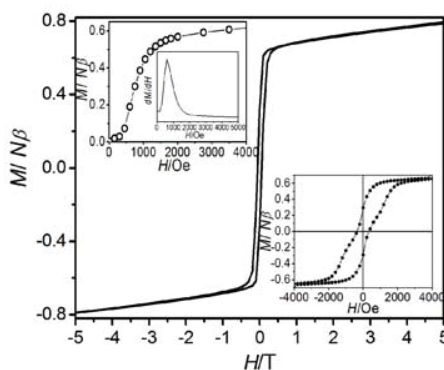


Figure 95 Field dependence of the magnetization for **V-3** at 2 K. The insets show the initial plot in a low field (left) and the hysteresis loop (right).

Temperature dependence of the magnetic susceptibility of **V-4** at 2–310 K under the field of 10 kOe is presented in Figure 96. The $\chi_m T$ value of $2.86 \text{ cm}^3 \text{ K mol}^{-1}$ at 310 K is much higher than the spin-only value of high-spin Co^{II} ions, owing to the orbital contributions of octahedral Co^{II} ions. Upon cooling the temperature, the $\chi_m T$ values decrease gradually and show the cusp around 15 K with the $\chi_m T$ value of $0.57 \text{ cm}^3 \text{ K mol}^{-1}$, after that the $\chi_m T$ values drop sharply down to $0.09 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The plot of $\chi_m T$ vs. T at small fields in the temperature range of 2–30 K is depicted in Figure 96, inset. Below 16 K, the abrupt increases in $\chi_m T$ values are observed under the field below 100 Oe, the susceptibility becomes

field dependent. At small field of 10 Oe, $\chi_m T$ shows an abrupt increase to a maximum value of $9.86 \text{ cm}^3 \text{ K mol}^{-1}$ at 12 K before decreasing in the lowest temperature region. The upturn of $\chi_m T$ below 16 K suggests uncompensated magnetic moments of the system arising from spin canting of the antiferromagnetically coupled Co^{II} ions.^[117, 121] The data above 150 K obeys the Curie-Weiss law with a Curie constant $C = 3.99(6) \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = -119(5) \text{ K}$. The C is much larger than the expected spin-only value, which indicates the significant orbital contribution of Co^{II} in an octahedral surrounding.^[109] The large negative θ value suggests the strong spin-orbital coupling of Co^{II} ions in an octahedral field and the antiferromagnetic coupling between Co^{II} ions within 3D framework of **V-4**.

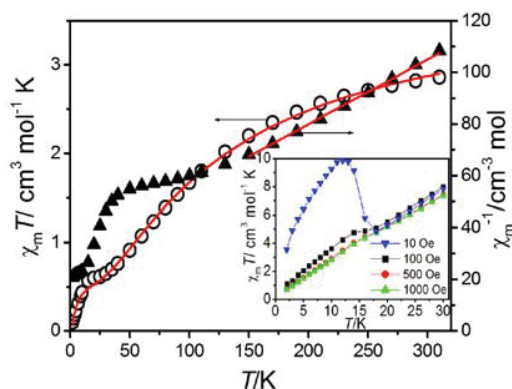


Figure 96 Temperature dependence of $\chi_m T$ (○) and χ_m^{-1} (▲) of **V-4** from 2 to 310 K at $H = 10 \text{ kOe}$. The solid lines correspond to the best fit (see the text). The inset shows the $\chi_m T$ vs. T plot of **V-4** below 30 K at small fields.

To estimate both magnetic exchange interactions and the spin-orbit coupling effect in the temperature range of 2–310 K for low-dimensional Co^{II} systems, the simple phenomenological equation (5.2) is used. The fitted parameters are $A + B = 3.90 \text{ cm}^3 \text{ K mol}^{-1}$, practically equivalent to the Curie constant obtained from the Curie-Weiss law in the high temperature range, $3.99 \text{ cm}^3 \text{ K mol}^{-1}$. The E_1/k is $+112(8) \text{ K}$ which is of the same magnitude as those reported for Co^{II} complexes (the order of $+100 \text{ K}$).^[136, 137, 139–141] For the antiferromagnetic coupling $E_2/k = +4.4(2) \text{ K}$, corresponding to $J = -8.8 \text{ K}$, according to the Ising chain approximation, $\chi_m T \propto \exp(+J/2kT)$. It is noticeable that the small E_2/k value is very close to those reported value for compound **V-2** ($E_2/k = +4.1(2) \text{ K}$), which contains the same alternating double EO and double EE azido- Co^{II} chain. It is indication of the overall antiferromagnetic coupling within the 1D azido- Co^{II} chain. However, the E_1/k value of **V-4** is much higher than that of **V-2** ($E_1/k = +61(2) \text{ K}$) implying that **V-4** presents the stronger spin-orbit coupling of Co^{II} ions in an octahedral field, corresponding to the observation of higher Curie and Weiss constants of **V-4**.

As a further proof for the presence of the spin canting, the temperature dependencies of the ZFC and the FC magnetization were measured at a low field of 10 Oe, as shown in Figure 97, inset. The obvious divergence of the ZFC and FC plots below 16 K indicates the onset of a magnetized state, which is compatible with the maxima in χ' and the nonzero χ'' signal at 16 K in *ac* susceptibility at 997 Hz, indicative of a long-range magnetic ordering (Figures 98). The isothermal magnetization with a field up to 5 T at 2 K is depicted in Figure 97. The initial increase of magnetization shows a positive curvature to 0.198 $N\beta$ at 5 T, far from the theoretical saturation magnetization of Co^{II} ion and no saturation is observed, which is indicative of the overall antiferromagnetic coupling between Co^{II} ions. A hysteresis loop of **V-4** is clearly observed when the field is less than 1 T, giving a coercive field of ≈ 450 Oe and remanent magnetization of $\approx 0.004 N\beta$. These results indicate that the spin canting effect between overall antiferromagnetically coupled Co^{II} ions leads to residual spins. The canting angle (α) is estimated to be about 0.11° based on the equation $\alpha = \sin^{-1} M_r/M_s$ ($M_s = 2.16 N\beta$ for octahedral Co^{II} at 2 K).

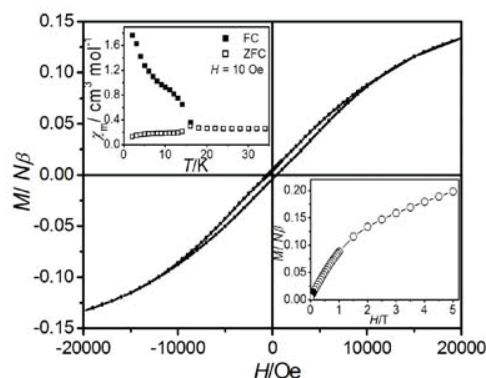


Figure 97 Hysteresis curve of **V-4** at 2 K. The insets show the field dependence of initial magnetization (right) and the ZFC-FC plots of **V-4** at 10 Oe (left).

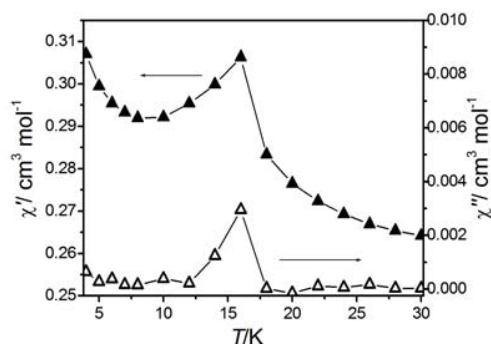


Figure 98 Temperature dependence of the *ac* susceptibility for **V-4** at $H_{\text{dc}} = 0$ Oe, $H_{\text{ac}} = 3$ Oe, with frequency of 997 Hz.

Remarkably, 2D layer of **V-3** exhibits the coexistence of big canting angle and metamagnetic phenomena whereas 3D framework of **V-4** only displays the canted antiferromagnetism with smaller canting angle. As it is known that two mechanisms lead to spin canting behavior (equation 1.16): (i) single-ion magnetic anisotropy and (ii) antisymmetric exchange interaction.^[59, 106] However, the spin canted structures are not compatible with both crystal structures of **V-3** and **V-4** because of the presence of an inversion center between the bridged Co^{II} sites, which forbids the occurrence of antisymmetric interactions. It is noticeable that the canted antiferromagnets in the presence of an inversion center between metal sites have been often observed in corresponding complexes that contain the 1D chain of alternating double EO and double EE azido-bridged metal(II) ions. Generally, these complexes were crystallized in low crystal systems (monoclinic and triclinic lattices) and display inversion center between metal sites. The 1D chain complexes with *cis*-bidentate chelating coligands are widely found in this magnetic system while the 2D layer and 3D framework structures are rarely observed. The isotropic Mn^{II} complexes usually exhibit the overall antiferromagnetic interaction within the 1D alternating ferromagnetic and antiferromagnetic chains and their magnetostructural correlations have been investigated entirely.^[117, 118, 123, 141] Whereas the metamagnetism and weak ferromagnetism due to canted antiferromagnetic system are usually observed in anisotropic ones (Co^{II}, Fe^{II} and Ni^{II} complexes).^[121, 122, 155] However some spin canting of 1D Mn^{II} complexes were also reported, which are due to the possible distortion in the crystal structure at low temperature.^[117, 120, 141] Consequently, the observation of spin canting for **V-3** and **V-4** should be attributed to the competition of ferromagnetic and antiferromagnetic interactions within intrachain of the alternating double EO and double EE azido bridging mode together with a relevant single-ion anisotropy of octahedral cobalt(II) ions and a possible structure phase transition at low temperature.^[117, 120-122, 155]

Obviously from the structural data, compound **V-3** which was crystallized in orthorhombic system with high centrosymmetric space group *Immm*, presented the disordered amino group on ampyz moiety and disordered terminal EO azido bridge arising from related crystallographic mirror planes and inversion center. It supposes that these disordered positions and inversion centers between the Co^{II} sites somewhere are possibly demolished at very low temperature and develop to the exact atomic location in the crystal lattice with the lower space group. Therefore, the antisymmetric coupling for **V-3** possibly exists at low temperature together with the single-ion anisotropy of octahedral Co^{II} ion yielding big canting angle for **V-3**, as similarly observed in other reported weak ferromagnets with large canting angles (Table 5.7). Moreover the interchain and the interlayer weak antiferromagnetic coupling of **V-3** which originate from *trans*-ampyz bridging shortly between the azido Co^{II} chain and the interlayer hydrogen bonding between NH₂ on ampyz and symmetric double EE azido bridges, would justify for the observed maximum of susceptibility at $H_c < 600$ Oe. In a magnetic field below 600 Oe, the residual magnetic moments due to spin canting on the chains are weak antiferromagnetically coupled to each other (Figure 5.31, inset). In stronger fields above 600 Oe, the amplitude of the applied magnetic field can

overcome the interchain and interlayer weak antiferromagnetic coupling leading to the observed metamagnetic-like behavior of **V-3**. However, because of the great spin-orbit coupling of Co^{II} ions, the magnetic interaction might be more complicated. Generally, the coexistence of spin canting and metamagnetism is found in the system consisting of a large anisotropy, which leads to a significant spin canting through increasing the possibility of antisymmetric exchange and may induces a metamagnetic transition in the presence of competing interactions within the structure.^[157, 159, 162-166]

It is worthwhile to compare the magnetic properties of **V-2**, **V-3** and **V-4** with the reported Co^{II} complexes containing similar alternating double EO and double EE azido bridging mode, as shown in Table 1. The comparison demonstrates that all compounds are hard magnets at 2 K ($H_c \approx 300$ -500 Oe) and only compound **V-3** which is in the highest-symmetry space group, shows the coexistence of big spin canting angle and metamagnetism whereas the others display very small spin canting angle. This unusual feature of **V-3** could be attributed to the abovementioned significant antisymmetric exchange interaction between Co^{II} ions and the single-ion anisotropy of Co^{II} ion. In addition, the interlayer hydrogen bonding between NH₂ of ampyz and symmetric double EE azido bridges in **V-3** which are not found in other structures, might play the important role on the presence of the field-induce metamagnetic phase transition.

Table 1 Structural and magnetic data for Co^{II} complexes containing the alternating double EO and double EE azido bridging mode.

Compound ^a	[Co(dpa)(N ₃) ₂] _n	V-2	V-3	V-4
Dimension	1D	2D	2D	3D
Co-ligand	<i>cis</i> -chelating	<i>trans</i> -bridging	<i>trans</i> -bridging	<i>cis</i> -bridging
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	$\bar{P}$ 1	<i>Immm</i>	<i>P</i> 2 ₁ / <i>n</i>
Co $\tilde{\text{N}}\text{Co}$ (deg)	103.7	102.25(14)	101.7(3)	98.90(7)
δ (deg) ^b	36.0	33.8(1)	0	12.57(6)
Co...Co (Å) ^c	9.294	8.322(2)	7.1808(12)	7.1119(14)
Magnetic behavior	Canted AF	Canted AF	Canted AF, metamagnetism	Canted AF
θ (K)	−40.0 ^e	−58(2) ^d	−61.8(13) ^d	−119(5) ^d
T_N (K)	12.4	12	10	16
$M_r(N\beta)$ ^f	0.002	0.002	0.29	0.004
H_c (Oe) ^g	500	300	350	450
α (deg) ^h	0.05	0.05	7.7	0.11
Ref.	[121]	this work	this work	this work

^a Abbreviations: 2,2'-bpe = 1,2-bis(2-pyridyl)ethylene and dpa = 2,2'-dipyridylamine. ^b The dihedral angle between the mean plane of Co(μ_2 -1,3 N₃)₂Co and the Co-N-N plane. ^c The shortest Co...Co distance among alternating double EO and double EE azido-Co^{II} chains. ^d The best fit to Curie-Weiss law above 150 K. ^e The best fit to Curie-Weiss law above 210 K. ^f Remanent magnetization at 2 K. ^g Coercive field at 2 K. ^h Canting angle based on the equation $\alpha = \sin^{-1}M_r/M_s$ ($M_s = 2.16 N\beta$).

In comparison with **V-3**, compound **V-4** and the others which were crystallized in lower crystal systems, reveal very small canting angles. This result indicates that the major magnetic anisotropy of octahedral Co^{II} ion in **V-4** plays a key role on spin canting as well as a minor magnitude of antisymmetric coupling between Co^{II} ions which possibly arises from a distortion in the crystal framework, suppressing the inversion center at low temperature. Abovementioned compound **V-4** shows the very close antiferromagnetic coupling E_2/k value to that reported for **V-2** but the Weiss constant and E_1/k value are much higher, which point to the very strong spin-orbital coupling of octahedral Co^{II} ions of **V-4**. This extra inherent anisotropy of the Co^{II} ions for **V-4** might provide an additional contribution to a larger degree of spin canting, resulting to the observation of the higher M_r and the larger canting angle when comparing with **V-2** and $[\text{Co}(\text{dpa})(\text{N}_3)_2]_n$. The T_N of **V-4** is slightly higher than other complexes owing to the closest $\text{Co}\cdots\text{Co}$ distance among the magnetic chains in 3D covalent framework of **V-4**.

4. Conclusions

The introduction of the amine group to the pyz ring in Cu^{II} carboxylate systems contributes to the structural networks mostly by amending from higher dimension to lower dimension when comparing with pyz spacer, as found in $[\text{Cu}(\text{HCO}_2)_2(\text{pyz})]_n$ ^[31] revealing a 3D framework, whereas compound **III-1** shows a 2D wavy network. The structure is attributed to the more pronounced steric effect in ampyz which possibly causes the carboxylate group to organize itself to reduce the steric effect, as found in **III-5**. Here malonate acts as tridentate ligand bridging between Cu^{II} centers to build a 2D stairlike layer, instead of acting as tetradentate bridging three Cu centers to build 3D framework, like in the pyz system.^[29] However, the ampyz spacer in addition effectively provides other weaker interactions, such as hydrogen bonding and π - π stacking in which it is not only stabilizing within the coordination network but also contributing the stability of whole supramolecular lattice structure which is not observed in pyz system. For instance, compound **III-4** reveals a 2D sheet which is composed of double-stranded chains acting as SBU, connected by ampyz spacers, whereas it is not found in those of the Cu^{II} -pyz systems. For **III-2** and **III-3**, the structures exhibit a 2D sheet stabilized *via* the hydrogen bonding between polymeric chains. Magnetic properties of **III-1** and **III-5** reveal weak ferromagnetic and weak antiferromagnetic spin exchange interactions between adjacent Cu^{II} ions *via* μ_2 -*syn-anti* carboxylates and μ_2 -ampyz with the spin exchange parameters of $J_{\text{inter}}/k = +6.9$ K and $J_{\text{intra}}/k = -2.3$ K, for **III-1** and $J_{\text{inter}}/k = +7.4$ K and $J_{\text{intra}}/k = -2.2$ K for **III-5**, respectively. Magnetic behaviors of **III-2-4** exhibit very strong antiferromagnetic interactions *via* four μ_2 -*syn-syn* carboxylates bridging between Cu^{II} ions which is well-known for the classical paddle-wheel Cu^{II} complexes.

Furthermore, by using versatile ligand ampyz in sulfate system, three metal supramolecular assemblies with a lack of coordination bridges **IV-1-3** and a Cd^{II} coordination polymer **IV-4** were successfully

synthesized. The Cd^{II} ion (ionic radius = 124 pm for 8-coordination)^[167] has a larger accessible space for arranging the bridging ampyz and bridging sulfato group leading to the 2D coordination network. In contrast, the smaller Co^{II} (ionic radius = 75 pm for 6-coordination)^[168] and Fe^{II} (ionic radius = 78 pm for 6-coordination)^[168] ions give isostructural assemblies of monomeric complexes which contain intermolecular π - π stacking and hydrogen bonding interactions stabilizing the whole structures. The water desorption/resorption processes trigger the reversible crystal-to-amorphous transformation with chromotropism for compounds **IV-1-3**. Although the lack of coordination bridge maintaining the skeleton of the framework structures in **IV-1-3**, the original crystalline phases are recovered from collapsed amorphous structures by the restoration of water molecules. On the other hand, the coordination bridges in **IV-4** play an important role for preserving the crystallinity in dehydrated phase thus the reversible structural phase transformation in **IV-4** is observed. The selective methanol accommodation with chromotropism in dehydrated **IV-1A** is observed which could be attributed to the proper size of methanol and weak host-guest interactions causing the changes of the *d*-orbital energy in distorted octahedral geometry. However the **IV-1A·MeOH** is unstable in air. The original crystalline phase **IV-1''** is easily recovered after the evaporation of methanol at room temperature which is indication of high selective recognition of **IV-1A** to water molecules. This work is beneficial to expand the field of the crystal engineering by controlling the weak interaction of coordination moieties.

In case of 2D-1D Co(II) 3,5-pyridinedicarboxylate frameworks, compounds $[\text{Co}(\text{pydc})(\text{H}_2\text{O})_2]_n$ (**IV-5**) and $[\text{Co}(\text{pydc})(\text{H}_2\text{O})_4]_n(\text{H}_2\text{O})_n$ (**IV-6**) have been successfully synthesized with 2D and 1D structural arrangement. The pydc acts as a tridentate ligand bridging between Co centers to build a 2D layer in **IV-5**, and a didentate bridging fashion to form 1D zig-zag chain in **IV-6**. Moreover, the pydc spacer in addition provides other weaker interactions, such as hydrogen bonding and π - π stacking in which it is not only stabilizing within the coordination network but also contributing the stability of whole framework structure. We have been able to demonstrate that the water molecules in both compounds can be reversibly exchanged along with the change in color of the sample. The reversibility of the solid transformation has been supported by spectroscopic techniques, elemental analysis, TGA and XRPD and shows that **IV-5** and **IV-6** exhibit water induced crystal-to-amorphous transformation with chromotropism. Furthermore, upon reintroduce of the water molecules, the original structure of **IV-6** could be generated from the dehydrated forms of both **IV-5** and **IV-6**. A striking contrast for this system is that the 2D honeycomb-like layer structure of **IV-5** can be transformed readily to the 1D zig-zag chain of **IV-6**, but not vice versa. The results suggest that **IV-6** is thermodynamically more stable than **IV-5** and the water molecules function as template molecules. They are essential for inducing the zig-zag chain structure when exposed to the enrichment water vapor and the weak interactions (hydrogen bonds and π - π stacking) pay an important role in the reversible phase transformation. Therefore, the conspicuous response of the dehydrated and

rehydrated samples to the presence of water suggests that these compounds could be employed as humidity sensors.

In the last complex system, two novel cobalt(II) azido inorganic-organic hybrid materials containing 2,2'-bpe have been obtained. The 2,2'-bpe can serve as either terminal coligand in monodentate coordination in **V-1** or ditopic bridging spacer in *trans* position in **V-2** with which molecular magnets of different lattice dimensionalities were developed. The 1D chain of **V-1** contains the rare mixing geometries of Co^{II} ions in a unique $[-5-5-6-]_n$ sequence of coordination number bridged by double EO mode of azide. The adjacent chains are assembled by C-H $\cdots\pi$ interaction and the intermolecular hydrogen bonds, stabilizing 2D sheet of **V-1**. The magnetic behavior of **V-1** reveals the metamagnetic transition which may be due to the presence of weak interchain antiferromagnetic interactions among the strong ferromagnetism of double EO Co^{II} azido chains. In contrast, compound **V-2** is 2D wavy coordination polymer containing the alternating double EO and double EE bridging modes of azides and exhibits a weak ferromagnetism due to spin canting. In case of the versatile ampyz spacer, two high dimensional cobalt(II) azido inorganic-organic hybrid frameworks, which contain similarly alternating double EO and double EE azido-bridged Co^{II} chain were obtained from the different preparative methods. The high symmetric square-grid structure of **V-3** from layer diffusion method which consists of *trans*-ampyz bridging between octahedral Co^{II} centers in axial positions, presents the coexistence of a big spin canting angle and metamagnetism below 10 K. The canting angle is estimated to be 7.7° and the critical field for metamagnetic phase transition is $\approx$ 600 Oe at 2 K. The interlayer hydrogen bonding between amino group of ampyz spacer and symmetric double EE azido bridges plays an important role on the field-induce metamagnetic phase transition. The spin canting of **V-3** could be attributed to the significant antisymmetric exchange arising from the structure phase transition at low temperature and the great role of magnetic anisotropy of Co^{II} ion. Whereas 3D framework containing *cis*-ampyz bridging among Co^{II} centers of **V-4** was synthesized from hydrothermal technique. It was crystallized in lower space group and exhibited only small spin-canted antiferromagnetism below 16 K. It is suggests that the large magnetic anisotropy in **V-4** might contribute a spin canting together with small antisymmetric coupling between Co^{II} ions, arising from a distortion in the crystal net at low temperature, which is frequently found in the related complexes containing the same bridging mode of azide. These results will provide the merit for future investigations and demonstrate the importance of the crystal engineering of inorganic-organic hybrid framework in the field of molecular-based magnetic materials.

5. References

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OUTPUT OF THE RESEARCH

Ph.D Students:

- 1) Dr. Pongthipun Phuengphai (2007-2010): “Design of Metal Organic Frameworks (MOFs) and Their Functions Towards Catalysis and Anion-exchange” Doctor of Philosophy Thesis in Chemistry, Graduate School, Khon Kaen University.
- 2) Dr. Jaurup Boonmak. (2006-2011): “Structural Diversity, Dynamic Structural Transformations and Magnetic Properties of Inorganic-Organic Hybrid Frameworks” Doctor of Philosophy Thesis in Chemistry, Graduate School, Khon Kaen University.

Publication papers:

- 1) J. Boonmak, S. Youngme, N. Chaichit, G.A. van Albada, and J. Reedijk, “Series of copper(II) coordination polymers containing aminopyrazine and different carboxylato bridges: Syntheses, structures and magnetic properties”, *Cryst. Growth des.*, 2009, **9**, 3318-3326.
- 2) P. Phuengphai, S. Youngme, P. Kongsaree, C. Pakawatchai, N. Chaichit, S. J. Teat, P. Gamez and J. Reedijk, “Drastic steric effects from, respectively, a hydrogen, a methyl and an ethyl group on the coordination network of a zinc(II)-4,4'-bipyridine-carboxylato ternary system”, *CrystEngComm*, 2009, **11**, 1723-1732.
- 3) C. Ramon, I. rio de P.R. Moreira, S. Youngme, K. Siriwong, N. Wannarit and F. Illas, “Toward the Design of Ferromagnetic Molecular Complexes: Magnetostructural Correlations in Ferromagnetic Triply Bridged Dinuclear Cu(II) Compounds Containing Carboxylato and Hydroxo Bridges” *Inorg. Chem.*, 2010, **49**, 285-294.
- 4) Cheansirisomboon, S. Youngme, C. Pakawatchai and N. Chaichit, “Synthesis and crystal structure of two new dinuclear oxalato-bridged copper(II) complexes containing bis(2-pyridyl)amine as a ligand”, *Mendeleev Commun.*, 2010, **20**, 109–110.
- 5) J. Boonmak, M. Nakano, N. Chaichit, C. Pakawatchai, and S. Youngme, “Water-induced reversible structural phase transformation with chromotropism in metal supramolecular frameworks containing aminopyrazine and sulfate anions”, *Dalton Trans.*, 2010, **39**, 8161 – 8167.
- 6) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk, “Catalytic properties of a series of coordination networks: cyanosilylation of aldehydes catalyzed by Zn(II)-4,4'-bpy-carboxylato complexes”, *Dalton Trans.*, 2010, **39** (34), 7936-7942.
- 7) N. Wannarit, N. Chaichit, C. Pakawatchai, and S. Youngme, “New trinuclear carbonato-bridged copper(II) complexes: synthesis, crystal structure, and spectroscopic properties” *Russ. J. Coord. Chem.*, 2010, **36**, (10), 778–785.
- 8) J. Boonmak, M. Nakano, S. Youngme, “Structural diversity and magnetic properties in 1D and 2D azido-bridged cobalt(II) complexes with 1,2-bis(2-pyridyl)ethylene” *Dalton Trans.*, 2011, **40**, 1254-1260.

- 9) J. Boonmak, M. Nakano, N. Chaichit, C. Pakawatchai, S. Youngme, "Spin Canting and Metamagnetism in 2D and 3D Cobalt(II) Coordination Networks with Alternating Double End-On and Double End-to-End Azido Bridges" *Inorg. Chem.*, 2011, **50**, 7324-7333.
- 10) N. Wannarit, K. Siriwong, N. Chaichit, S. Youngme, R. Costa, I.P.R. Moreira, F. Illas, "New series of triply-bridged dinuclear Cu(II) compounds: synthesis, crystal structure, magnetic properties and theoretical study" *Inorg. Chem.*, 2011, **50** (21), 10648–10659.
- 11) N. Wannarit, K. Siriwong, N. Chaichit, S. Youngme, " Multiple-Layer Heterometallic MnII-AgI Coordination Polymers Constructed from $[AgI_2(CN)_3]^-$ and $[AgI(CN)_2]^-$ Units " *Transition Met. Chem.*, 2012, **37**, 79-84.
- 12) P. Phuengphai, S. Youngme, I. Mutikainen, P. Gamez, J. Reedijk, "A series of related 2D coordination polymers based on [copper(II)-4,4'-bpy-carboxylato] building blocks" *Polyhedral*, 2012, **42**, 10-17.

Honor and Awards:

- 1) S. Youngme, CST Distinguished Chemist Award 2010 (Inorganic Chemistry)
- 2) S. Youngme, Excellent Researcher Award 2010: Gold Metal Researcher Award
- 3) P. Phuengphai, Professor Dr. Thab Neelanithi's Foundation Distinguished Dissertation Award in 2010
- 4) P. Phuengphai, Surindra Rajabhat University Researcher Distinguished Achievement Award in 2010
- 5) P. Phuengphai, Dissertation Graduate student Distinguished KKU Thesis Award in 2011
- 6) J. Boonmak, Merck-CST Distinguished Dissertation Award 2011 by The Chemical Society of Thailand under the Patronage of Her Royal Highness Princess Chulabhorn Mahidol.
- 7) J. Boonmak, Student Best Poster Award in the 12th International Conference on Molecule-Based Magnets, Beijing, China.
- 8) A. Cheansirisomboon "IUPAC Young Chemist Awards" supported by IUPAC, RSC and Bangkok Bank at 14th Asian Chemical Congress (ACC), Bangkok, Thailand.
- 9) N. Wannarit, The Best Outstanding Poster Presentation Award at PERCH-CIC congress VII, Pattaya, Chonburi, Thailand..

Presentations:

- 1) S. Youngme "Design of metal organic frameworks and their functions towards catalysis, anion-exchange and dynamic structural transformation"*Invited as a keynote lecture at at Pure and*

Applied Chemistry International Conference(PACCON), Bangkok, Thailand. 5-7 January 2011.

- 2) S. Youngme “Frameworks of Zn^{II} -4,4'-bipyridine-carboxylate and M^{II} -2-aminopyrazine-sulfate ($M^{II} = Co, Fe$ and Cd) and their functions toward catalysis, anion-exchange and dynamic behaviors” **Invited as a keynote lecture** at at 37th Congress on Science and Technology of Thailand, Bangkok, Thailand. 10-12 October 2011.
- 3) S. Youngme “Frameworks of Zn^{II} -4,4'-bipyridine-carboxylate and M^{II} -2-aminopyrazine-sulfate ($M^{II} = Co, Fe$ and Cd) and their functions toward catalysis, anion-exchange and dynamic behaviors” **Invited as a keynote lecture** at at 3rd Asian Conference on Coordination Chemistry (3rd ACCC), New Delhi, India. 17-20 October 2011.
- 4) S. Youngme “Metal-Organic Frameworks and their Functional Toward Anion-exchange, Catalysis, Magnetism and Dynamic structural Transformation with Chromotropism” **Invited as a keynote lecture** at at The 4th International Conference on Science and Technology for Sustainable Development of the Greater Mekong Sub-region (4th STGMS), at Pullman Khon Kaen Raja Orchid Hotel, Khon Kaen, Thailand. 23-24 January 2012
- 5) P. Phuengphai, S. Youngme, J. Reedijk “Framework Engineering of $Zn(II)$ /4,4'-bipy Porous Coordination Polymers and Carboxylate-regulator: Synthesis, Structures and Thermal properties” **Poster presented at the 33th Congress on Science and Technology of Thailand (STT-33)**, 18-20 October 2007. Nakorn Sri Thammarat, Thailand.
- 6) P. Phuengphai, J. Reedijk and S. Youngme, “Framework Engineering of $Zn(II)$ /4,4'-bpy Porous Coordination Polymers and Carboxylate-regulator; Synthesis, structures and thermal properties” **Poster presented at The Royal Golden Jubilee Ph.d Program RGJ-Ph.D. Congress IX (RGJ-Ph.D IX)**, April 4-6, 2008, Jomtien Palm Beach Hotel and Resort, Chonburi, Thailand.
- 7) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk “Framework Engineering of $Zn(II)$ /4,4'-bipy Porous Coordination Polymers and Carboxylate-regulator: Synthesis, Structures and Thermal properties”. **Poster presented at the Holland Research School of Molecular Chemistry (HRSMC)**, 27 November 2008, Vrije University, Amsterdam, the Netherlands.
- 8) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk “Framework Engineering of $Zn(II)$ /4,4'-bipy Porous Coordination Polymers and Carboxylate-regulator: Synthesis, Structures and Thermal properties” **Oral presented at the 10th Netherlands Catalysis and Chemistry Conference (NCCC)**, 2-4 March 2009, Noordwijkerhout, the Netherlands.
- 9) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk “Framework Engineering of $Zn(II)$ /4,4'-bipy Porous Coordination Polymers and Carboxylate-regulator: Synthesis, Structures and Thermal properties” **Poster presented at the 1st Hybrid Materials Conference**, 14-19 March 2009, Tours, France.

- 10) P. Phuengphai, S. Youngme, P. Kongsaree, C. Pakawatchai, N. Chaichit, S. J. Teat, P. Gamez and J. Reedijk, "Drastic steric effects from, respectively, a hydrogen, a methyl and an ethyl group on the coordination network of a zinc(II)–4,4'-bipyridine–carboxylato ternary system" **Oral presented** at at the 33th Congress on Science and Technology of Thailand (STT-35), 14-17 October 2009. Choburi, Thailand.
- 11) P. Phuengphai, S. Youngme, P. Kongsaree, C. Pakawatchai, N. Chaichit, S. J. Teat, P. Gamez and J. Reedijk, "Drastic steric effects from, respectively, a hydrogen, a methyl and an ethyl group on the coordination network of a zinc(II)–4,4'-bipyridine–carboxylato ternary system" **Poster presented** the 2nd Asian Conference on Coordination Chemistry (2nd ACCC), 1-4 November 2009. Nanjing University, Nanjing, China.
- 12) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk, "Anion Exchange and Catalytic Properties of a Series of Coordination Networks: Cyanosilylation of Aldehydes Catalyzed by Zn(II)-4,4'-bpy-carboxylato Complexes" **Oral presented** the 2nd Pure and Applied Chemistry International Conference (2nd PACCON), 21-23 January 2010. Ubonratchatani University, Ubonratchatani, Thailand.
- 13) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk, "Design of Metal Organic Frameworks (MOFs) and Their Functions Towards Catalysis and Anion-exchange" **Oral presented** the 2nd Academic Conference (2nd SIFF), 14-24 January 2010. Surindra Rajabhat University, Surin, Thailand.
- 14) J. Boonmak, "Structural diversity, dynamic structural transformations and magnetic properties of inorganic-organic hybrid frameworks containing aminopyrazine spacer" **Invited lecture at CST award in Pure and Applied Chemistry International Conferences 2012 (PACCON 2012)**, Chiang Mai, Thailand. January 11-13, 2012
- 15) J. Boonmak, M. Nakano, N. Chaichit, C. Pakawatchai, S. Youngme, "Spin canting and metamagnetism in 2D and 3D cobalt(II) coordination networks with alternating double end-on and double end-to-end azido bridges" **Poster presented at 14th Asian Chemical Congress (14ACC)**, Bangkok, Thailand. September 5-8, 2011.
- 16) J. Boonmak, M. Nakano, N. Chaichit, C. Pakawatchai, S. Youngme, "Water-induced reversible structural phase transformation with chromotropism in metal supramolecular frameworks containing aminopyrazine and sulfate anions" **Oral presentation at NanoThailand 2010**, Thailand Science Park Convention Center (NSTDA) Pathumthani, Thailand. November 8 – 20, 2010.
- 17) J. Boonmak, M. Nakano, S. Youngme, "Structural diversity and magnetic properties in 1D and 2D azido-bridged Co(II) complexes with 1,2-bis(2-pyridyl)ethylene" **Poster presented at The Inaugural CU-IMS Joint Symposium: The Overseas Sokendai Lecture in Bangkok 2010**, Department of Chemistry, Faculty of Science, Chulalongkorn University. October 19–21, 2010.

- 18) J. Boonmak, M. Nakano, S. Youngme, "Structural diversity and magnetic properties in 1D and 2D azido-bridged Co(II) complexes with 1,2-bis(2-pyridyl)ethylene" **Poster presented at The 12th International Conference on Molecule-Based Magnets (ICMM12th)**, Beijing, China. October 8-12, 2010.
- 19) J. Boonmak, N. Chaichit, C. Pakawatchai, G.A. van Albada, J. Reedijk, S. Youngme "Series of Copper(II) Coordination Polymers Containing Aminopyrazine and Different Carboxylato Bridges: Syntheses, Structures and Magnetic Properties" **Poster presented at The 59th Symposium on Coordination Chemistry of Japan (JSCC59)**, Bunkyo-machi, Nagasaki-city, Nagasaki University, Japan. Sep. 25–27 2009.
- 20) J. Boonmak, N. Chaichit, C. Pakawatchai, M. Nakano, S. Seki, S. Youngme "Syntheses, Crystal Structures, and Magnetic Studies of Cobalt(II) Azido Coordination Networks Containing *N,N'*-Ditopic Spacers" **Oral presentation at JENESYS Programme 2009 General Meeting and Mini Symposium**, Institute for molecular science, Okazaki, Japan. July 31, 2009.
- 21) J. Boonmak, N. Chaichit, C. Pakawatchai, G.A. van Albada, J. Reedijk, S. Youngme "A Series of Copper(II) Coordination Polymers Containing Aminopyrazine and Different Carboxylato Bridges: Syntheses, Structures and Magnetic Properties" **Poster presented at the 6th PERCH-CIC Congress**, Chonburi, Thailand. 3–6 May 2009.
- 22) J. Boonmak, N. Chaichit, S. Youngme, "Metal-directed supramolecular assemblies and coordination polymer based on aminopyrazine with sulfate anions" **Poster presentation at RGJ-Ph.D. Congress X**, Jomtien Palm Beach Hotel&Resort, Pattaya, Chonburi, Thailand, Apr. 3 – 5, 2009.
- 23) J. Boonmak, N. Chaichit, S. Youngme "Copper coordination polymers containing aminopyrazine with various carboxylato bridges" **Oral presentation at 34th Congress on Science and Technology of Thailand**, Queen Sirikit National Convention Center, Bangkok, Thailand. Oct. 31 – Nov. 2, 2008.
- 24) N. Wannarit, S. Youngme, K. Siriwong, R. Costa, I.P.R. Moreira, and F. Illas "Magnetostructural correlations in ferromagnetic triply bridged dinuclear Cu(II) compounds containing carboxylato and hydroxo bridges Inorganic chemistry". **Poster presented at PERCH-CIC congress VII**, Pattaya, Chonburi, Thailand. 4-7 May 2011.
- 25) N. Wannarit, S. Youngme, K. Siriwong, R. Costa, I.P.R. Moreira, and F. Illas "Toward the Design of Ferromagnetic Molecular Complexes: Magnetostructural correlations in ferromagnetic triply bridged dinuclear Cu(II) compounds containing carboxylato and hydroxo bridges Inorganic chemistry". **Poster presented at 14th Asian Chemical Congress (ACC)**, Bangkok, Thailand. 5-8 September 2011.

- 26) N. Wannarit, C. Pakawatchai and S. Youngme. “Two Novel Manganese(II) Coordination Polymers Constructed by Dicyanoargentate Bridges”. ***Poster presented*** at 37th Congress on Science and Technology of Thailand, Bangkok, Thailand. 10-12 October 2011.

APPENDICES

PUBLICATION PAPERS OF PART I

- 1) P. Phuengphai, S. Youngme, P. Kongsaree, C. Pakawatchai, N. Chaichit, S. J. Teat, P. Gamez and J. Reedijk, "Drastic steric effects from, respectively, a hydrogen, a methyl and an ethyl group on the coordination network of a zinc(II)-4,4'-bipyridine-carboxylato ternary system", *CrystEngComm*, 2009, **11**, 1723-1732.
- 2) P. Phuengphai, S. Youngme, P. Gamez and J. Reedijk, "Catalytic properties of a series of coordination networks: cyanosilylation of aldehydes catalyzed by Zn(II)-4,4'-bpy-carboxylato complexes", *Dalton Trans*, 2010, **39** (34), 7936-7942.
- 3) P. Phuengphai, S. Youngme, I. Mutikainen, P. Gamez, J. Reedijk, "A series of related 2D coordination polymers based on [copper(II)-4,4'-bpy-carboxylato] building blocks" *Polyhedral*, 2012, **42**, 10-17.

Drastic steric effects from, respectively, a hydrogen, a methyl and an ethyl group on the coordination network of a zinc(II)–4,4′-bipyridine–carboxylato ternary system†

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The combination of a [zinc(II)–4,4′-bpy] coordination moiety with, respectively, formate, acetate and propionate ligands leads to the formation of the compounds $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (**1**), $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**) and $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(\mathbf{4,4'}\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (**3**). The molecular structures determined by single-crystal X-ray diffraction data reveal significant changes, which are apparently due to the sole different steric hindrance between a H atom (formate, compound **1**), a methyl group (acetate, compound **2**) and an ethyl group (propionate, compound **3**). The three coordination materials have been fully characterized and their thermal decomposition behavior has been investigated. The 3D (**1**), 1D (**2**) and 2D (**3**) networks exhibit voids that contain the counter-ions and guest molecules as well, namely water for compounds **1** and **2**, and water/4,4′-bpy for compound **3**.

Introduction

During the past 15 years, the field of coordination polymer research has become an extremely prolific area of chemistry.^{1–3} In this context, a number of crystal engineering investigations are aimed at trying to understand how a variety of factors, like the metal ions, reaction conditions and secondary co-ligands,⁴ may affect the molecular structures and/or properties of coordination polymers.^{5–7}

Coordination polymer networks, also known as metal–organic frameworks (MOFs),⁸ are based upon self-assembly between metal ions (typically transition-metal ions) characterized by inherent preferences in coordination geometry and at least dinucleating ligands.⁹ (Poly)carboxylato ligands are commonly being used to generate MOFs of diverse topologies.¹⁰ Moreover, the combination of metal–carboxylato building blocks with a secondary co-ligand (usually a dinucleating N-donor ligand, such as 4,4′-bipyridine, **4,4′-bpy**) allows a considerable enhancement of the structural diversity of the coordination materials.¹¹ Actually, numerous remarkable coordination

networks built from **4,4′-bpy** and carboxylato ligands have been reported in the literature,^{12–19} for which the nature of the carboxylato molecule plays an important structural role.^{20–23}

In the present study, the effect of the steric hindrance of different carboxylato ligands (formate, acetate and propionate ligands) on the solid-state structure of the corresponding coordination materials has been investigated. Thus, three multicomponent polymeric networks have been synthesized from zinc(II) ions, **4,4′-bpy** and a carboxylato ligand, whose single-crystal X-ray structures reveal a significant influence of a hydrogen (formate), a methyl (acetate) and an ethyl (propionate) group on the assembly of the coordination framework. The compounds $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (**1**), $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**) and $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(\mathbf{4,4'}\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (**3**) have been synthesized and characterized and their thermal stability has been examined.

Results and discussion

Crystal structure of $\{[\text{Zn}_3(\mathbf{4,4'}\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (**1**)

The 3D molecular structure of compound **1** exhibits four different types of zinc(II) ions, each with octahedral N_2O_4 coordination environments (Fig. 1). The basal plane of the octahedron around Zn1 is formed by four oxygen atoms belonging to three formate ligands. The axial positions are occupied by two pyridine N-donors from two different (bridging) **4,4′-bpy** moieties (for the atom Zn3, the **4,4′-bpy** units act as monodentate ligands; see green **4,4′-bpy** ligands in Fig. 2). The formate ligand [O2, O12] acts as a bridging $\mu\text{-O, O'}$ ligand, connecting Zn1 to Zn3 (Fig. 1). The formate ligand [O3, O8] functions as a $\mu_3\text{-O, O, O'}$ ligand, bridging Zn1 and Zn3 and connecting the {Zn1, O3, Zn3} unit to an adjacent Zn4 ion

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† Electronic supplementary information (ESI) available: X-Ray powder diffraction patterns for compounds **1–3** (Fig. S1–S3). CCDC reference numbers 699370–699372. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901607d

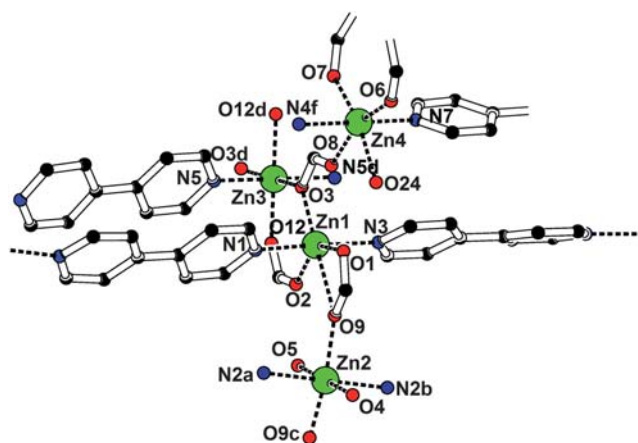


Fig. 1 Representation of the asymmetric unit of **1** showing the atom labeling scheme for the zinc(II) ions. The perchlorate anions, the lattice water molecules and the H atoms are not shown for clarity. Symmetry operations: $a = 1 - x, y, 1/2 - z$; $b = 1 - x, y, 3/2 - z$; $c = 1 - x, -y, 1 - z$; $d = x, -y, -1/2 + z$; $f = 3/2 - x, 1/2 + y, 3/2 - z$.

(through the oxygen atom O8). The third formate ligand [O1, O9] is chelating the atom Zn1 (Fig. 1) and is coordinated as well (through the atom O9) to a neighbouring Zn2 ion, thus acting as a μ -O,O',O' ligand.

The Zn–O and Zn–N bond distances are in normal ranges for this type of chromophore (Table 1).^{21,24} The coordination angles, varying from 53.31(9) to 122.98(11)° (Table 1), reflect a strong distortion of the octahedron which is principally due to the very small bite angle of the chelating formate ligand.

The basal plane of the octahedron around Zn2 is constituted of two oxygen atoms (O9 and O9c) from two μ -O,O',O'-formate ligands and two water oxygen atoms (O4 and O5). Zn2 lies on a two-fold axis and is coordinated by two different 4,4'-bpy moieties (N2a and N2b) at the axial positions. The Zn–O and

Table 1 Selected bond lengths (Å) and angles (°) for **1**^a

Zn1–O1	2.100(3)	Zn2–O4	2.054(5)
Zn1–O2	2.048(3)	Zn2–O5	2.062(5)
Zn1–O3	2.082(3)	Zn2–O9	2.095(3)
Zn1–O9	2.639(3)	Zn2–O9c	2.095(3)
Zn1–N1	2.168(3)	Zn2–N2a	2.198(4)
Zn1–N3	2.171(3)	Zn2–N2b	2.198(4)
Zn3–O3	2.149(3)	Zn4–O6	2.036(5)
Zn3–O3d	2.149(3)	Zn4–O7	2.065(4)
Zn3–O12	2.082(3)	Zn4–O8	2.192(3)
Zn3–O12d	2.082(3)	Zn4–O24	2.144(4)
Zn3–N5	2.126(3)	Zn4–N4f	2.150(4)
Zn3–N5d	2.126(3)	Zn4–N7	2.163(4)
O1–Zn1–O3	122.98(11)	O4–Zn2–O9	97.25(9)
O3–Zn1–O2	100.69(12)	O9–Zn2–O5	82.75(9)
O2–Zn1–O9	83.07(9)	O5–Zn2–O9c	82.75(9)
O9–Zn1–O1	53.31(9)	O9c–Zn2–O4	97.25(9)
N1–Zn1–N3	175.19(15)	N2a–Zn2–N2b	180
O3–Zn3–O12	87.99(11)	O6–Zn4–O7	114.80(18)
O12–Zn3–O3d	92.01(11)	O7–Zn4–O8	84.76(13)
O3d–Zn3–O12d	87.99(11)	O8–Zn4–O24	77.31(13)
O12d–Zn3–O3	92.01(11)	O24–Zn4–O6	83.12(18)
N5–Zn3–N5d	180	N4f–Zn4–N7	178.21(16)

^a Symmetry operations: $a = 1 - x, y, 1/2 - z$; $b = 1 - x, y, 3/2 - z$; $c = 1 - x, -y, 1 - z$; $d = x, -y, -1/2 + z$; $f = 3/2 - x, 1/2 + y, 3/2 - z$.

Zn–N bond distances can be considered as normal for this type of coordination environment (Table 1).²⁵ The basal angles ranging from 82.75(9) to 97.25(9)° indicate a distortion of the octahedral geometry, attributed to constraints induced by the bridging of the μ -O,O',O'-formate ligands to Zn1.

The N₂O₄ coordination environment around the Zn3 ion, which lies on an inversion centre, is an almost perfect octahedron (the basal angles vary from 87.99(11) to 92.01(11); Table 1), with four in-plane oxygen atoms belonging to distinct formate ligands (O3, O12, O3d and O12d; Fig. 1). The axial positions are occupied by the nitrogen atoms N5 and N5d from two 4,4'-bpy ligands. The Zn–O and Zn–N bond lengths are in common ranges.²¹

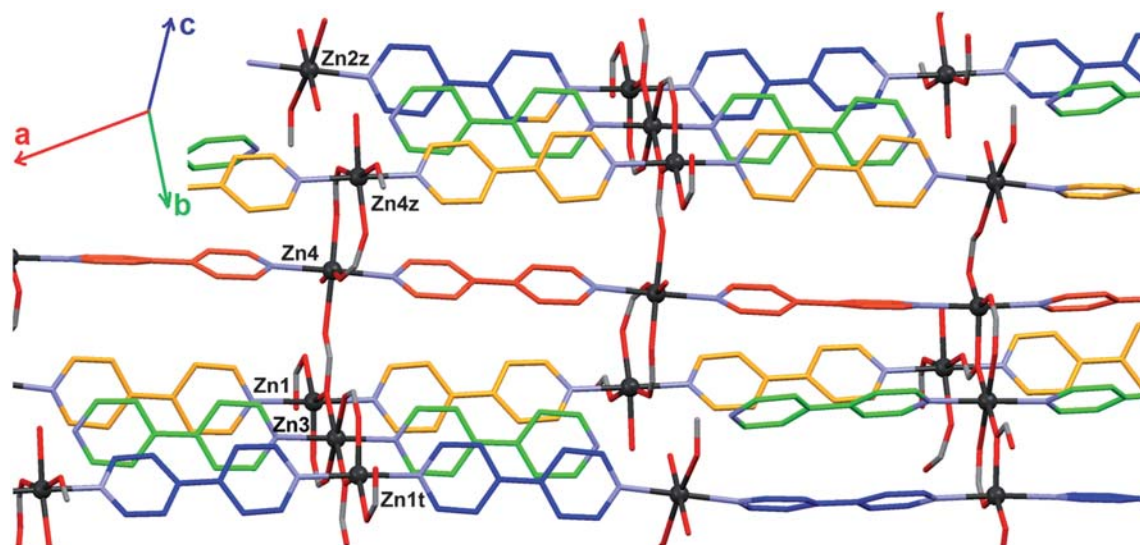


Fig. 2 3D coordination network of Zn^{II}, 4,4'-bipyridine and formate. The 4,4'-bpy ligands involved in the formation of trinuclear zinc units are shown in blue, green and orange for comparison with compounds **2** and **3**. The 4,4'-bpy ligands generating a 1D chain are depicted in red. Symmetry operations: $t = 1/2 - x, -1/2 + y, 1/2 - z$; $z = 1 - x, y, 3/2 - z$.

The distorted octahedral geometry around Zn4 (the basal angles range from 77.31(13) to 114.80(18)°) is most likely due to the bite angle of the μ -O,O'-formate ligands (oxygen atoms O6 and O7), connecting Zn4 to a symmetry-related Zn4 ion (see Fig. 2). The Zn–O and Zn–N bond distances are in normal ranges.²⁵

The self-assembly between these bridging N- and O-ligands and zinc(II) ions gives rise to a remarkable 3D architecture (Fig. 2). The metal–organic framework is formed from trinuclear [Zn1, Zn3, Zn1] clusters which are connected through two 4,4'-bpy ligands (yellow and blue 4,4'-bpy ligands in Fig. 2) to the Zn2 and Zn4 ions, generating 1D, triple-stranded infinite chains. These chains showing π – π interactions between three 4,4'-bpy units (with centroid-to-centroid distances ranging from 3.491(4) to 3.839(4) Å) are connected to each other *via* a different infinite single chain exhibiting the sequence {Zn1, Zn4, Zn4, Zn1, Zn2,...} (chain built from the orange 4,4'-bpy ligands in Fig. 2). This spatial arrangement produces a unique heptanuclear coordination metallacycle (Fig. 3).

The organization of these heptanuclear motifs in the crystal lattice gives rise to the formation of channels which are filled by disordered perchlorates and water molecules (Fig. 4).

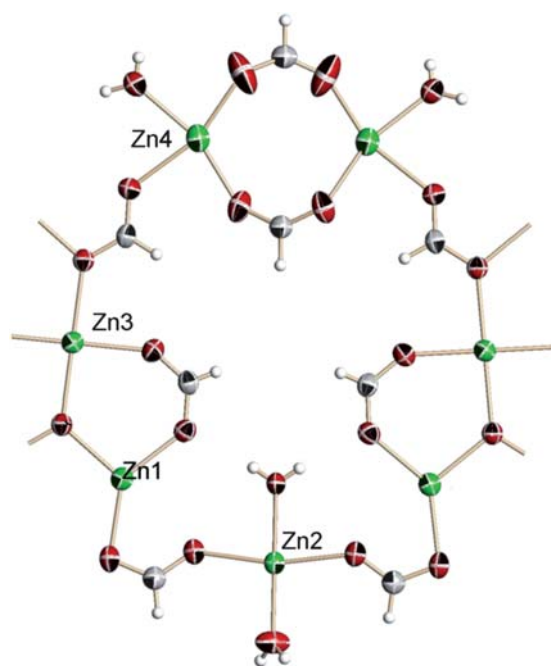


Fig. 3 Heptanuclear building unit constituting the channel walls in **1**.

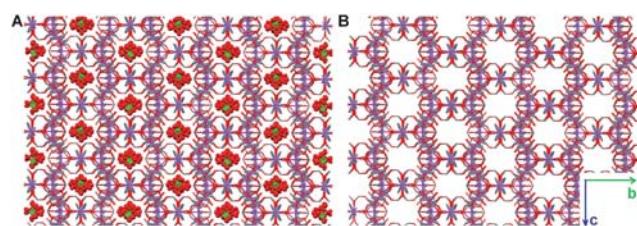


Fig. 4 (A) Channels filled with disordered perchlorate anions (shown in the space-filling mode) and water molecules. (B) Empty channels for compound **1**.

Crystal structure of $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**)

The simple replacement of formate by acetate during the synthetic procedure (used to prepare **1**) produces significant structural changes in the crystal lattice of the resulting coordination compound $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**). As is shown in Fig. 5, **2** only exhibits two types of zinc(II) ions, namely Zn1 and Zn2 (instead of four different zinc ions for compound **1**; see above).

Zn1 is characterized by a strongly distorted octahedral coordination environment, owing to the small bite angle of the μ -O,O',O' bridging mode of one of the two acetato ligands (the angle O3–Zn1–O4 is only 58.34(12)°; Table 2). The basal plane is constituted of four oxygen atoms belonging to two acetato ligands (O1, O3 and O4) and one water molecule (O5). The octahedron is completed by two 4,4'-bpy nitrogen atoms (N1 and N2a), at the axial positions. The Zn–O and Zn–N bond distances can be considered as normal for this type of ZnN_2O_4 coordination environment (Table 2).

Zn2 lies on an inversion centre. The coordination environment around the Zn2 ion is an almost perfect octahedron, since the basal angles, varying from 87.73(13) to 92.27(13)°, are close to the ideal value of 90°. At the basal plane, Zn2 is coordinated by four oxygen atoms (O2, O3, O2c and O3c) from different acetato ligands. The axial positions are occupied by nitrogen atoms N3

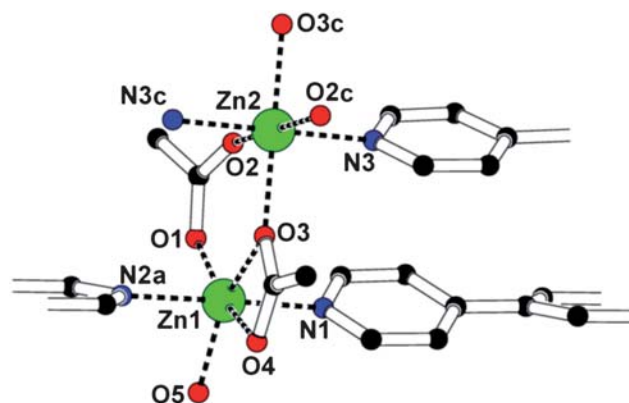


Fig. 5 Representation of the asymmetric unit of **2** showing the atom labeling scheme for the zinc(II) ions. The hexafluoridophosphate anions, the lattice water molecules and the H atoms are not shown for clarity. Symmetry operations: $a = x, -y + 1, z$; $c = 1 - x, 1 - y, 1 - z$.

Table 2 Selected bond lengths (Å) and angles (°) for **2**^a

Zn1–O1	1.995(4)	Zn2–O2	2.076(3)
Zn1–O3	2.218(3)	Zn2–O3	2.160(3)
Zn1–O4	2.241(4)	Zn2–N3	2.177(4)
Zn1–O5	2.060(3)		
Zn1–N1	2.168(4)		
Zn1–N2a	2.211(4)		
O1–Zn1–O3	104.77(13)	O2–Zn2–O3	87.73(13)
O3–Zn1–O4	58.34(12)	O3–Zn2–O2c	92.27(13)
O4–Zn1–O5	92.86(13)	N3–Zn2–N3c	180
O5–Zn1–O1	104.03(13)		
N1–Zn1–N2a	178.29(12)		

^a Symmetry operations: $a = x, -y + 1, z$; $c = 1 - x, 1 - y, 1 - z$.

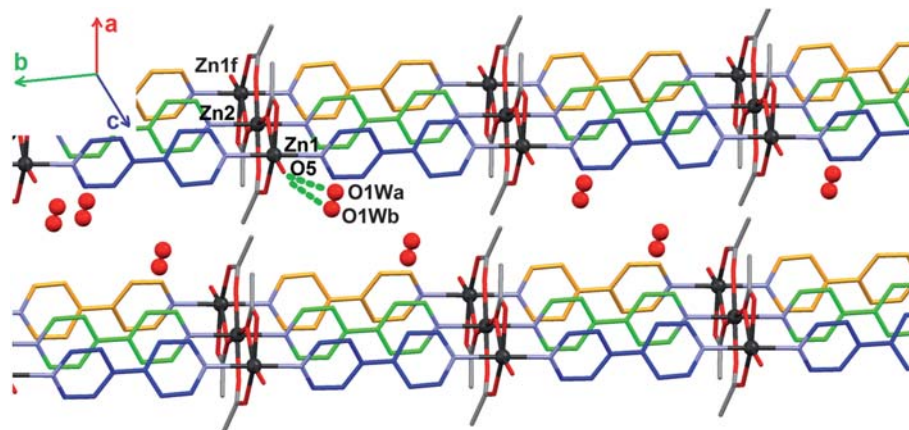


Fig. 6 1D coordination network in **2** of Zn^{II} , 4,4'-bipyridine and acetate. The 4,4'-bpy ligands involved in the formation of trinuclear zinc units are shown in blue, green and orange for comparison with compounds **1** and **3**. Symmetry operations: $a = x, -y + 1, z$; $b = x, 1 + y, z$; $f = 2 - x, 1 - y, 2 - z$.

and N3c, belonging to two 4,4'-bpy ligands (lying on an inversion centre) at common distances.

Zn2 is bridged to two symmetry-related Zn1 ions *via* two $\mu\text{-O, O'}$ - and two $\mu\text{-O, O'}$ -acetato ligands, generating a linear trinuclear [Zn1, Zn2, Zn1] cluster, analogous to the [Zn1, Zn3, Zn1] triad observed in **1** (see Fig. 2 and 6).

The [Zn1, Zn2, Zn1] clusters are connected to each other through coordination of the zinc ions by 4,4'-bpy ligands, producing a 1D chain, constituted of three single zinc chains, indicated by the blue, green and yellow 4,4'-bpy ligands in Fig. 6. Contrary to **1**, the triple-stranded chains in **2** are not connected to each other through a single-stranded coordination chain (see orange chain in Fig. 2). This interconnection is most likely prevented by the steric bulk of the acetato methyl groups (Fig. 7). However, the 1D chains are closely packed, which only allows the coordination of a small molecule, namely a water molecule (O5 in Fig. 6 and 7) at the two external positions of the [Zn1, Zn2, Zn1] triad. These coordinated water molecules are hydrogen-bonded to disordered lattice water molecules ($\text{O5} \cdots \text{O1Wb} = 2.717(16) \text{ \AA}$ and $\text{O5} \cdots \text{O1Wa} = 2.806(19) \text{ \AA}$). Similarly to the ClO_4^- ions in **1**,

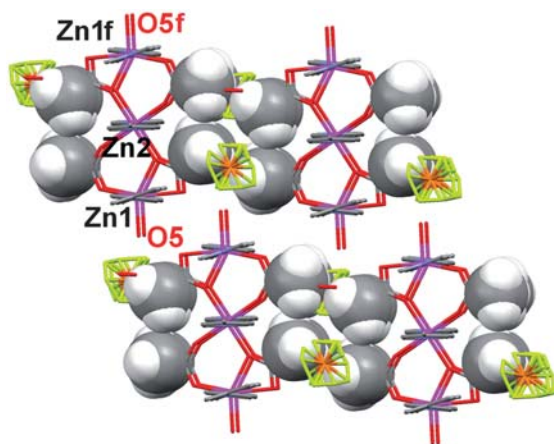


Fig. 7 Illustration of the steric bulk in **2** resulting from the acetato methyl groups (shown in the space-filling mode), which prevents the interconnection of the triple-stranded chains. Symmetry operation: $f = 2 - x, 1 - y, 2 - z$.

the PF_6^- anions occupy the voids in the crystal lattice of **2** and apparently do not play a significant role in the formation of the framework (since their only interactions occur with the disordered lattice water molecules; the $\text{F} \cdots \text{O}$ contact distances are in the range $2.89(3) - 2.98(2) \text{ \AA}$). Actually, the compound $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})\}_n$ has been previously reported by Woodward *et al.* (CSD refcode: CERFUB).²¹ The X-ray structure of this compound exhibits the same 1D framework, therefore confirming the non-involvement of the PF_6^- or ClO_4^- anions in the network formation.

Crystal structure of $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(4,4'\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (**3**)

The steric effect on the molecular architecture has been further investigated by using a propionato ligand during the synthesis of the coordination assembly. Thus, the solid-state structure of compound $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(4,4'\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (**3**), bearing ethyl groups, shows significant differences compared to that of **2** (holding CH_3 groups) and **1** (characterized by H groups).

The 2D molecular structure of compound **3** (Fig. 8) exhibits three different types of zinc(II) ions with octahedral N_2O_4 (Zn1) and N_3O_3 (Zn2, Zn3) geometries.

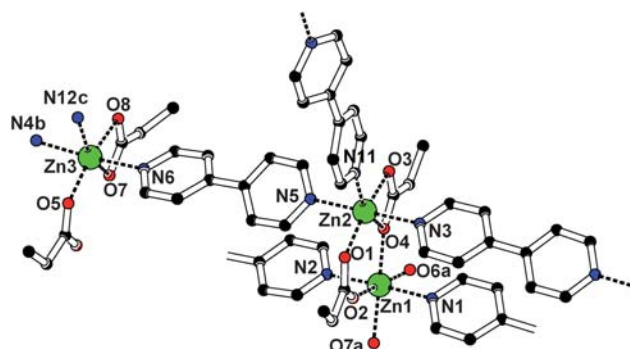


Fig. 8 Representation of the asymmetric unit of **3** showing the atom labeling scheme for the zinc(II) ions. The perchlorate anions, the lattice water molecules and the H atoms are not shown for clarity. Symmetry operations: $a = -x, -y + 1, -z$; $b = x - 1, y, z - 1$; $c = -x, -y + 2, -z$.

Table 3 Selected bond lengths (Å) and angles (°) for **3**^a

Zn1–O2	2.119(2)	Zn2–O1	2.003(2)
Zn1–O4	2.133(2)	Zn2–O3	2.166(2)
Zn1–O6a	2.083(2)	Zn2–O4	2.218(2)
Zn1–O7a	2.152(2)	Zn2–N3	2.202(3)
Zn1–N1	2.174(3)	Zn2–N5	2.198(3)
Zn1–N2	2.167(3)	Zn2–N11	2.121(3)
Zn3–O5	1.995(2)	O2–Zn1–O4	89.74(9)
Zn3–O7	2.215(2)	O4–Zn1–O6a	89.58(10)
Zn3–O8	2.168(2)	O6a–Zn1–O7a	91.47(9)
Zn3–N6	2.206(3)	O7a–Zn1–O2	89.22(9)
Zn3–N4b	2.198(3)	N1–Zn1–N2	176.37(11)
Zn3–N12c	2.108(3)		
O1–Zn2–O4	105.33(9)	O5–Zn3–O7	103.28(9)
O4–Zn2–O3	59.55(9)	O7–Zn3–O8	59.57(9)
O3–Zn2–N11	95.36(10)	O8–Zn3–N12c	96.89(10)
N11–Zn2–O1	99.75(11)	N12c–Zn3–O5	100.31(11)
N3–Zn2–N5	178.24(11)	N6–Zn3–N4b	175.86(11)

^a Symmetry operations: a = $-x, -y + 1, -z$; b = $x - 1, y, z - 1$; c = $-x, -y + 2, -z$; d = $-x + 1, -y + 1, -z + 1$.

Zn1 exhibits an almost perfect octahedral environment with basal angles ranging from 89.22(9) to 91.47(9)° (Table 3). The basal plane is constituted of four oxygen atoms belonging to two μ -O,O'-propionato ligands (O2 and O6a) and two μ -O,O',O'-propionato ligands (O4 and O7a). The axial positions are occupied by two different **4,4'-bpy** ligands which connect Zn1 to symmetry-related Zn1 ions, generating a polymeric chain. The Zn–N and Zn–O bond lengths are comparable to those of the ZnN_2O_4 coordination units of the previous compounds.

Zn2 is coordinated at the basal plane of the octahedron by three oxygen atoms and one nitrogen atom from two propionato ligands (O3, O4 and O1) and one **4,4'-bpy** ligand (N11). The axial positions are occupied by two **4,4'-bpy** ligands (N3 and N5), linking Zn2 to two symmetry-related Zn3 ions, generating a polymeric chain exhibiting the sequence {Zn2, Zn3, Zn2, Zn3,...}. The Zn–O and Zn–N bond distances are in normal ranges for this type of coordination moiety.^{24,26} The basal angles

varying from 59.55(9) to 105.33(9)° (Table 3) are indicative of a strong distortion of the octahedron, attributed to the small bite angle of the μ -O,O'-propionato ligand (O4–Zn2–O3 = 59.55(9)°).

The coordination environment around the Zn3 ion is comparable to that of Zn2. The ZnN_3O_3 unit exhibits analogous Zn–O

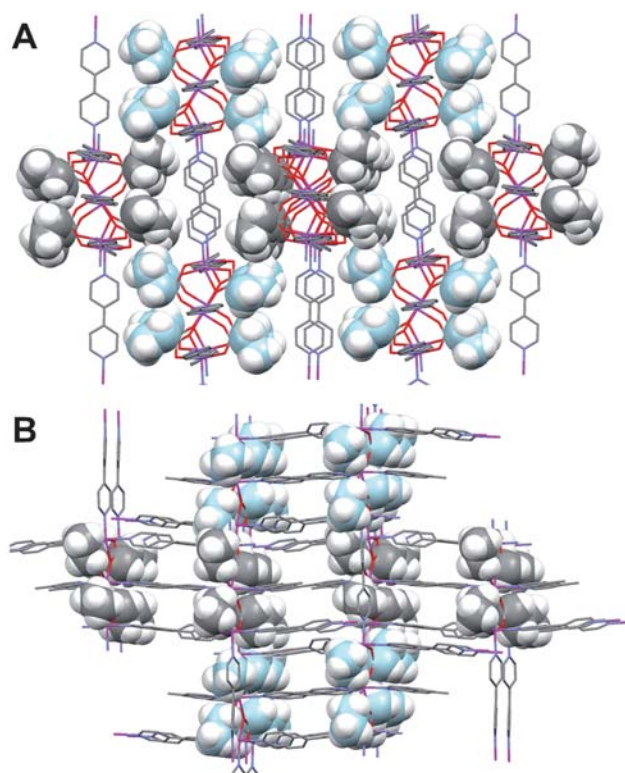


Fig. 10 Illustrations of the steric hindrance due to the propionato ethyl groups (shown in the space-filling mode, in grey and light blue) in **3**, which prevents close contacts between the 1D chains.

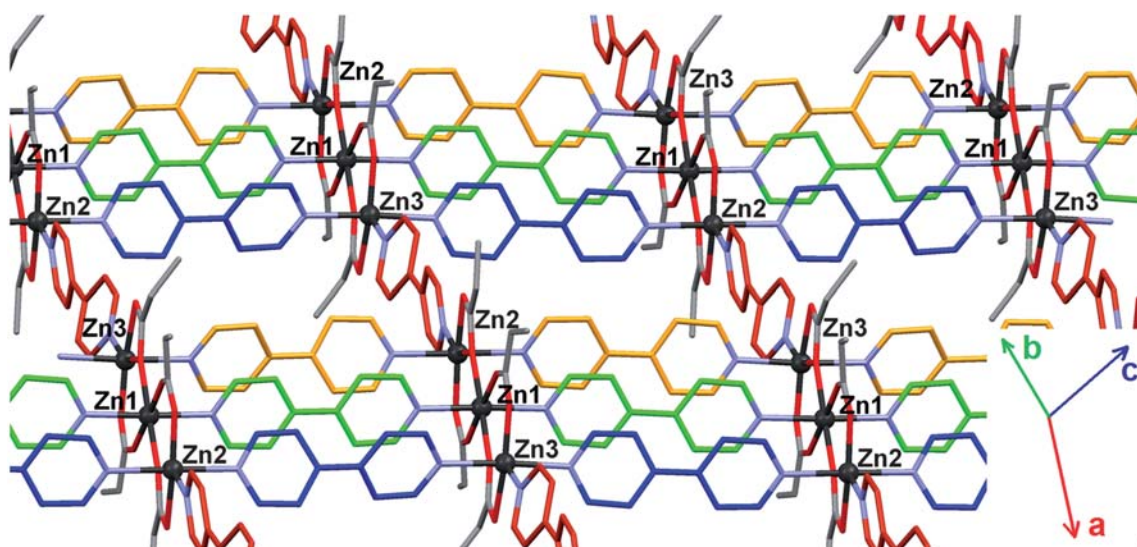


Fig. 9 2D coordination network in **3** of Zn^{II} , 4,4'-bipyridine and propionate. The **4,4'-bpy** ligands involved in the formation of trinuclear zinc units are shown in blue, green and orange for comparison with compounds **1** and **2**. The **4,4'-bpy** ligands connecting 1D three-leg ladders are shown in red.

and Zn–N bond lengths (to those of Zn2), which can be considered as normal (Table 3).²⁷ Similarly to Zn2, the coordination geometry around Zn3 is a strongly distorted octahedron, resulting from the small O7–Zn3–O8 angle of 59.57(9)° characterizing the coordination of the propionato ligand (Fig. 8).

The trinuclear [Zn1, Zn2, Zn3] clusters are connected to each other, in a head-to-tail fashion, through the coordination of the

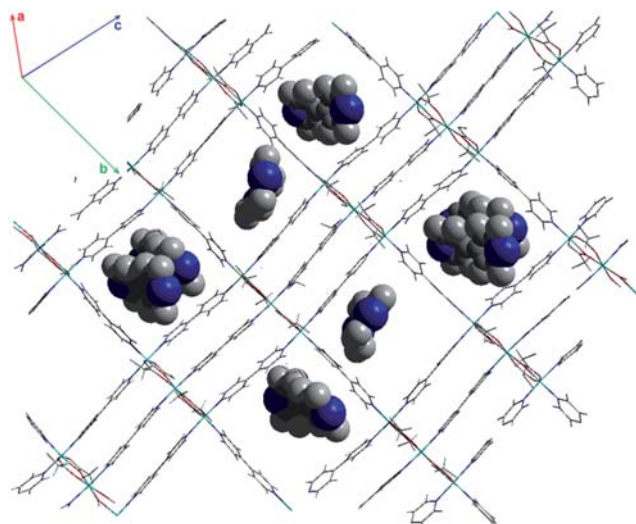


Fig. 11 Representation of the 2D network of compound **3**, illustrating the large cavities which contain non-coordinated **4,4'**-bpy ligands (space-filling mode).

zinc ions by **4,4'**-bpy ligands, producing a 1D chain exhibiting the sequence {Zn1, Zn1, Zn1,...} for the central metal ion and {Zn2, Zn3, Zn2, Zn3,...} for the external zinc ions. This arrangement gives rise to triple-stranded chains, illustrated by the blue, green and yellow **4,4'**-bpy ligands in Fig. 9. These coordination polymeric chains are closely related to those observed for compound **2** (see Fig. 6 and 9) and reassemble part of the network of compound **1** (see Fig. 2 and 9). In contrast to the methyl groups in **2**, the ethyl groups of the propionato ligands in **3** do not allow a close packing of the triple-stranded polymeric chains (see Fig. 7 and 10), as the result of steric constraints. Consequently, the trinuclear zinc(II) units in **3** are more separated from each other than those in **2** (Fig. 7 and 10A). Indeed, the shorter intermolecular Zn...Zn separation distance is 9.391(3) Å for compound **3**, while the shorter intermolecular Zn...Zn distance is 5.557(3) Å for **2**.

This spatial organization allows the coordination of **4,4'**-bpy ligands at the two external positions of the trizinc moieties (orange **4,4'**-bpy ligands coordinated to Zn3 and Zn2; Fig. 9), connecting the triple-stranded chains to each other to form a 2D network. The herringbone-type architecture (Fig. 10A and 11) exhibit large cavities that can accommodate bulky guest molecules, namely non-coordinated **4,4'**-bpy ligands which are hydrogen-bonded to lattice water molecules (N10...O1w = 2.960(8), N9...O4w = 2.908(7) Å and N8...O3w = 2.827(10) Å). In addition, these large voids contain disordered perchlorate anions, which do not significantly interact with the metal–organic framework, but are hydrogen bonded to lattice water molecules (O15...O2w = 2.889(12) Å, O12...O3w = 2.831(15) Å and O12b...O3w = 2.882(15) Å).

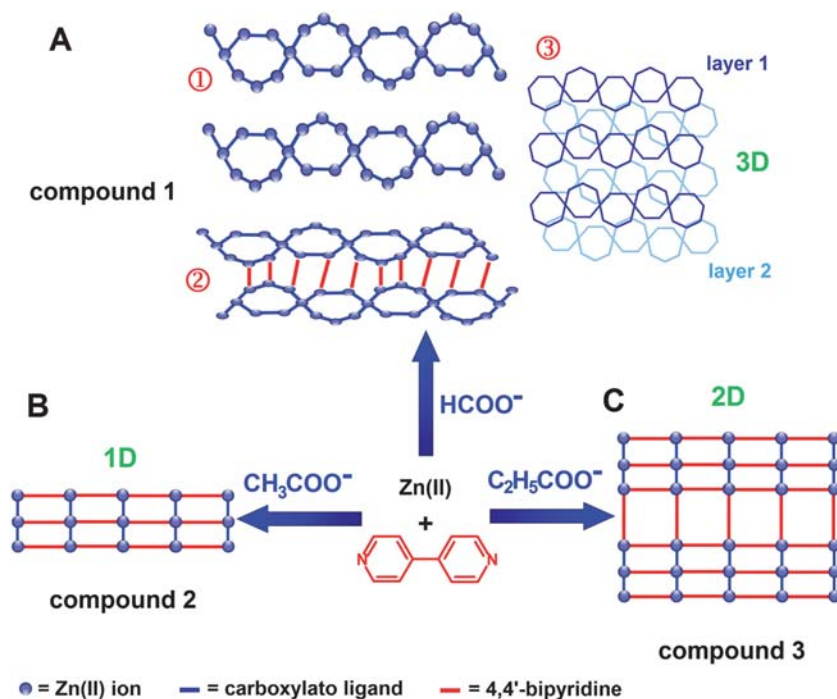


Fig. 12 Coordination networks of A) compound **1** (3D), B) compound **2** (1D) and C) compound **3** (2D). A-①: 1D chains packed in a parallel fashion, forming a 2D layer; A-②: connection of two chains through **4,4'**-bpy ligands; A-③: packing of slightly shifted layers.

Coordination networks

The use of slightly different carboxylato moieties as secondary co-ligands of $[\text{Zn}(\text{II})/4,4'\text{-bpy}]$ coordination units, applying the same reaction conditions, leads to the formation of drastically distinct networks (Fig. 12).

The combination $[\text{Zn}^{\text{II}}/4,4'\text{-bpy}/\text{formate}]$ generates an intricate 3D framework (Fig. 12A). The bridging of zinc(II) ions by formate ligands produces a 1D chain constituted of heptanuclear rings (see Fig. 3 and 12A-①). These chains are arranged in a parallel fashion, resulting in a 2D layer. Each layer is linked to one layer above and to one layer below through coordinated 4,4'-bipyridines (red lines in Fig. 12A-②). Since each chain is connected to two chains above and to two chains below, this spatial organization creates a 3D framework of slightly shifted layers (Fig. 12A-③).

The sole replacement of formate by acetate results in the formation of 1D network (Fig. 12B). This simple framework is built from trinuclear acetato-bridged units that are linked to two adjacent ones, to form a three-leg ladder.

The use of propionate as co-ligand yields a 2D network (Fig. 12C) which presents similarities with the previous one. Actually, the framework of **3** contains the three-leg ladders observed in solid-state structure of **2**. These three-leg ladders are connected to each other *via* 4,4'-bpy ligands (vertical red lines in Fig. 12C).

It should be noted that, albeit the three coordination networks are different, they show some common features. Indeed, all three structures exhibit trinuclear carboxylato-bridged moieties as secondary building units (SBUs). Moreover, infinite $\{-\text{Zn}-(4,4'\text{-bpy})-\}_n$ chains are observed for the three compounds (see for instance, the red $\{-\text{Zn}4-(4,4'\text{-bpy})-\}_n$ chains in Fig. 2, and the blue $\{-\text{Zn1}/\text{Zn2}-(4,4'\text{-bpy})-\}_n$ chains in Fig. 6 and 9, respectively). Finally, one should notice that the zinc(II) ions have similar coordination environments, regardless of the carboxylato co-ligand used. Therefore, the structural diversity of the frameworks obviously originates from different steric constraints induced by the carboxylato ligands.

Comparison between the frameworks of **1**, **2** and **3** and those of related compounds found in the Cambridge Structural Database

Eight coordination frameworks exclusively constructed from zinc(II) ions, 4,4'-bipyridine ligands and bridging carboxylato units are found in the Cambridge Structural Database (CSD ConQuest version 1.11; Refcodes: ALUPUS,^{14,15,28} CERFOV,²¹ CERFUB,²¹ DELTAQ,¹⁹ EYELID,¹⁷ JODFIS,¹³ NEWTIT¹⁸ and QEQBIY¹²). Representations of these frameworks are shown in Fig. 13.

From the eight compounds, three, *i.e.* CERFOV, CERFUB and QEQBIY, show frameworks that are comparable to those of **2** and **3**. Actually, as already mentioned above, the compound with refcode CERFUB²¹ is isostructural to **2**. The sole difference between CERFUB and **2** lies in the distinct lattice anions, respectively, ClO_4^- and PF_6^- . This demonstrates that the two anions have no influence on the network formation. The 2D triple-chain sheet architectures of CERFOV²¹ and QEQBIY¹² are comparable to that of **3**. The remaining five compounds exhibit 1D networks (ALUPUS, EYELID, JODFIS and

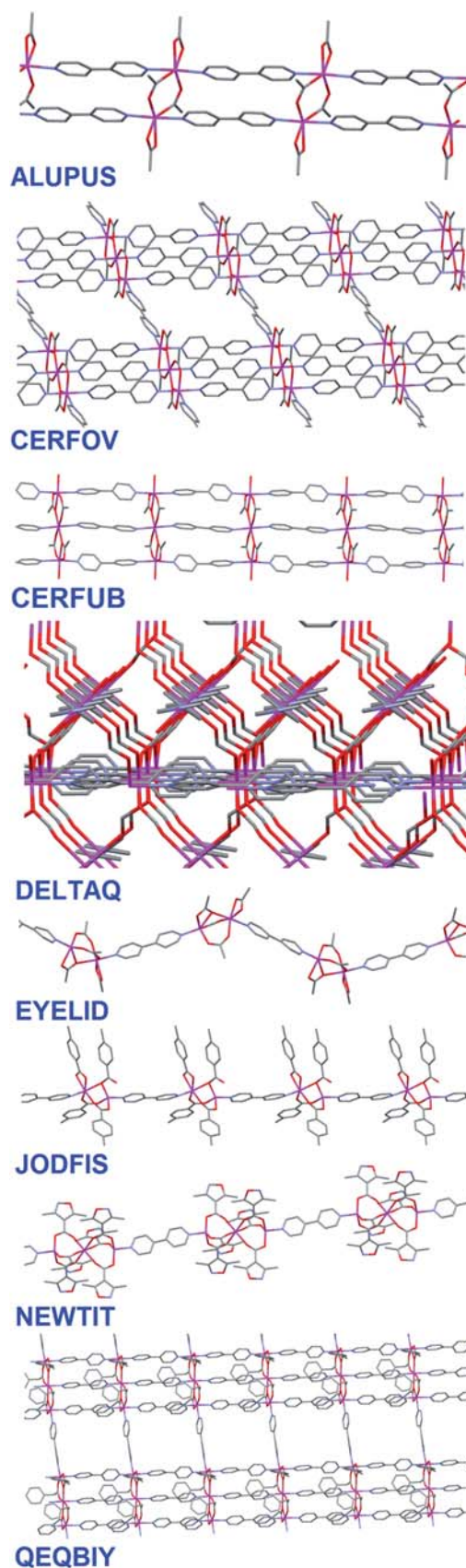


Fig. 13 Representations of the coordination networks exhibited by the seven $[\text{Zn}^{\text{II}}/4,4'\text{-bpy}/\text{carboxylato}]$ -based compounds found in the CSD.

NEWTIT) or a 3D framework (DELTAQ). Interestingly, the only 3D structure found in the CSD (DELTAQ) contains formate co-ligands. In the present study, a 3D network is observed as well when formate is used as secondary ligand. Therefore, the lower steric hindrance exerted by the formate ligand appears to favour the formation of 3D structures. Finally, it has to be noted that all carboxylato units act as bridging ligands, linking two or three zinc(II) atoms (for the formate ligand, polymeric $\text{Zn}^{\text{II}}/\text{HCOO}^-$ structures are observed). The resulting zinc clusters are connected to each other through the 4,4'-bipyridine ligands.

Thermogravimetric analysis

The thermal decomposition behavior of compound **1** (Fig. 14) reveals a first weight loss in the temperature range 143–201 °C, corresponding to four water molecules (experimental value, 5.50%; calculated, 6.03%). From 202 °C, compound **1** starts to decompose. When **1** is heated up to 800 °C, a white residue is obtained, which is most likely ZnO.

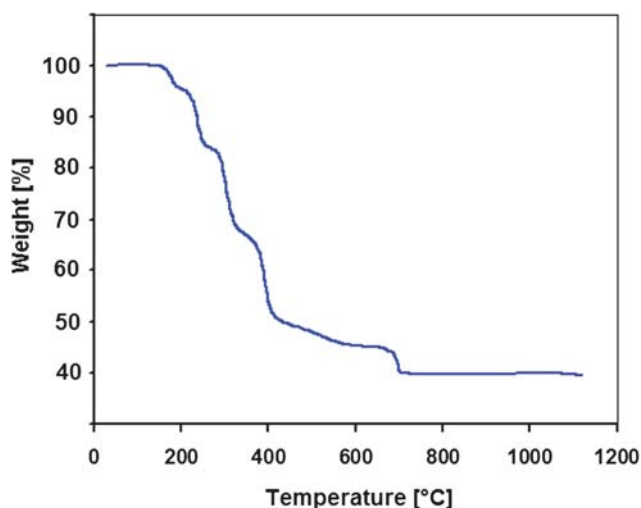


Fig. 14 Thermogravimetric analysis of compound **1**.

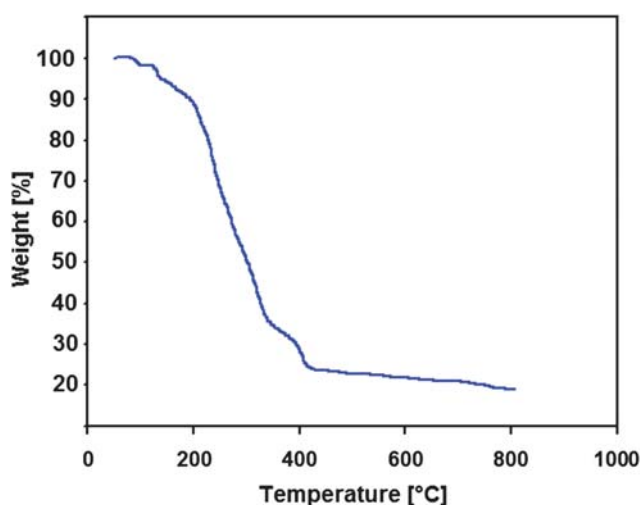


Fig. 15 Thermogravimetric analysis of compound **2**.

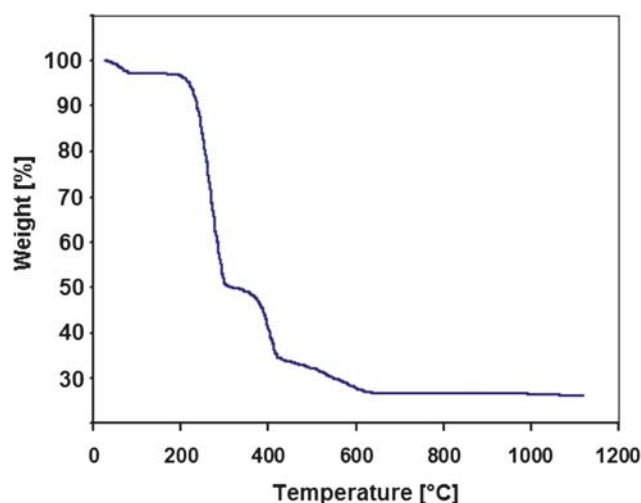


Fig. 16 Thermogravimetric analysis of compound **3**.

The thermogravimetric analysis of compound **2** (Fig. 15) shows a first weight loss in the temperature range 71–170 °C, characterizing the loss of four water molecules (experimental value, 5.82%; calculated, 5.70%). In the temperature range 171–429 °C, the decomposition of the coordination material is observed. As for **1**, a white residue (ZnO) is obtained when **2** is heated to 800 °C.

The thermal analysis of **3** (Fig. 16) exhibits a two-stage decomposition of the material. A first weight loss of 3.50% is observed in the temperature range 92–195 °C, which corresponds to the release of four lattice water molecules (calculated 4.15%). In the temperature range 196–630 °C, compound **3** degrades. As for compounds **1** and **2**, a white residue (ZnO) is obtained when the sample is heated to 800 °C.

Conclusions

One of the most important challenges that remains in crystal engineering is crystal structure prediction. As properly stated by Desiraju,²⁹ the main objective of the crystal engineering chemist is to try to understand intermolecular interactions in the context of crystal packing and to use such knowledge to rationally design new materials with anticipated molecular structures and desired physical and chemical properties.

In the present study, the influence of small secondary ligands, namely common monocarboxylato ligands, on the overall solid-state structure of [zinc(II)–4,4-bpy–carboxylato] coordination compounds has been investigated. This study shows that the change from a formate ligand to an acetato and a propionato ligand gives rise to the formation of drastically distinct metal–organic frameworks, as the result of the different steric bulk of the carboxylato unit involved. Such studies are of great interest for the crystal engineering chemist, as they contribute to increase the knowledge about crystallization processes and molecular structure prediction.

Experimental

All starting materials were commercially available and used as received. IR spectra were recorded on a Perkin-Elmer Spectrum

One FTIR spectrophotometer as KBr discs in the range 4000–450 cm^{-1} . C, H, and N analyses were performed on a Perkin-Elmer PE2400 CHNS/O. Thermogravimetric analyses were carried out using a Perkin-Elmer Pyris Diamond analyzer in flowing nitrogen at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. X-ray powder diffraction (XRPD) data for **1–3** were obtained using a Phillips Xpert Pro equipped with an X'celerator, with Cu $K\alpha$ radiation ($\lambda \approx 1.5408 \text{ \AA}$), in the 2θ range 10–45. The diffraction patterns were recorded at room temperature (see Fig. S1–S3, ESI).†

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (**1**)

An aqueous solution (10 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.302 g, 1.0 mmol) was added to an ethanolic solution (10 mL) of **4,4'-bpy** (0.157 g, 1.0 mmol). An aqueous solution (10 mL) of NaO_2CH (sodium formate; 0.149 g, 2.0 mmol) was subsequently added, followed by 0.141 g of KClO_4 (1.0 mmol) under continuous stirring. The resulting colourless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, colourless crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield = 0.262 g (66% based on Zn). Elemental analyses calculated for $\text{C}_{39}\text{H}_{40}\text{Cl}_2\text{N}_7\text{O}_{20}\text{Zn}_3$: C, 39.24; H, 3.38; N, 8.21. Found: C, 39.22; H, 3.31; N, 8.22%. IR data (cm^{-1}): 3400s, 1609s, 1588s, 1536w, 1413m, 1384m, 1348w, 1224w, 1117s, 1089s, 807s, 630s. The purity and homogeneity of compound **1** were confirmed by X-ray powder diffraction (see Fig. S1).†

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**)

An aqueous solution (15 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.306 g, 1.0 mmol) was added to a solution of **4,4'-bpy** (0.157 g, 1.0 mmol) in ethanol (10 mL). Next, an aqueous solution (20 mL) of NaO_2CCH_3 (sodium acetate; 0.138 g, 2.0 mmol) and an aqueous solution (10 mL) of KPF_6 (0.185 g, 1.0 mmol) were added under continuous stirring. A few drops of CH_3COOH 98% were subsequently added to the reaction mixture, yielding a clear colorless solution. This solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing colorless needle crystals of **2** after a few days. Yield = 0.290 g (70% based on Zn). Elemental analyses calculated for $\text{C}_{38}\text{H}_{44}\text{F}_{12}\text{N}_6\text{O}_{12}\text{P}_2\text{Zn}_3$: C, 36.14; H, 3.51; N, 6.66. Found: C, 36.41; H, 3.24; N, 6.30%. IR data (cm^{-1}): 3400s, 3045s, 1603s, 1520s, 1490s, 1419s, 133m, 1219s, 1070s, 1195s, 1100s, 1074s 1046m, 1015m, 846s, 838s, 643m, 630m, 560s. The purity and homogeneity of compound **2** were confirmed by X-ray powder diffraction (see Fig. S2).†

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(4,4'\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (**3**)

An aqueous solution (10 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.313 g, 1.0 mmol) was added to a solution of **4,4'-bpy** (0.158 g, 1.0 mmol) in ethanol (10 mL). Subsequently, an aqueous solution (10 mL) of $\text{NaCOOCH}_2\text{CH}_3$ (sodium propanoate; 0.201 g, 2.0 mmol) was added, followed by KClO_4 (0.152 g, 1.0 mmol) under continuous stirring. Next, a few drops of $\text{CH}_3\text{CH}_2\text{COOH}$ 98% were added,

yielding a clear colourless solution, which was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. Colorless crystals were collected from the solution by filtration after several days. Yield = 0.385 g (68% based on Zn). Elemental analyses calculated for $\text{C}_{72}\text{H}_{76}\text{Cl}_2\text{N}_{12}\text{O}_{20}\text{Zn}_3$: C, 50.97; H, 4.52; N, 9.91. Found: C, 51.19; H, 4.84; N, 9.91%. IR data (cm^{-1}): 3392s, 1609s, 1578s, 1552s, 1466m, 1419m, 1222w, 1107s, 1067s, 1046m, 808s, 631s. The purity and homogeneity of compound **3** were confirmed by X-ray powder diffraction (see Fig. S3).†

Crystallography

The X-ray single-crystal data for all compounds were collected at 293(2) K on a 1 K Bruker SMART CCD area detector diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at a detector distance of 4.5 cm and swing angle of -35° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0, 88, and 180°) and each exposure of 40 s covered 0.3° in ω . Data reduction and cell refinements were performed using the program SAINT.³⁰ An empirical absorption correction by using the SADABS³¹ program was applied, which resulted in transmission coefficients ranging from 0.690 to 0.820, 0.642 to 0.823 and 0.600 to 0.680 for compounds **1**, **2** and **3**, respectively. The structures were solved by direct methods and refined by full-matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package.³² All hydrogen atoms were located geometrically and refined isotropically except the hydrogen atoms of the propionate group in compound **3**. The molecular graphics were created by using the SHELXTL-PC³² package.

Table 4 Crystal and refinement data for compounds **1**, **2** and **3**

Compound	1	2	3
Empirical formula	$\text{C}_{39}\text{H}_{40}\text{Cl}_2\text{N}_7\text{O}_{20}\text{Zn}_3$	$\text{C}_{38}\text{H}_{44}\text{F}_{12}\text{N}_6\text{O}_{12}\text{P}_2\text{Zn}_3$	$\text{C}_{72}\text{H}_{76}\text{Cl}_2\text{N}_{12}\text{O}_{20}\text{Zn}_3$
Formula weight	1193.79	1262.84	1696.46
T/K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P-1$	$P2_1/c$
$a/\text{\AA}$	26.8795(12)	10.6952(7)	18.506(4)
$b/\text{\AA}$	19.1415(8)	11.4831(7)	18.838(4)
$c/\text{\AA}$	21.2041(9)	11.7638(7)	25.568(5)
$\alpha/^\circ$	90	101.558(2)	90
$\beta/^\circ$	122.078(2)	116.757(2)	119.90(3)
$\gamma/^\circ$	90	95.574(2)	90
$V/\text{\AA}^3$	9244.2(7)	1234.58(13)	7727(3)
Z	8	1	4
$D_{\text{calc}}/\text{g cm}^{-3}$	1.716	1.699	1.458
μ/mm^{-1}	1.748	1.619	1.071
$F(000)$	4856	638	3504
θ range/ $^\circ$	2.22–21.99	2.02–30.35	2.16–27.48
GOF	1.030	1.007	1.023
Final R indices ^a	$R1 = 0.0465$	$R1 = 0.0648$	$R1 = 0.0562$
$[I > 2\sigma(I)]$	$wR2 = 0.1116$	$wR2 = 0.1666$	$wR2 = 0.1223$
R indices (all data)	$R1 = 0.0623$	$R1 = 0.0895$	$R1 = 0.0897$
	$wR2 = 0.1206$	$wR2 = 0.1867$	$wR2 = 0.1332$
Largest difference peak and hole/ $e \text{ \AA}^{-3}$	0.727, -0.981	1.460, -1.905	0.417, -0.564

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

The crystal and refinement details of all compounds are listed in Table 4.

For compound **1**, displacement parameter restraints were used in modelling the percholates and the bpy ligands. Even with these, the displacement parameter ratio (maximin) of a few atoms is around 4.5 : 1, and the anisotropic parameters for the perchlorate are larger than ideal. Geometric restraints were used in modelling the chlorates.

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Catalytic properties of a series of coordination networks: cyanosilylation of aldehydes catalyzed by Zn(II)-4,4'-bpy-carboxylato complexes†

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Three porous crystalline coordination polymers, *i.e.* the three-dimensional framework $\{[\text{Zn}_3(4,4'\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (**1**), the one-dimensional three-leg ladder $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**), and the two-dimensional layered network $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(4,4'\text{-bpy})_2(\text{H}_2\text{O})_4\}_n$ (**3**), have been investigated. All networks exhibit voids that contain the counter-ions and guest molecules, namely water for compounds **1** and **2**, and water/4,4'-bpy for compound **3**. In addition, compounds **2** and **3** are further stabilized by hydrogen bonds and π - π stacking interactions to form intricate supramolecular frameworks. The removal and reintroduction of guest water molecules for compounds **2** and **3** have been explored for their dynamic structural transformation. Interestingly, all Zn(II) compounds are active heterogeneous catalysts for the high-yield cyanosilylation of acetaldehydes in dichloromethane.

Introduction

Porous coordination polymers (PCPs), also known as metal-organic frameworks (MOFs), may be assembled from various molecular building blocks; therefore, diverse architectures and functions can be achieved.^{1–3} MOFs may find potential applications in molecular adsorption and separation processes,^{1–3} ion-exchange,^{4–6} catalysis,⁷ sensor technology,⁸ and optoelectronics.⁹ The design of porous coordination polymers does not only allow the preparation of light materials with high porosity, but also the generation of desirable regular networks. PCPs are engineered by linking building blocks at their coordination sites *via* multi-functional linkers into perfect and esthetic architectures, whose topology is pre-defined by the arrangement of the coordination sites and the orientation and number of the binding groups in the linker. Despite extensive studies, applications of porous compounds are still quite limited compared to that of zeolites. Inorganic materials with inner cavities, such as zeolites are known to bind many organic molecules in the hollow spaces and often exhibit unique catalytic properties for a number of organic reactions, in which high regioselectivity, stereoselectivity, and shape selectivity are observed.^{10–15} Reports of catalytic studies involving coordination polymers have been relatively scarce.^{16–29} While most of these investigations have dealt with some significant successes in enantioselective catalysis,^{17,18} there has been little focus thus far on probing the selectivity with substrates of comparable size to the pore dimensions.^{27,29}

Only few catalytic applications of carboxylato-bridged porous coordination polymers have been reported.^{4–7} The cat-

alytic and dynamic structural transformation of three coordination polymeric architectures for which preliminary results were published,³⁰ namely the 3D $\{[\text{Zn}_3(4,4'\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (**1**), the 1D $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (**2**) and the 2D $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](4,4'\text{-bpy})_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4\}_n$ (**3**), are herein reported.

Experimental

Preparation of the coordination polymers

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (1**)³⁰.** An aqueous solution (10 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.302 g, 1.0 mmol) was added to an ethanolic solution (10 mL) of 4,4'-bpy (0.157 g, 1.0 mmol). An aqueous solution (10 mL) of NaCOOH (sodium formate; 0.149 g, 2.0 mmol) was subsequently added, followed by 0.141 g of KClO_4 (1.0 mmol) under continuous stirring. The resulting colorless solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, colorless crystals were obtained. The crystals were filtered, washed with the mother liquid and dried in air. Yield = 68%.

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (2**) and $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](4,4'\text{-bpy})_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4\}_n$ (**3**)³⁰.** Complexes **2** and **3** have also been obtained following the synthetic procedure applied for compound **1**, using sodium acetate for **2** and sodium propionate for **3** in place of sodium formate (compound **1**). Yield = 78% (**2**) and 70% (**3**).

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_{3.5}(\mu\text{-O}_2\text{CH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_2\}_n$ (1**) doped with Cu^{2+} (**1a**) and Mn^{2+} (**1b**).** An aqueous solution (10 mL) of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.308 g, 1.0 mmol) was added to an ethanolic solution (10 mL) of 4,4'-bpy (0.158 g, 1.0 mmol). An aqueous solution (10 mL) of NaCOOH (sodium formate; 0.148 g, 2.0 mmol) was subsequently added, followed by 0.141 g of KClO_4 (1.0 mmol) and 0.003 g (0.002 mmol) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (or 0.003 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.002 mmol)) under continuous

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† Electronic supplementary information (ESI) available: Figures (S1–S3) with XRPD, IR spectroscopy and EPR at RT and 70 K for the 3 compounds. CCDC reference numbers 699370–699372. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c001659b

stirring. The resulting solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature. After several days, light-green crystals of **1a** were obtained (light-pink crystals for **1b**). The crystals were filtered, washed with the mother liquor and dried in air. Yield = 66%. The IR spectra of **1a** and **1b** are similar to that of **1**.

Synthesis of $\{[\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$ (2**) and $\{[\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4](4,4'\text{-bpy})_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4\}_n$ (**3**) doped with Cu^{2+} and Mn^{2+} , **2a**, **2b**, **3a** and **3b**.** Complexes **2a**, **2b**, **3a** and **3b** can also be obtained applying the same synthetic procedure as for **1a** and **1b**, using sodium acetate and Cu^{2+} for **2a** (Mn^{2+} for **2b**) and potassium propionate and Cu^{2+} for **3a** (Mn^{2+} for **3b**). The IR spectra and XRPD patterns of the doped compounds are comparable to those of the corresponding parent compounds, respectively **2** and **3**.

Characterization

FTIR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}). Elemental analyses for C, H and N were performed with a Perkin-Elmer 2400 analyzer. Thermogravimetric analyses were carried out using a Perkin-Elmer Pyris Diamond analyzer in flowing nitrogen at a heating rate of 10 $^\circ\text{C min}^{-1}$. The X-band powder EPR spectra were obtained on polycrystalline samples at room temperature and at 77 K with a Bruker EMXplus spectrometer with DPPH ($g = 2.0036$) as a reference. X-Ray powder diffraction (XRPD) data were recorded at room temperature using a Phillips Xpert Pro equipped with an X'celerator, with Cu-K α radiation ($\lambda \approx 1.5408 \text{ \AA}$), in the 2θ range 10–45 $^\circ$.

Catalytic reactions

A typical cyanosilylation reaction was performed as follows: 40 mg (0.006 mmol, 0.2 mmol of Zn(II)) of MOF catalyst was suspended in 5 mL of dry dichloromethane (CH_2Cl_2) or tetrahydrofuran (THF), followed by the addition of the aldehyde (1.5 mmol) and trimethylsilyl cyanide (3 mmol). The reaction mixtures were stirred at room temperature under argon. The reaction conversions were determined by gas chromatography (GC) analysis. The catalytic recyclability was checked three times with the same batch of catalyst, and no obvious decrease in activity was observed. For the filtration test, the catalyst was separated after a reaction time of 5 h and the solution was divided into two equal portions. Hereafter, one portion was stirred with fresh catalyst, while the second one was stirred without MOF catalyst.

Results and discussion

Synthesis and structure

Crystalline materials were obtained for all three compounds prepared from zinc(II) ions, 4,4'-bpy and carboxylate ligands in ethanol– H_2O solvent mixture. Other solvent combinations were used, *i.e.* methanol– H_2O and acetone– H_2O , but the solvent pair ethanol– H_2O gave the best result in terms of yield and quality of crystals. The three compounds exhibit different topologies, induced by the different carboxylate ligands used.³⁰ The MOF

compounds are insoluble in most organic solvents, except dimethyl sulfoxide and *N,N'*-dimethylformamide.

The combination Zn(II)/4,4'-bpy/formate generates an intricate 3D framework of **1**. The bridging of zinc(II) ions by formate ligands produces a 1D chain constituted of heptanuclear rings (Fig. 1(a)). The complete replacement of formate by acetate results in the formation of a 1D network (compound **2**; Fig. 1(b)). This simple framework is built from trinuclear acetato-bridged units that are linked to two adjacent ones, to form a three-leg ladder. The use of propionate as co-ligand yields a 2D network (Fig. 1(c)) which presents similarities with **2**. In fact, the framework of **3** contains the three-leg ladders observed in the solid-state structure of **2**. In **3**, these three-leg ladders are further connected to each other *via* 4,4'-bpy ligands.

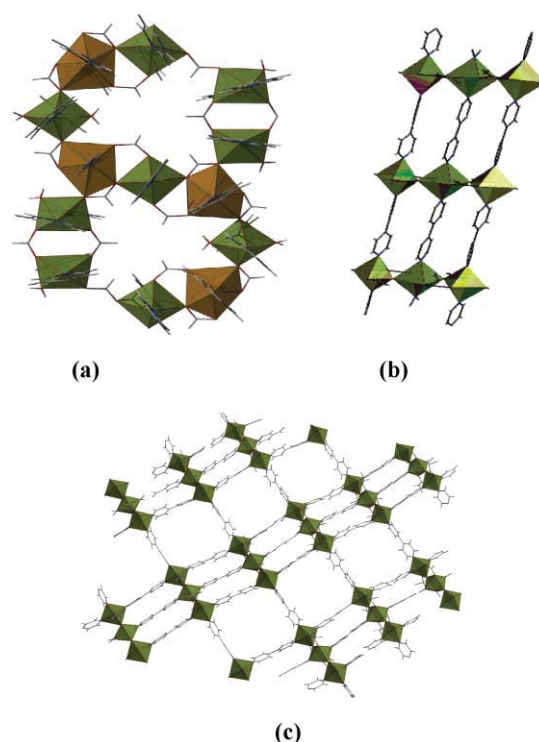


Fig. 1 (a) Perspective view of the 3D framework of **1**; (b) perspective view of the 1D three-leg ladder observed for **2** and; (c) perspective view of a 2D layer of **3**. The counter anions and the lattice water molecules have been omitted for clarity.

Zn(II) compounds doped with Cu(II) and Mn(II)

The three zinc(II) compounds were prepared in the presence of doping amounts of paramagnetic metal ions ($\text{Cu}(\text{II})$ and $\text{Mn}(\text{II})$) to investigate the potential cation-exchange properties of MOFs with structure retention, and analyze the coordination geometry(ies) around the Zn(II) ions. The doped materials were prepared in ethanol– H_2O , using Zn(II)/Cu(II) and Zn(II)/Mn(II) ratios of 95:5, and in the presence of one equivalent of 4,4'-bpy ligand. All doped compounds have been characterized by XRPD, IR spectroscopy and EPR at RT and 70 K (see Figs. S1–S3,†). The IR spectra of the doped compounds are similar to that of the original Zn(II) compound, thus indicating that the structure and therefore the environment around the zinc(II) centers are not altered.

For instance, the polycrystalline EPR spectrum of the trinuclear Zn(II) compound **2** doped with Cu(II) shows signals revealing the presence of two different types of Cu(II) species. Each one is characterized by a four-lines hyperfine pattern with $g_{//} = 2.343$ and 2.275 ; (with $A_{//} = 124$ and 126 ; red and blue dots in Fig. 2(a)) $g_{\perp} = 2.094$ and 2.094 in agreement with a distorted-octahedral geometry.³¹ No super-hyperfine splitting is resolved. These EPR data are clearly indicative of the occurrence of two different environments for the Zn(II) ions in **2**, which have been replaced by Cu(II) ions. Actually, a close observation of the molecular structure of **2** clearly reveals the presence of two distinct coordination geometries for the Zinc(II) ions, a highly distorted octahedron (site I in Fig. 2(b)) and a perfect octahedron (site II in Fig. 2(b)).¹³ Each trinuclear zinc unit in **2** is formed by two external sites I and one central site II. The doping with Mn(II) ions leads to a heteronuclear compound, whose EPR spectrum shows only one set of six lines, characterizing a Mn(II) species (Fig. 3(a)). These data suggest that only one from the two potential coordination sites has experienced ion exchange. Most likely Mn(II) ions are only capable of occupying site II (Fig. 3(b)), since Mn(II) has the tendency to form regular octahedral complexes. The polycrystalline EPR spectra of **1** and **3** doped with Cu(II) and Mn(II) exhibit similar features, thus suggesting comparable ion-exchange properties (Fig. S1, ESI†).

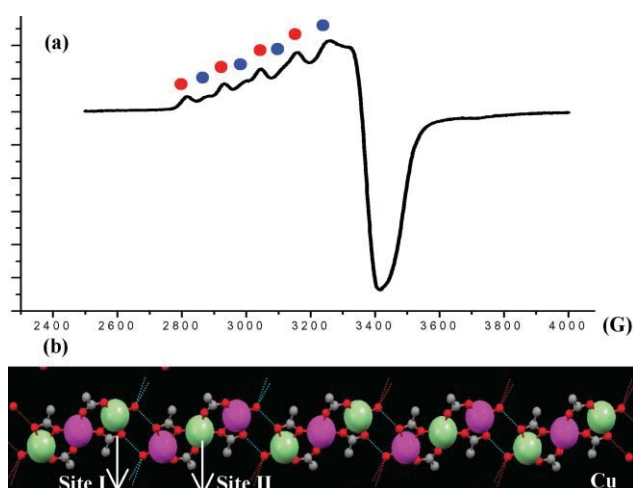


Fig. 2 (a) Polycrystalline EPR spectrum of **2** doped with Cu(II), recorded at 70 K. The two species are illustrated by blue and red dots. (b) Trinuclear Zn(II) units of **2** where zinc(II) ions (pink) have been replaced by Cu(II) ions (green) in two different sites (sites I and II).

The influence of the nature of the doping metal ion, namely Cu(II) and Mn(II), has been successfully investigated by EPR. This study illustrates the flexibility of the coordination geometry of Cu(II) compared to Mn(II). Such investigations are of great interest in the context of potential cation-exchange properties of MOFs with structure retention.

Removal and reintroduction of guest molecules

The single-crystal X-ray structures of **1–3** reveal the presence of lattice water molecules, indicating a potential porosity of the materials. Thus, all three room-temperature stable compounds exhibit open channels that are occupied by guest water molecules. The

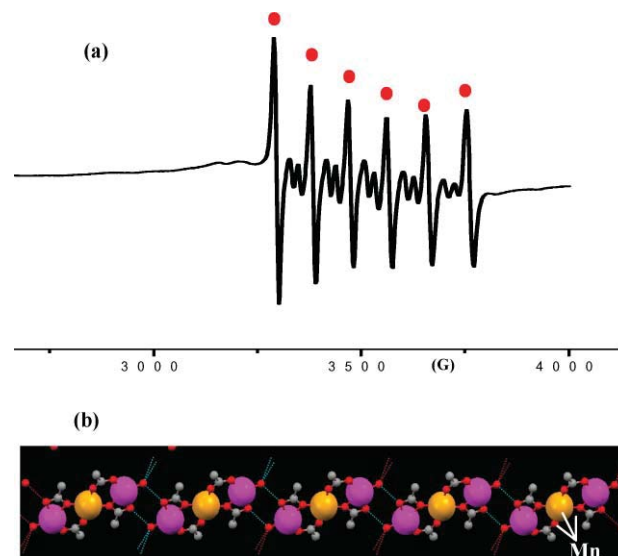


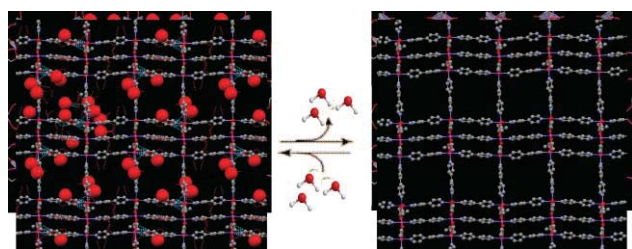
Fig. 3 (a) Polycrystalline EPR spectrum of **2** doped with Mn(II), recorded at 70 K and (b) Trinuclear Zn(II) units of **2** where only the central Zn(II) sites have been replaced by Mn(II) ions.

possibility of generating microporous frameworks by removing the guest molecules has therefore been investigated. Hence, the stability of the different frameworks upon removal/reintroduction of the guest molecules has been monitored in detail, using TGA and XRPD techniques.

In the TGA curves of all compounds,³⁰ the first weight loss of 5.50% for **1**, 5.82% for **2** and 3.50% for **3** in the temperature range 71–201 °C, corresponds to the loss of the coordinated waters and guest water molecules. The loss of the coordinated aqua ligands is not observed below about 180 °C, apparently as the result of their strong coordination to the Zn(II) centers. Upon evacuation at 140 °C for 8 h under reduced pressure, compounds **2** and **3** experience weight losses consistent with the removal of all water molecules, behaving as second generation porous coordination polymers which have rigid vacant channels formed after the removal of guest molecules (Scheme 1) as is clear from the main peaks of XRPD patterns.³² While the weight losses of compound **1** consist of all water molecules and four formate groups when elevating the temperature to 140 °C for 8 h under vacuum, the loss four formate groups does affect the framework skeleton. X-Ray power diffraction reveals the structure change, but this compound remains a microcrystalline solid, as evidence by XRPD pattern (Fig. 4(a)) according to the result of the elemental analysis and corresponds to the formula of $\text{Zn}(4,4'\text{-bpy})_{2.5}(\text{ClO}_4)_2$, calcd.: C 45.86, H 3.07, N 10.70; found: C 44.67, H 3.01, N 10.56. (Table 1). So, the zinc(II)-formate compound **1** containing **4,4'-bpy** organic ligand is unstable at high temperature. On the other hand after removal of the guest molecules from crystalline **3**, the XRPD pattern of the resulting material **3c** is almost identical to the theoretical one of starting material **3** (Fig. 4(c)). These data clearly suggest that **3c** exhibits the original structure of **3** with empty channels. This behavior is also observed for compound **2** (Fig. 4(b)), therefore indicating that the solid-state structures of **2** and **3** do not collapse when the water molecules are taken out. Interestingly, the guest water species can be reintroduced into the evacuated samples of the

Table 1 Elemental analyses of compounds **1–3** and of the products after removal and after reintroduction of the guest water molecules

Compound	Element	Exp.	Cal.	After removal of water		After water reintroduction (exp.)
				Exp.	Cal.	
1	C	39.22	39.23	44.67	41.76	41.43
	H	3.31	3.37	3.01	2.88	3.50
	N	8.22	8.21	10.56	8.74	8.96
2	C	36.41	36.40	38.68	38.33	37.04
	H	3.23	3.33	2.80	3.50	3.16
	N	6.30	6.70	7.81	7.06	7.09
3	C	51.19	50.97	53.19	53.23	49.30
	H	4.84	4.51	4.09	4.22	3.93
	N	9.91	9.91	10.36	10.35	9.51

**Scheme 1** Framework of **3** showing rigid vacant channels formed after the removal of water molecules

three compounds by simple immersion in water for 48 h, as confirmed by XRPD measurements (Fig. 4), and elemental analyses (Table 1). In case of compound **1**, the elemental analysis data after reintroduction of water indicates the formula to be $\text{Zn}(4,4'\text{-bpy})_2(\text{H}_2\text{O})(\text{ClO}_4)_2$, calcd.: C 40.39, H 3.05, N 9.42; found: C 41.43, H 3.50, N 8.96 (Table 1). Thus, after removal of the water/formate molecules, the microporous solids $\text{Zn}(4,4'\text{-bpy})_{2.5}(\text{ClO}_4)_2$ (**1c**), $\{\text{Zn}_3(4,4'\text{-bpy})_3(\mu\text{-O}_2\text{CCH}_3)_4(\text{PF}_6)_2\}_n$ (**2c**) and $\{\text{Zn}_3(4,4'\text{-bpy})_4(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_4(\text{ClO}_4)_2(4,4'\text{-bpy})_2\}_n$ (**3c**) are generated with retention of the original frameworks (of compounds **2** and **3**). Such microporous materials with high-thermal stabilities and host–guest properties are relatively rare and have therefore great potential for practical applications.

Catalytic properties

Porous MOFs **1–3** have been tested as heterogeneous catalysts for the cyanosilylation of acetaldehyde and benzaldehyde. Thus, the selectivity and activity of the 3D (**1**), 1D (**2**) and 2D (**3**) coordination polymers have been examined. Typically, the powdered catalyst (**1–3**) is suspended in dichloromethane (CH_2Cl_2) or tetrahydrofuran (THF). The aldehydic substrate and trimethylsilyl cyanide (1 : 2 molar ratio) are subsequently added at room temperature and the reaction is carried out for 24 h (Scheme 2).^{27,29} The course of the reactions has been monitored by gas chromatography (GC).

**Scheme 2** Cyanosilylation of acetaldehyde and benzaldehyde**Table 2** Cyanosilylation of aldehydes catalyzed by compounds **1–3**

Catalyst	Types	Substrate	Solvent	Time/h	Conversion (%)
1	3D	Acetaldehyde	CH_2Cl_2	24	95
		Acetaldehyde	THF	24	38
		Benzaldehyde	CH_2Cl_2	24	22
2	1D	Acetaldehyde	CH_2Cl_2	24	71
		Acetaldehyde	THF	24	30
		Benzaldehyde	CH_2Cl_2	24	21
3	2D	Acetaldehyde	CH_2Cl_2	24	86
		Acetaldehyde	THF	24	57
		Benzaldehyde	CH_2Cl_2	24	22

Blank reactions have been performed by carrying the cyanosilylation of acetaldehyde and benzaldehyde without catalyst, at 25 °C. These test reactions give only conversions of 18% for acetaldehyde and 10% for benzaldehyde, after a reaction time of 24 h. When 40 mg of solid **1** is used as catalyst, a conversion of 95% of acetaldehyde is reached after 24 h reaction time in CH_2Cl_2 (Table 2 and Fig. 5). This high conversion suggests first that **1** acts as a very efficient catalyst for this reaction, and that both acetaldehyde and trimethylsilyl cyanide can diffuse swiftly through the pores to attain the Lewis metallic sites, to generate 2-(methylsiloxy)propionitrile with a yield of 95% (71% when using **2** and 86% with **3**).

When benzaldehyde, a sterically more demanding substrate, is used under similar reaction conditions, a conversion of only 22% is observed (21% for **2** and 22% for **3**; Table 2). This significantly lower reactivity suggests that the dimension of the channels of the MOF plays an important role and leads to size selectivity.

Next, the influence of another organic solvent, namely THF, on the conversion of acetaldehyde has been examined for each MOF catalyst. It has been found that the reaction is less efficient in THF, which may be explained by a competitive binding of the substrate and the solvent to the metal site. This competitive binding obviously does not occur with CH_2Cl_2 .

For instance, in THF, compound **1** promotes the conversion of only 38% acetaldehyde (30% for **2** and 57% for **3**; Table 2). The cationic nature and Lewis acidity of the Zn^{2+} center may play a role and lead to significantly different in the conversion (Fig. 6).

In contrast to the reactions performed in CH_2Cl_2 , **3** is more efficient than **1** in THF (Table 2). These disparities regarding the distinct catalytic activities in CH_2Cl_2 and THF may be explained by structural features characterizing both compounds. As reported earlier,¹³ the 3D framework of **1** exhibits channels filled by disordered perchlorate anions. The crystal packing of

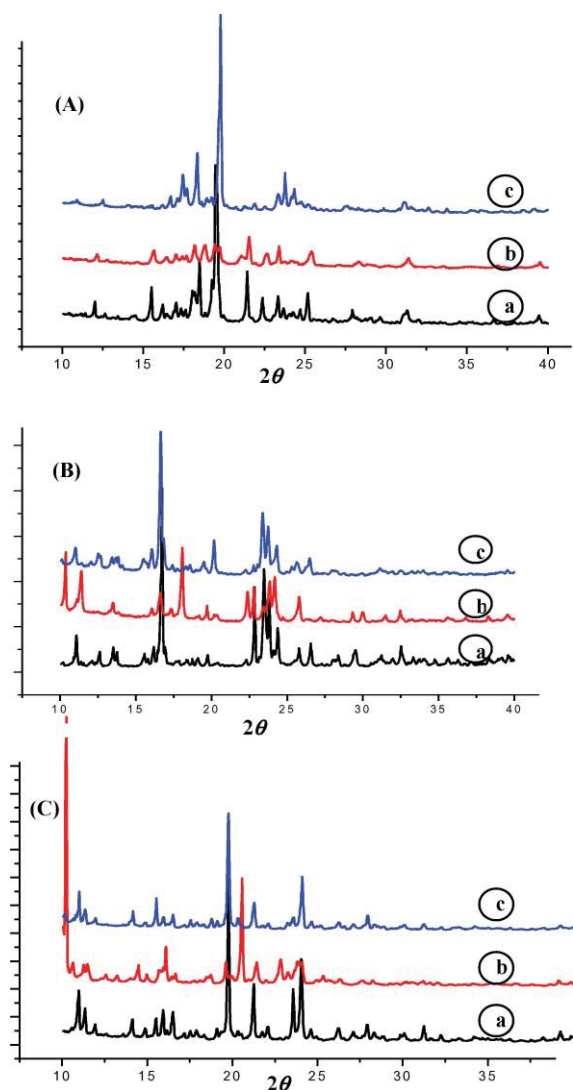


Fig. 4 (A) XRPD patterns of (a) **1** as-synthesized, (b) after removal of the guest water molecules, and (c) after reintroduction of the guest water molecules. (B) XRPD patterns of (a) **2** as-synthesized, (b) after removal of the guest water molecules, and (c) after reintroduction of the guest water molecules. (C) XRPD patterns of (a) **3** as-synthesized, (b) after removal of the guest water molecules, and (c) after reintroduction of the guest water molecules.

the 2D framework of **3** generates huge cavities filled with non-coordinated 4,4'-bipyridine (**4,4'-bpy**) molecules. Most likely, the slightly more polar solvent THF is capable of displacing the **4,4'-bpy** guest molecules of **3** (which is obviously not the case with CH_2Cl_2), therefore increasing the accessibility of the aldehydic substrate to the metal centers.

The catalytic activities of compounds **1–3** for the cyanosilylation of aldehydes have been compared with those of other porous coordination frameworks. Fujita and co-workers reported the first coordination polymeric catalyst, *i.e.* $\{\text{Cd}(\text{4,4'-bpy})_2(\text{NO}_3)_2\}_n$,²³ for the cyanosilylation of aldehydes. This square network material is highly shape-selective, which is illustrated by the inclusion of *ortho*-dihalogenobenzenes, whereas the *meta*- and *para*-isomers do not form clathrates. Shape specificity has been observed as well with this compound for the cyanosilylation of aldehydes. For

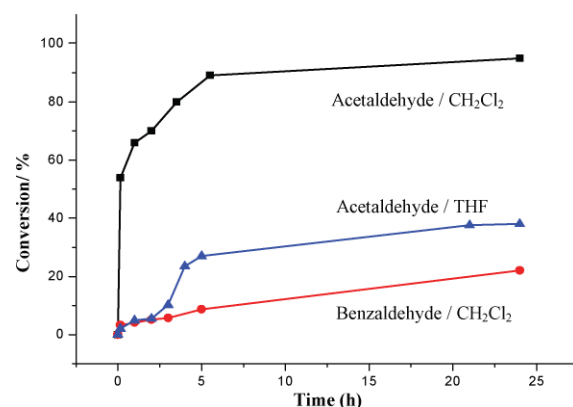


Fig. 5 Cyanosilylation of acetaldehyde and benzaldehyde with MOF **1** as catalyst.

example, the conversion of 2-tolualdehyde (40%) is significantly higher than that of 3-tolualdehyde (19%). In addition, α - and β -naphthaldehydes are good substrates in which can be converted with yields of 62% and 84%, respectively. The more sterically-demanding 9-anthraldehyde is hardly cyanosilylated. These shape specificities may be ascribed to the size of the cavity of the network material. In 2004, the same research group synthesized $\{\text{Cd}(\text{4,4'-bpy})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}\}_n$,³³ a square network to investigate mechanistic aspects of this cyanosilylation reaction. Thus, the catalytic study has been extended to the cyanosilylation of imines to gain some mechanistic insights in the heterogeneous catalysis mediated by the coordination compound. It has been found that the substrate accommodated in the square cavity, can easily coordinate to the Cd^{2+} center of the next network layer. It has therefore been suggested that the active sites exist mainly around the surface of the solid. They noted that, given a surface-promoted reaction, the catalytic activity of this porous polymer is remarkably high. Moreover, the $\text{Cd}(\text{II})$ center is more cationic and stronger Lewis acidic than mononuclear $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Size-selective reactions involving a MOF catalyst have been recently reported for $\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{CH}_3\text{OH})_{10}]_2$ (H_3BTT = 1,3,5-benzenetris tetrazol-5-yl),²⁹ wherein Mn^{2+} ions exposed on the surface of the framework might serve as potential Lewis acidic sites. Indeed, this MOF catalyzes the cyanosilylation of aromatic aldehydes and ketones, as well as the Mukaiyama-aldol reaction. In each case, a pronounced size-selectivity effect consistent with the pore dimensions is observed.

Heterogeneity

The heterogeneity of the catalytic reaction has been probed for the cyanosilylation of acetaldehyde in THF, mediated by compound **1**. Thus, the catalyst (compound **1**) has been filtered out after a reaction time of 5 h, corresponding to an acetaldehyde conversion of 24% (Fig. 7). The filtrate has been stirred for 24 h and no further conversion of the substrate is observed (about 25% conversion; Fig. 7). This result clearly demonstrates that no homogeneous catalytic species is present in solution. Next, the filtrate has been divided into two equal parts. The first part has been stirred with fresh catalyst **1** while the other one has been stirred without catalyst. In the filtrate without catalyst, the reaction does not proceed further, whereas in the catalyst-containing suspension, the conversion of the substrate is observed, reaching 38% after 24 h

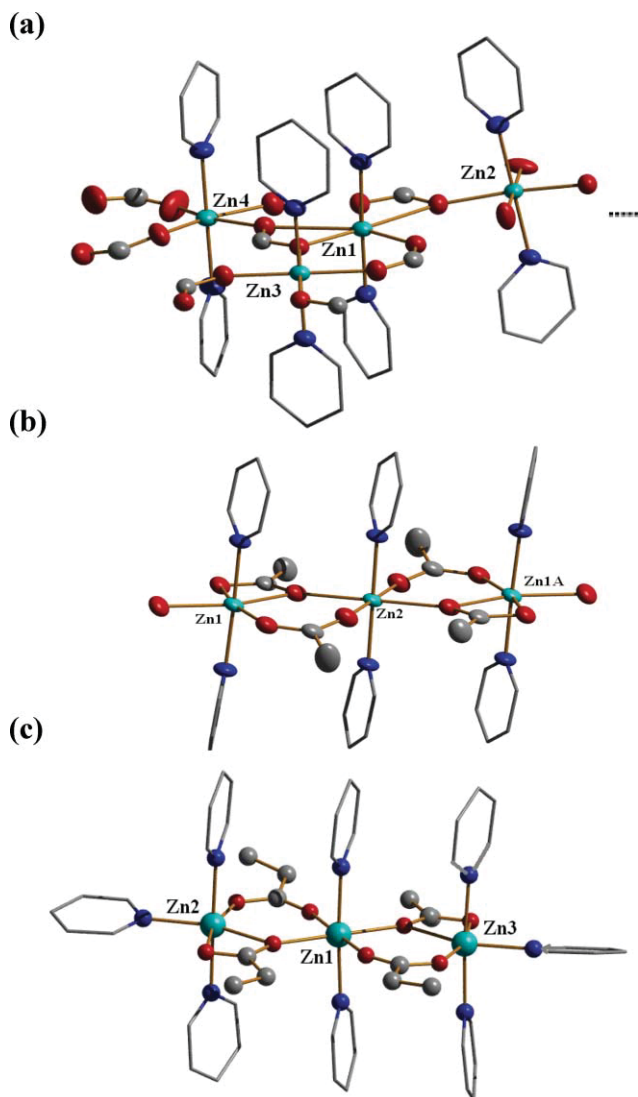


Fig. 6 Representation of the asymmetric units of (a): **1**, (b): **2** and (c): **3**, showing the atom-labeling schemes for the zinc(II) ions. The perchlorate anions and the lattice water molecules are not shown for clarity.

(Fig. 7). Thus, the catalytic activity of Zn(II)-4,4'-bpy-carboxylate originates from the presence of the solid catalyst and is not due to molecular species that dissolve into the solution. Furthermore, the isolated catalyst (by filtration after a reaction time of 24 h) can be reused without apparent loss of activity.

Conclusions

In summary, the present study, describes the host–guest and catalytic properties of three coordination polymers, belonging to the second generation of porous coordination compounds. The removal/reintroduction of water guest molecules is accompanied by a crystalline-to-crystalline structural transformation of the material, which exhibits rigid vacant host channels. Interestingly, the Zn(II) compounds are effective heterogeneous catalysts for the high-yielding cyanosilylation of acetaldehyde in dichloromethane. Moreover, the MOF catalysts show size-selective behaviors since acetaldehyde is efficiently converted whereas the conversion of benzaldehyde is significantly lower.

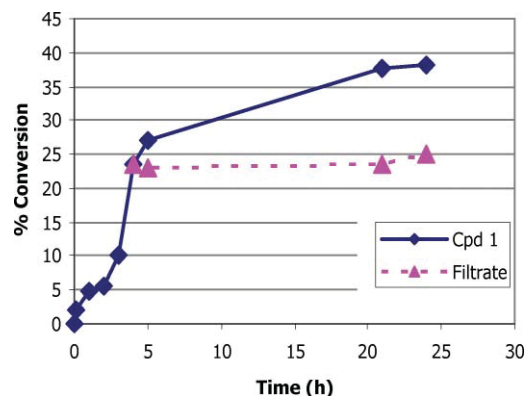


Fig. 7 Cyanosilylation of acetaldehyde in THF catalysed by **1**.

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A series of related 2D coordination polymers based on [copper(II)-**4,4'-bpy**-carboxylato] building blocks

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ABSTRACT

Different combinations of three building blocks, namely the coordination moiety [copper(II)-**4,4'-bpy**], a carboxylato co-ligand (formate or acetate) and an anion (ClO_4^- , NO_3^- or PF_6^-), lead to the formation of the three compounds, namely $\{[\text{Cu}_3(\textbf{4,4'-bpy})_3(\mu\text{-OOCCH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_6\}_n$ (**1**), $\{[\text{Cu}(\textbf{4,4'-bpy})(\mu\text{-OOCCH}_3)(\text{NO}_3)]\}_n$ (**2**) and $\{[\text{Cu}_2(\textbf{4,4'-bpy})_2(\mu\text{-OOCCH}_3)_3](\text{PF}_6)(\text{H}_2\text{O})\}_n$ (**3**). The molecular structures determined by single-crystal X-ray diffraction reveal notable (4,4) topology, regardless of the different mono-carboxylato groups (formate for **1** and **2** and acetate for **3**) and anions. Compound **1**, synthesized from Cu(II), **4,4'-bpy**, ClO_4^- and formate as co-ligand, exhibits a 2D coordination network based on trinuclear chain secondary building units. With coordinating NO_3^- anions (instead of non-coordinating ClO_4^-), a distinct structural motif, i.e. a 2D framework assembled from dinuclear chain secondary building units, is obtained (compound **2**). The replacement of the formate ligands by acetate units in compound **3**, gives rise to a 2D framework which is assembled from tetranuclear chain secondary building units. The three new coordination compounds have been characterized and tested for their catalytic properties. All compounds show catalytic activities for the selective cyanosilylation of aldehydes.

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1. Introduction

Numerous Porous Coordination Polymers (PCPs) with diverse architectures and functions have been developed through the self-assembly of molecular building blocks [1–5]. PCPs may find potential applications in molecular adsorption and separation processes [1–3], ion-exchange [4], catalysis [5], sensor technology [6], and optoelectronics [7]. The formation of such frameworks is highly influenced by several factors such as the specific coordination features of the metal ion used, the structural characteristics of the multidentate ligands, the counter ions, etc. [8]. In some cases, a subtle alteration of one of these factors can lead to the creation of significantly distinct framework architectures.

The incorporation of guest ions or small molecules in PCPs may result in the modification of their network structures [9]; such host–guest materials may be used as chemical sensors or ion-exchange compounds [10]. For instance, Kitagawa et al. successfully constructed a series of porous Cu(II)/**4,4'-bpy** coordination polymers with different anions [11].

However, for the construction of PCPs with **4,4'-bpy**, the ligand conformation would be expected to have a significant effect on the structure of the final product. Since the pioneering work of Robson and co-workers in 1990 [12], the *exo*-bidentate (divergent) ligand **4,4'-bpy** is widely used as building blocks to synthesize coordination polymers. Carboxylates have also been used to form moderately robust (zeolitic) frameworks [13] in which the O-donor ligands exhibit distinct bridging modes and a strong tendency to generate large tightly bound metal clusters [14,15].

An effective strategy to assemble cavity-containing PCPs is to use different spacer units to connect the metal ions [16]. Hence, several remarkable examples applying this approach have been reported, including the ligand combination of **4,4'-bpy** and oxalate, and **4,4'-bpy** and pyridine-4-carboxylate [17]. Nevertheless, the development of synthetic routes to produce systems containing two or more different bridging ligands is much less explored, and it is generally yet not possible to predict either their composition or structure. Therefore, more investigation is required for the rational design and synthesis of mixed-ligand coordination networks.

In the present study, the effects of the steric hindrance of different carboxylato ligands (formate and acetate ligands) as well as the

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influence of the nature of the anion used on the solid-state structure of the corresponding coordination materials have been investigated. Thus, three multicomponent polymeric networks have been synthesized from copper(II) ions, **4,4'-bpy** (4,4'-bipyridyl) and a carboxylato ligand. The single-crystal X-ray structures of these PCPs reveal a significant influence of the formate and acetate groups on the assembly of the coordination frameworks. The three new compounds, exhibiting different anions, have been identified as the 2D frameworks $\{[\text{Cu}_3(\text{4,4'-bpy})_3(\mu\text{-OOCH})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_6\}_n$ (**1**), the $\{[\text{Cu}(\text{4,4'-bpy})(\mu\text{-OOCH})(\text{NO}_3)]\}_n$ (**2**) and the $\{[\text{Cu}_2(\text{4,4'-bpy})_2(\mu\text{-OOCCH}_3)_3](\text{PF}_6)(\text{H}_2\text{O})\}_n$ (**3**). Only few catalytic applications of copper(II) carboxylato-bridged porous coordination polymers have been reported [18]. The catalytic properties of the heterogeneous copper(II)-**4,4'-bpy**-carboxylato compounds in the hydrosilylation of aldehydes has been investigated.

2. Experimental

2.1. Materials and physical measurements

All commercially available reagents were used as received. The single-crystal X-ray data were collected at 173(2) K on a Nonius Kappa CCD diffractometer. FTIR spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}). Elemental analyses for C, H and N were performed with a Perkin–Elmer 2400 analyzer. Thermogravimetric analyses were carried out using a Perkin–Elmer Pyris Diamond analyzer in flowing nitrogen at a heating rate of 10 $^\circ\text{C min}^{-1}$. The X-band powder EPR spectra were obtained on polycrystalline samples at room temperature, and at 70 K with a Bruker EMX plus spectrometer with DPPH ($g = 2.0036$) as a reference. X-ray powder diffraction (XRPD) data were recorded at room temperature using a Phillips Xpert Pro equipped with an X'celerator, with Cu K α radiation ($\lambda \approx 1.5408 \text{ \AA}$), in the 2θ range 10–45 $^\circ$.

2.1.1. Synthesis of **1**

A warm solution of **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) was added to a warm aqueous solution (10 mL) of Cu (NO_3) $_2$ ·3H $_2\text{O}$ (0.241 g, 1.0 mmol). Next, a warm aqueous solution

(10 mL) containing NaOOCH (0.136 g, 2.0 mmol) and KClO $_4$ (0.138 g, 1.0 mmol) was added under continuous stirring. A few drops of HCOOH 98% were subsequently added to the reaction mixture. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **1** after a few days. Yield: 70%. A microcrystalline sample of compound **1** was prepared in the same manner. The purity and homogeneity were confirmed by X-ray powder diffraction (see Fig. S1A). Elemental analysis (%) for C $_{34}\text{H}_{44}\text{Cl}_2\text{Cu}_3\text{N}_6\text{O}_{24}$ (Fw = 1182.28 g mol $^{-1}$) *Anal.* Calc.: C, 34.54; H, 3.75; N, 7.11. Found: C, 34.56; H, 4.18; N, 7.33%. IR (cm^{-1}): $\nu_{\text{as}}(\text{COO})$ 1569, $\nu_{\text{s}}(\text{COO})$ 1417, $\delta(\text{O}-\text{C}-\text{O})$ 643, $\nu(\text{ClO}_4)$ 1104–1045.

Caution! Although no problems were encountered in this work, perchlorate salts are potentially explosive and should be handled in small quantities.

2.1.2. Synthesis of **2**

A warm solution containing **4,4'-bpy** (0.156 g, 1.0 mmol) in ethanol (10 mL) and NaOOCH (0.136 g, 2.0 mmol) in water (10 mL) was added to an aqueous solution (10 mL) of Cu(NO_3) $_2$ ·3H $_2\text{O}$ (0.241 g, 1.0 mmol) under continuous stirring. A few drops of HCOOH 98% were subsequently added to the reaction mixture. The resulting blue solution was allowed to stand unperturbed for the slow evaporation of the solvent at room temperature, producing blue crystals of **2** after a few days. Yield: 82%. A microcrystalline sample of compound **2** was prepared in the same manner. The purity and homogeneity were confirmed by X-ray powder diffraction (see Fig. S1B). Elemental analysis (%) for C $_{11}\text{H}_9\text{CuN}_3\text{O}_5$ (Fw = 326.75 g mol $^{-1}$) *Anal.* Calc.: C, 40.43; H, 2.78; N, 12.86. Found: C, 40.02; H, 3.01; N, 12.84%. IR (cm^{-1}): $\nu_{\text{as}}(\text{COO})$ 1575, $\nu_{\text{s}}(\text{COO})$ 1416, $\delta(\text{O}-\text{C}-\text{O})$ 644, $\nu(\text{NO}_3)$ 1374.

2.1.3. Synthesis of **3**

Compound **3** was prepared following the procedure used to synthesize compound **1**, but with a different carboxylate salt and counter anion (i.e. NaO $_2$ CCH $_3$ and PF $_6^-$). The blue crystals formed were collected, washed with ethanol, and dried in air. Yield: 72%. A microcrystalline sample of compound **3** was prepared using the same manner. The purity and homogeneity were confirmed by X-ray powder diffraction (see Fig. S1C). Elemental analysis (%)

Table 1
Crystal and refinement data for compounds **1**–**3**.

Compound	1	2	3
Empirical formula	C $_{34}\text{H}_{44}\text{Cl}_2\text{Cu}_3\text{N}_6\text{O}_{24}$	C $_{11}\text{H}_9\text{CuN}_3\text{O}_5$	C $_{26}\text{H}_{27}\text{Cu}_2\text{F}_6\text{N}_4\text{O}_7\text{P}$
Formula weight	1182.28	326.75	779.57
<i>T</i> (K)	173(2)	173(2)	173(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>P2</i> $_1$ / <i>c</i>	<i>Pnma</i>	<i>P2</i> $_1$ / <i>c</i>
<i>a</i> (Å)	12.294(2)	7.634(2)	11.708
<i>b</i> (Å)	11.071(2)	11.074(2)	15.839
<i>c</i> (Å)	16.729(3)	14.975(2)	18.196
α (°)	90.00	90.00	90.00
β (°)	91.09(3)	90.00	117.34
γ (°)	90.00	90.00	90.00
<i>V</i> (Å ^{3})	2276.5(7)	1266.0(4)	2997.4
<i>Z</i>	2	4	4
<i>D</i> _{calc} (g cm $^{-3}$)	1.725	1.714	1.727
μ (mm $^{-1}$)	1.600	1.748	1.561
<i>F</i> (000)	1206	660	1576
θ range (°)	3.05–27.59	3.52–27.56	2.19–27.58
Goodness-of-fit (GOF) on <i>F</i> ^{2}	1.016	1.141	0.995
Final <i>R</i> indices	<i>R</i> $_1$ = 0.0609	<i>R</i> $_1$ = 0.0309	<i>R</i> $_1$ = 0.0596
$[I > \sigma(I)]$	<i>wR</i> $_2$ = 0.1309	<i>wR</i> $_2$ = 0.0731	<i>wR</i> $_2$ = 0.1442
<i>R</i> indices (all data)	<i>R</i> $_1$ = 0.0991	<i>R</i> $_1$ = 0.0358	<i>R</i> $_1$ = 0.0946
	<i>wR</i> $_2$ = 0.1485	<i>wR</i> $_2$ = 0.0755	<i>wR</i> $_2$ = 0.1678
Largest difference peak and hole (e Å $^{-3}$)	0.941, −1.026	0.994, −0.635	0.716, −0.886

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Table 2
Selected bond lengths (Å) and angles (°) for **1**.^a

Cu1–O1	1.989(3)	Cu2–O4	2.011(4)
Cu1–O5a	1.990(3)	Cu2–O4b	2.011(4)
Cu1–N11	2.007(4)	Cu2–N31	2.012(5)
Cu1–N21	2.026(4)	Cu2–N41	2.013(5)
Cu1–O5	2.355(3)	Cu2–O3	2.309(3)
Cu1–O3b	2.593(3)	Cu2–O3b	2.309(3)
O1–Cu1–O5a	178.29(12)	O4–Cu2–O4b	179.9(2)
O1–Cu1–N11	89.67(14)	O4–Cu2–N31	89.94(11)
O5a–Cu1–N11	90.78(14)	O4b–Cu2–N31	89.94(11)
O1–Cu1–N21	87.89(14)	O4–Cu2–N41	90.06(11)
O5a–Cu1–N21	91.78(14)	O4b–Cu2–N41	90.06(11)
N11–Cu1–N21	175.56(15)	N31–Cu2–N41	180.000
O1–Cu1–O5	100.53(12)	O4–Cu2–O3	92.16(14)
O5a–Cu1–O5	77.80(13)	O4b–Cu2–O3	87.85(14)
N11–Cu1–O5	91.36(12)	N31–Cu2–O3	95.09(8)
N21–Cu1–O5	92.72(13)	N41–Cu2–O3	84.91(8)
O1–Cu1–O3b	55.41(12)	O4–Cu2–O3b	87.85(14)
O5–Cu1–O3b	153.88(12)	O4b–Cu2–O3b	92.16(14)
		N31–Cu2–O3b	95.09(8)
		N41–Cu2–O3b	84.91(8)
		O3–Cu2–O3b	169.82(17)

^a Symmetry operations: (a) 1 – x, y, 0.5 – z; (b) –x, y, 0.5 – z.**Table 3**
Selected bond lengths (Å) and angles (°) for **2**.^a

Cu1–O4	1.964(2)	Cu1–N1a	1.997(1)
Cu1–N1	1.997(1)	Cu1–O5b	2.008(2)
Cu1–O1	2.287(2)	Cu1–O4a	2.559(2)
O4–Cu1–N1a	90.43(5)	O4–Cu1–N1	90.43(5)
N1a–Cu1–N1	172.81(11)	O4–Cu1–O5b	173.64(9)
N1a–Cu1–O5b	89.18(5)	N1–Cu1–O5b	89.18(5)
O4–Cu1–O1	82.25(9)	N1a–Cu1–O1	93.59(5)
N1–Cu1–O1	93.59(5)	O5b–Cu1–O1	104.11(9)
		O4a–Cu1–O5b	55.79(5)

^a Symmetry operations: (a) x, 0.5 – y, z; (b) –0.5 + x, y, 0.5 – z.

for C₂₆H₂₇Cu₂F₆N₄O₇P (Fw = 779.57 g mol^{–1}) Anal. Calc.: C, 40.06; H, 3.49; N, 7.19. Found: C, 39.76; H, 3.50; N, 6.94%. IR (cm^{–1}): ν_{as}(COO) 1564, ν_s(COO) 1417, δ(O–C–O) 645, ν(PF₆) 834–823.

2.2. Catalytic properties

A typical cyanosilylation reaction was performed as follows: 40 mg (0.006 mmol, 0.2 mmol of Cu(II) MOF catalyst was suspended in 5 mL of dry dichloromethane (CH₂Cl₂) or tetrahydrofuran (THF), followed by the addition of the aldehyde (1.5 mmol) and trimethylsilyl cyanide (3 mmol). The reaction mixtures were stirred at room temperature under argon. The reaction conversions were determined by gas chromatography (GC) analysis. The catalytic recyclability was checked three times with the same batch of catalyst, and no obvious decrease in activity was observed. For the filtration test, the catalyst was separated after a reaction time of 5 h and the solution was divided into two equal portions. Hereafter, one portion was stirred with fresh catalyst, while the second one was stirred without MOF catalyst.

2.3. Crystal structure determination

Data collections on single crystals of **1–3** were performed with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). DENZO-SMN was used for data integration and SCALEPACK corrected data for Lorentz-polarization effects [19]. The structures of all compounds were solved by direct methods with the package SIR92 [20], and the refinement and all further calculations were carried out using the SHELX-TL suite [21].

Table 4
Selected bond lengths (Å) and angles (°) for **3**.^a

Cu1–O3a	1.962(3)	Cu2–O7	1.972(3)
Cu1–N31	2.008(3)	Cu2–O9b	1.984(3)
Cu1–N21	2.015(3)	Cu2–N11c	2.006(3)
Cu1–O5	2.060(3)	Cu2–N41d	2.008(3)
Cu1–O1	2.175(3)	Cu2–O9	2.366(3)
		Cu2–O12	2.739(3)
O3a–Cu1–N31	91.38(14)	O7–Cu2–O9b	175.41(13)
O3a–Cu1–N21	92.11(14)	O7–Cu2–N11c	87.30(12)
N31–Cu1–N21	175.08(15)	O9b–Cu2–N11c	92.99(12)
O3a–Cu1–O5	144.60(12)	O7–Cu2–N41d	87.39(12)
N31–Cu1–O5	90.94(14)	O9b–Cu2–N41d	92.34(12)
N21–Cu1–O5	88.21(13)	N11c–Cu2–N41d	174.67(13)
O3a–Cu1–O1	125.72(14)	O7–Cu2–O9	105.39(12)
N31–Cu1–O1	88.30(14)	O9b–Cu2–O9	79.19(12)
N21–Cu1–O1	86.85(14)	N11c–Cu2–O9	90.08(13)
O5–Cu1–O1	89.65(14)	N41d–Cu2–O9	90.81(13)
		O12–Cu2–O9	59.41(1)

^aSymmetry operations: (a) 1 – x, –y, –z; (b) 1 – x, 1 – y, –z; (c) –1 + x, 0.5 – y, –0.5 + z; (d) 1 + x, 0.5 – y, 0.5 + z.

All non-hydrogen atoms were refined anisotropically. The H atoms were introduced at calculated positions and refined with a fixed geometry with respect to their carrier atoms. The crystal and refinement details of the three compounds are listed in Table 1; selected bond lengths and angles are given in Tables 2–4.

3. Results and discussion

3.1. Crystal structure of {[Cu₃(4,4'-bpy)₃μ-OOCH)₄(H₂O)₂](ClO₄)₂(H₂O)₆]_n (**1**)

The 2D structure of compound **1** exhibits two different types of copper(II) ions, each with an elongated octahedral N₂O₄ coordination environment (Fig. 1).

The basal plane of the octahedron of Cu1 is formed by two oxygen atoms belonging to two formate ligands (O1 and O5a) and two 4,4'-bpy nitrogen atoms (N11 and N21). The octahedral geometry is completed at the axial positions by two oxygen atoms from two formate ligands (O3b and O5), with the Cu–O distances of 2.593(3) and 2.355(3) Å, respectively. The Cu–O and Cu–N bond distances [22] can be considered as normal for this type of CuN₂O₄ coordination environment (Table 2).

As a crystallographic inversion centre is located in the centre of the four-membered Cu1–O5–Cu1A–O5a ring, Cu1 is bridged to symmetry-related Cu1A ions via two monoatomic bridged μ-O,O'-formate ligands (O5 and O5a) and to Cu2 ions via one μ-O,O',O'-formate ligand. This spatial arrangement produces a linear trinuclear [Cu1A, Cu1, Cu2] cluster. These tricopper units

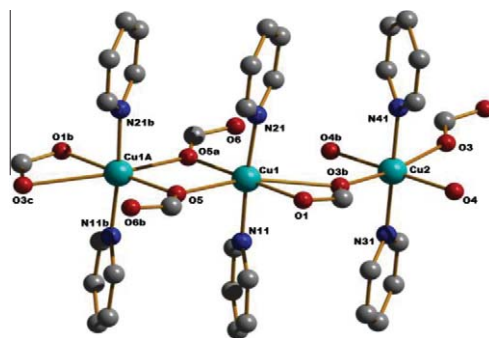


Fig. 1. Representation of the linear trinuclear unit of **1** showing the atomic labelling scheme for the two different copper(II) ions. The perchlorate anions, the lattice water molecules and the H atoms are not shown for clarity.

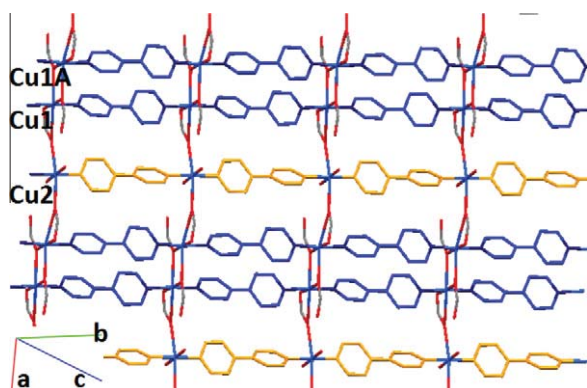


Fig. 2. 2D coordination network of **1**. The **4,4'**-bpy ligands connecting the trinuclear copper units are shown in blue and orange. (Color online.)

are linked via μ -formato- κ O bridges, producing a 1D polymeric chain, and each chain is connected through **4,4'**-bpy ligands to generate a (4,4) 2D layer in the crystallographic *b* direction (blue and orange **4,4'**-bpy ligands in Fig. 2).

The coordination environment around the Cu2 ion is best described as an elongated octahedron, whose basal angles, varying from 89.94(11) to 90.06(11)°, are close to the ideal value of 90°. This basal plane contains two water molecules (O4 and O4b) and two nitrogen atoms (N31 and N41) belonging to two **4,4'**-bpy ligands. The axial positions are occupied by two oxygen atoms (O3 and O3b) from different μ -O, μ O', μ O'-formato ligands at common distances (Cu2–O = 2.309 Å).

The 1D chains of {Cu2, Cu1, Cu1A} units are connected to each other through **4,4'**-bpy ligands, resulting in the formation of a (4,4) 2D framework based on trinuclear chain secondary building units (Figs. 2 and S3). The linear strands containing the metal centres Cu1A and Cu1 interact via π – π contacts between two **4,4'**-bpy units (centroid-to-centroid distances ranging from 3.467(4) to 3.682(4) Å; blue **4,4'**-bpy ligands in Fig. 2). The two coordinated water molecules (O4 and O4b in Fig. 3) are hydrogen bonded to lattice water molecules (O4...O6Wb = 2.745(4) and O4...O9Wa = 2.663(4) Å), which are located between the closely packed 2D layers. In addition, the intricate crystal packing of **1** exhibits anion– π contacts [23]. Indeed, each perchlorate ion is involved in weak intermolecular anion– π interactions with two **4,4'**-bpy rings from adjacent chains (Fig. S4), characterized by O(ClO₄)[−]...C contact distances in the range 4.267(12)–4.539(12) Å. The occurrence of these non-covalent contacts results in the formation of a three-dimensional supramolecular structure.

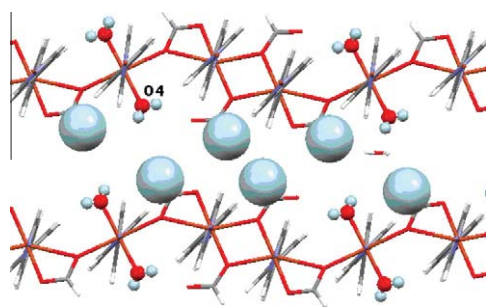


Fig. 3. Illustration of the solid-state structure of **1** showing the absence of steric bulk due to the formate ligands (whose hydrogen atom is shown in the space-filling mode), hence allowing the coordination of two water molecules (O4 and O4b) to the Cu2 centre.

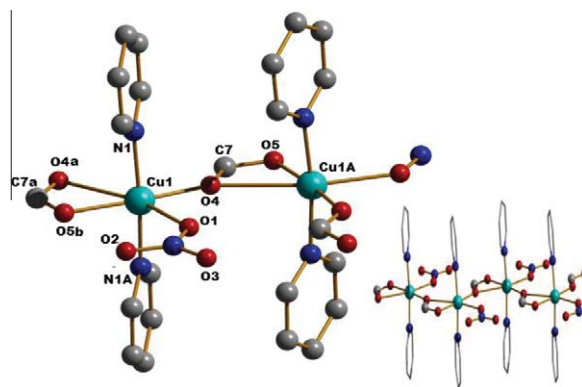


Fig. 4. Left: representation of the dinuclear unit of **2** with the atom-labelling scheme. Right: formation of a 1D chain through formate bridges.

3.2. Crystal structure of $\{[\text{Cu}(\text{4,4'}\text{-bpy})(\mu\text{-OOCH})(\text{NO}_3)]_n\}$ (**2**)

The simple replacement of perchlorate in compound **1** by nitrate during the synthetic procedure produces structural changes in the crystal lattice of the resulting coordination compound $\{[\text{Cu}(\text{4,4'}\text{-bpy})(\mu\text{-OOCH})(\text{NO}_3)]_n\}$ (**2**) which lead to changes in the crystallographic symmetry. As is shown in Figs. 4 and 2 only exhibits one type of copper(II) ion, namely Cu1 (instead of two different copper(II) ions for compound **1**; see above). Cu1 is best described as a distorted octahedral N_2O_4 coordination environment consisting of four oxygen atoms belonging to two formate ligands (O4, O4a and O5b), and one monodentate NO_3^- ligand (O1) in the basal plane (Fig. 4). The octahedron is completed by two nitrogen atoms belonging to two **4,4'**-bpy ligands (N1 and N1a) at the axial positions with Cu–N distances of 1.997(1) Å. The Cu–O and Cu–N bond distances [22] can be considered as normal for this type of CuN_2O_4 chromophore (Table 3), with CuO_4 as the equatorial plane and two additional axial ligands. Cu1 is bridged to symmetry-related Cu1A ions via one monoatomic bridged μ -O, μ O', μ O'-formato ligand (O4 and O5), generating a dinuclear $[\text{Cu1}, \text{Cu1A}, \dots]$ moiety. These dicopper units are linked via formate μ -O bridges, producing a 1D polymeric chain (Fig. 4 right).

The {Cu1, Cu1A, Cu1, Cu1A, ...} chains are connected to each other, through coordination of the copper(II) ions by **4,4'**-bpy ligands (blue **4,4'**-bpy ligands in Fig. 5), producing a (4,4) 2D layer based on dinuclear chain secondary building units. However, the 2D framework can be described as the assembly from analogous dinuclear chains (Fig. 5) exhibiting π – π interactions between **4,4'**-bpy units (with centroid-to-centroid distances ranging from

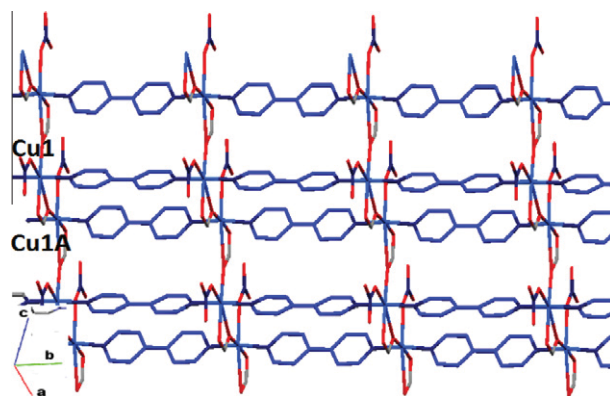


Fig. 5. 2D coordination network of **2**. The **4,4'**-bpy ligands coordinated to Cu1 and Cu1A are shown in blue. (Color online.)

4.294(4) to 4.279(4) Å), through formate μ -O bridges. In **2**, the nitrate anions are coordinated to the metal centres, while the perchlorate ions in **1** are located in the crystal lattice. This disparity may explain the closer packing of the coordination polymeric chains in **2**, compared to that in **1** (see Figs. 2 and 5). However, both compounds show the same (4,4) net. Hydrogen-bonding interactions between a nitrate oxygen atom and a pyridyl group are observed, with a $O \cdots H-C$ contact distance of 2.829(7) Å.

3.3. Crystal structure of $\{[Cu_2(4,4'-bpy)_2(\mu-OOCCH_3)_3](PF_6)(H_2O)]_n\}$ (**3**)

Next, the steric effect of a different carboxylato ligand, i.e. acetato instead of formate, on the molecular architecture of the resulting coordination network has been investigated. Thus, the solid-state structure of $\{[Cu_2(4,4'-bpy)_2(\mu-OOCCH_3)_3](PF_6)(H_2O)]_n\}$ (**3**) shows differences in local geometries by comparison with those of **1** and **2**. As is shown in Fig. 6, compound **3** also contains two types of copper(II) centres, generating two crystallographically unique chains namely pentacoordinated Cu1 and hexacoordinated Cu2 ions. Cu1 exhibits a coordination geometry in between a trigonal bipyramid and a square pyramid ($\tau_5 = 0.51$). The coordination environment around Cu1 is constituted of three oxygen atoms belonging to two *syn-syn* μ -O,O'-acetato ligands (O1 and O3a) and one *syn-anti* μ -O,O'-acetato ligand (O5), and two nitrogen atoms (N21 and N31) from two different **4,4'**-bpy ligands (Fig. 6). As a crystallographic inversion centre is located in the centre of the eight-membered ring, Cu1 is connected to a symmetry-related Cu1A ion via two *syn-syn* μ -O,O'-acetato ligands, and is linked to Cu2 through a μ -O,O'-acetato bridge.

The octahedral Cu2 ion is coordinated by four oxygen atoms from three acetato ligands (O7, O12, O9 and O9b) and two axial nitrogen atoms (N11c and N41d) belonging to two pyridyl groups (Cu–N distance of 1.997(1)). As a crystallographic inversion centre is located in the centre of the four-membered Cu2–O9b–Cu2A–O9 ring, Cu2 is bridged to a symmetry-related Cu2A ion via two μ -O,O'-acetato ligands, and is linked to Cu1. The resulting linear tetracopper [Cu2, Cu2A, Cu1A, Cu1] units form a polymeric [copper/acetato] chain (Fig. 7). These chains are connected to each other via **4,4'**-bpy ligands, generating a (4,4) 2D framework from the assembly of tetranuclear chain secondary building units (Fig. 8).

The Cu–O and Cu–N bond distances (Table 4) are in normal ranges for this type of coordination moiety [24]. The basal angles varying from 59.38(12) to 105.39(12)° (Table 4) are indicative of a large distortion of the octahedron, attributed to the small bite angle of the μ -O,O'-acetato ligand (O12–Cu2–O9b = 59.38(12)°) and to the long Cu–O basal distances of 2.739(3) and 2.366(3) Å.

The chains of [Cu1A, Cu1, Cu2, Cu2A] units are connected to each other through the coordination of the copper(II) ions by

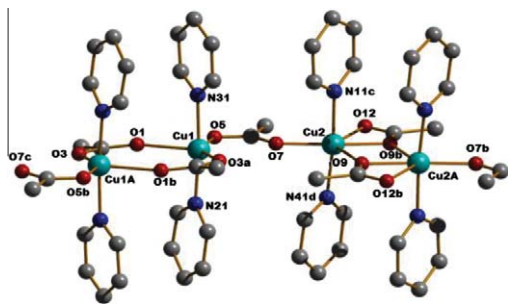


Fig. 6. Representation of the tetranuclear unit of **3**, with the atom-labelling scheme for the copper(II) ions. The hexafluoridophosphate anions, the lattice water molecules and the H atoms are not shown for clarity.

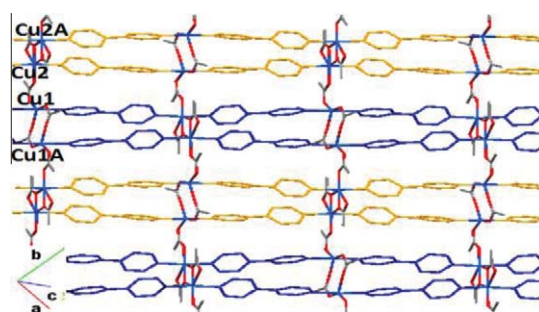


Fig. 7. 2D coordination network of **3**. The **4,4'**-bpy ligands involved in the formation of a (4,4) topology generating from the assembly of tetranuclear chain secondary building units are shown in blue and orange. (Color online.)

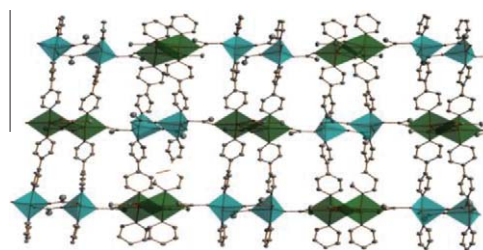


Fig. 8. Representation of the 2D coordination network of **3** illustrating the formation of chains of alternated dimers of five-coordinated (blue) and octahedral (green) copper(II) ions. (Color online.)

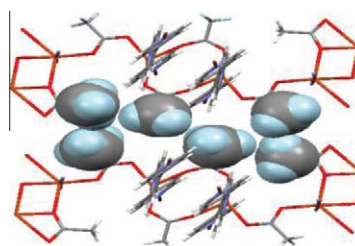
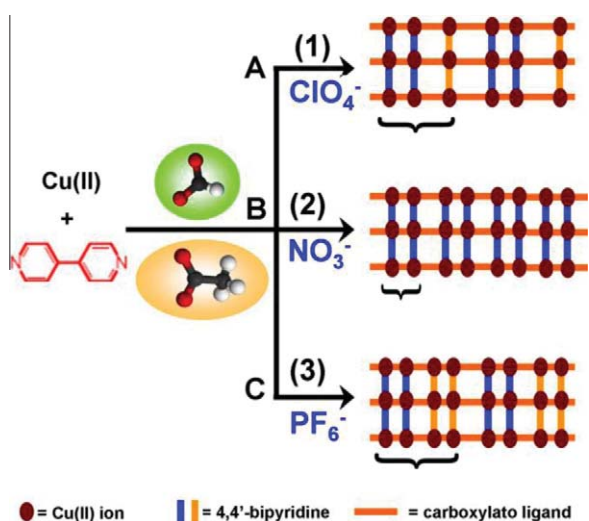


Fig. 9. Illustration of the steric bulk in **3** resulting from the acetato methyl groups (shown in the space-filling mode), preventing a close packing of the chains and not allowing the coordination of water molecules (in contrast to **1**; Fig. 3).

4,4'-bpy ligands, producing a (4,4) 2D layer based on tetranuclear chain secondary building units (blue and orange **4,4'**-bpy ligands in Fig. 7). This 2D spatial arrangement may be also described as the assembly of dinuclear chains of alternating dimers of five-coordinated and octahedral Cu^{II} ions (blue and orange coordination geometries in Fig. 8, respectively). In contrast to the hydrogen atoms of the formate ligands in **1**, the methyl groups of the acetato ligands in **3** do not allow a close packing of the polymeric chains (see Figs. 3 and 9), as the result of steric constraints. Consequently, the separation between the [copper(II)/carboxylato] chains in **3** is greater than that observed in **1** (Figs. 3 and 9). Indeed, the shortest intermolecular Cu $\cdots$ Cu separation distance is 9.544(12) Å for compound **3**, while the shortest intermolecular Cu $\cdots$ Cu distance is 7.855(11) Å for **1**.

The large lattice voids contain hexafluoridophosphate anions, which are hydrogen bonded to **4,4'**-bpy ligands from adjacent layers $F1 \cdots C26 = 3.169(12)$ and $F6 \cdots C13 = 3.126(15)$ Å. In addition, intermolecular anion– π interactions occur between each hexafluoridophosphate ion and **4,4'**-bpy units from contiguous layers. This intricate network of supramolecular bonds produces a three-dimensional structure.



Scheme 1. Coordination networks of (4,4) 2D layer of compounds **1–3** resulting from the assembly of trinuclear, dinuclear and tetranuclear secondary building units, respectively.

3.4. Anion effect on the geometries of **1** and **2**

Compounds **1** and **2** exhibit structural changes in the symmetry of the crystal lattice with small differences in local geometries, apparently resulting from the distinct anions used during their preparation [25]. However, both compounds have the same (4,4) topology. Compound **1** is a 2D layer based on trinuclear formate-bridged secondary building units while compound **2** is a 2D layer assembled from analogous dinuclear formate-bridged secondary building units (Schemes 1A and B). The ClO_4^- anions in **1** are located in the lattice cavities whereas the NO_3^- anions in **2** are coordinated to the copper(II) centres.

3.5. Effect of the carboxylate ligand on the geometries of **1** and **3**

The steric effect of a co-ligand on the resultant geometry has been investigated through the utilisation of slightly different monocarboxylate ligands, namely the formate and acetate moieties (Scheme 1A and C). The combination of Cu(II) ions, **4,4'**-bpy ligands and formate co-ligands in **1** generates a (4,4) 2D layer resulting from the assembly of trinuclear chain secondary building units with elongated octahedral geometry (Scheme 1A).

The replacement of formate ligands in **1** by acetate units in **3** produces a notably different 2D secondary building block, formed by tetranuclear acetate-bridged moieties that are linked to two neighbouring ones, to form 2D layers (Fig. 7 and Scheme 1C). The framework of **3** exhibits two different types of copper(II) ions (five-coordinated and distorted octahedral) which are alternating within each chain (Fig. 8). The framework of **1** shows two independent copper(II) chromophores with elongated octahedral geometries (Fig. S3). Thus, both compounds display distinct coordination geometries, most likely due to the different carboxylate co-ligands used.

3.6. Comparison between the frameworks of compounds **1–3** and other related compounds

Seven related coordination polymers have been reported in the literature, that exhibit copper(II) ions, **4,4'**-bpy ligands and bridging monocarboxylate co-ligands (Fig. 10). In these compounds, the copper(II) ions are connected by carboxylate bridges, yielding

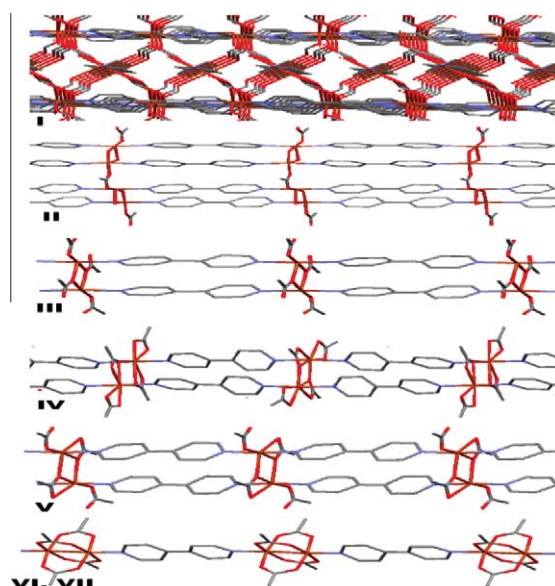


Fig. 10. Representations of the structure of related [Cu(II)/**4,4'**-bpy/carboxylato]-based coordination networks.

the three-dimensional structure $[\text{Cu}(\text{OOCCH}_3)_2(\text{4,4'}\text{-bpy})]_n$ (**I**) [26], the two-dimensional framework $\{[\text{Cu}_2(\text{4,4'}\text{-bpy})(\text{OOCCH}_3)(\text{OH})(\text{H}_2\text{O})](\text{H}_2\text{O})_2(\text{SiF}_6)]_n$ (**II**) [27], and the one-dimensional polymers $\{[\text{Cu}(\text{4,4'}\text{-bpy})(\text{OOCCH}_3)_2](\text{H}_2\text{O})_{2.5}\}_n$ (**III**) [28], $\{[\text{Cu}_2(\text{4,4'}\text{-bpy})_2(\mu\text{-OOCCH}_3)_2(\text{OOCCH}_3)_2](\text{H}_2\text{O})_n\}$ (**IV**) [29], $\{[\text{Cu}(\text{4,4'}\text{-bpy})(\text{OOCCH}_3)_2](\text{H}_2\text{O})_3\}_n$ (**V**) [30,31], $\{[\text{Cu}_2(\text{4,4'}\text{-bpy})(\text{OOCCH}_3)_4](\text{CH}_3\text{CN})_n\}$ (**VI**) [32], $\{[\text{Cu}_2(\text{4,4'}\text{-bpy})(\text{OOCCH}_3)_4](\text{DMF})_n\}$ (**VII**) [33]. Representations of these coordination polymers are shown in Fig. 10.

Among these seven compounds described earlier, only **II**, containing acetate co-ligands, exhibits (4,4) 2D sheet architecture resulting from the assembly of trinuclear chain secondary building units, like compound **3**. The formate-containing compound **I** displays a 3D structure while in the case of **1** and **2**, 2D networks are observed. The remaining five compounds exhibit double-stranded 1D polymeric chains for **III–V**, and 1D polymeric chains for **VI** and **VII** (Fig. 10). It is interesting to notice that compounds **VI** and **VII** are isostructural. In fact, the sole difference between them lies in the distinct guest solvent molecules, namely CH_3CN and DMF. Hence, it appears that the nature of these two solvents does not affect the subsequent network.

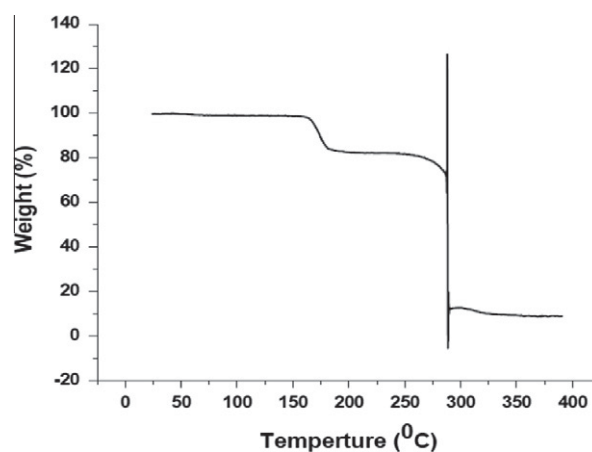
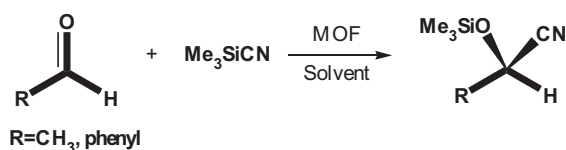


Fig. 11. Thermogravimetric analysis of compound **1**.



Scheme 2. Cyanosilylation reaction.

3.7. Thermogravimetric analysis

The thermal decomposition behaviour of the copper(II)-**4,4'**-bpy-carboxylato compound **1** (Fig. 11) reveals a first weight loss in the temperature range 160–250 °C, corresponding to eight water molecules and two formate groups (experimental value, 17.80%; calculated, 19.02%). Then compound **1** decomposes and could not be investigated above 280 °C, as metal–formate/acetato compound containing perchlorate anion and organic co-ligands are potentially explosive, see Fig. 11. In fact, decompositions were also observed for compounds **2** and **3** upon heating at high temperatures.

3.8. Electronic and EPR spectra

The electronic spectrum of **1** displays a broad peak centred at 15800 cm^{−1}, and a poorly resolved shoulder at approximately 12500 cm^{−1}. This feature characterizes an elongated octahedral geometry with an off-z-axis distortion. The d_{xz} , $d_{yz} \rightarrow d_{x^2-y^2}$ and d_{xy} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions may be assigned to the broad band and the low-energy shoulder, respectively. The spectrum of **2** exhibits a broad peak at 15200 cm^{−1}, in agreement with a distorted octahedral geometry having an off-z-axis, and assigned to the d_{xz} , d_{yz} , d_{xy} , $d_{x^2-y^2} \rightarrow d_{z^2}$ transitions. The electronic spectrum of **3** shows a higher-energy broad band centred at 16500 cm^{−1}, and a poorly resolved shoulder at approximately 12500 cm^{−1}. These spectroscopic data are consistent with the presence of distinct coordination geometries. Hence, the intermediate five-coordinate copper(II) environment is illustrated by the broad band at approximately 13000 cm^{−1}, and the distorted octahedral geometry by the broad band at approximately 15000–16500 cm^{−1}.

The X-band powder EPR spectra of polycrystalline samples of all compounds have been recorded at room temperature and at low temperature (70 K) (Fig. S2). The Cu(II)-**4,4'**-bpy-formato compound **1** shows an axial signal with $g_{\parallel} = 2.22$ and $g_{\perp} = 2.09$, which is typical for the $d_{x^2-y^2}$ ground state of an elongated octahedral geometry (Fig. S2A). No hyperfine splitting is resolved. The EPR spectrum of **2** exhibits an axial signal with $g_{\perp} = 2.18$ and $g_{\parallel} = 2.04$ (Figure S2B), which is typical for the d_{z^2} ground state of a distorted octahedral geometry. A comparable feature is observed as well for the Cu(II)-**4,4'**-bpy-acetato compound **3**, with a $g_{\perp} = 2.22$ and $g_{\parallel} = 2.09$, in agreement with the dominant characteristic of distorted octahedral chromophore in the compound (Fig. S2C).

3.9. Catalytic activity

Compounds **1–3** have been tested as heterogeneous catalysts for the cyanosilylation of acetaldehyde and benzaldehyde. Thus, the selectivity and activity of the 2D coordination polymers have been examined. Typically, the powdered catalyst (**1–3**) is suspended in dichloromethane (CH₂Cl₂) or tetrahydrofuran (THF). The aldehydic substrate and trimethylsilyl cyanide (1:2 molar ratio) are subsequently added at room temperature and the reaction is carried out for 24 h (Scheme 2) [34,35]. The course of the reactions has been monitored by gas chromatography (GC).

As can be seen, the three copper(II)-**4,4'**-bpy-carboxylato compounds are poorly active catalysts for the cyanosilylation of aldehydes. With **1**, a conversion of 29% of acetaldehyde is reached

Table 5
Cyanosilylation of aldehydes catalysed by compounds **1–3**.

Catalyst	Types	Substrate	Solvent	Time (h)	Conversion%
1	2D	Acetaldehyde	CH ₂ Cl ₂	24	29
		Acetaldehyde	THF	24	14
		Benzaldehyde	CH ₂ Cl ₂	24	2
2	2D	Acetaldehyde	CH ₂ Cl ₂	24	19
		Acetaldehyde	THF	24	16
		Benzaldehyde	CH ₂ Cl ₂	24	2
3	2D	Acetaldehyde	CH ₂ Cl ₂	24	14
		Acetaldehyde	THF	24	35
		Benzaldehyde	CH ₂ Cl ₂	24	2

after 24 h reaction time in CH₂Cl₂ (19% (**2**) and 14% (**3**); Table 5). With benzaldehyde, a sterically more demanding substrate, a conversion of only 2% is observed under similar reaction conditions (2% (**2**) and 2% (**3**); Table 5).

In addition, the conversion of acetaldehyde has been examined in THF for each MOF catalyst. It has been found that the reaction is poorly efficient as well in this solvent. Only a yield of 14% is achieved after 24 h when using **1** (16% (**2**) and 35% (**3**), Table 5).

In contrast to the reactions performed in CH₂Cl₂, **3** is more efficient than **1** in THF (Table 5). These disparities regarding the distinct catalytic activities in CH₂Cl₂ and THF may be explained by distinct structural packing features and interlayer distances for both compounds in the two different solvents. The interlayer space of **1** is occupied by perchlorate anions and is characterized by a distance of 8.471 Å (Fig. 12A). The crystal packing of **3** generates huge cavities filled with hexafluoridophosphate anions, and with a larger interlayer distance, i.e. 10.555 Å (Fig. 12B). Most likely, in the slightly more polar solvent THF, acetaldehyde and trimethylsilyl cyanide can diffuse swiftly through the large pores to attain the Lewis metallic sites, to generate 2-(methylsiloxy)propionitrile with a higher yield of 35% (14% when using **1**).

The catalytic properties of compounds **1–3** for the cyanosilylation of aldehydes have been compared with those of zinc(II) porous coordination frameworks reported earlier [5]. The lower catalytic activities of **1–3** suggest that the Lewis acidity of the copper(II) compounds is lower than that of the zinc(II) ones.

3.10. Heterogeneity

The heterogeneity of the catalytic reaction was probed for the cyanosilylation of acetaldehyde in THF, mediated by compound

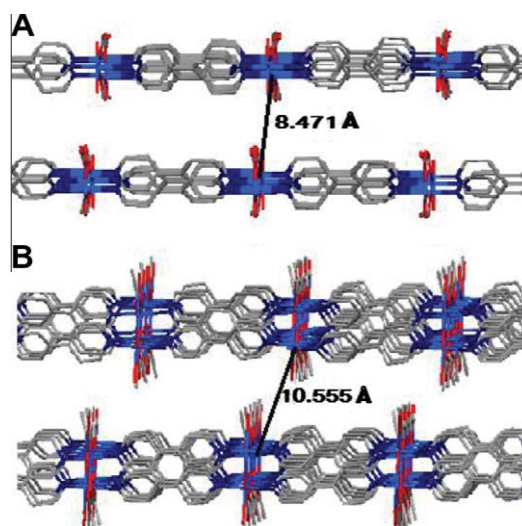


Fig. 12. Illustration of the interlayer distances of compounds **1** and **3**.

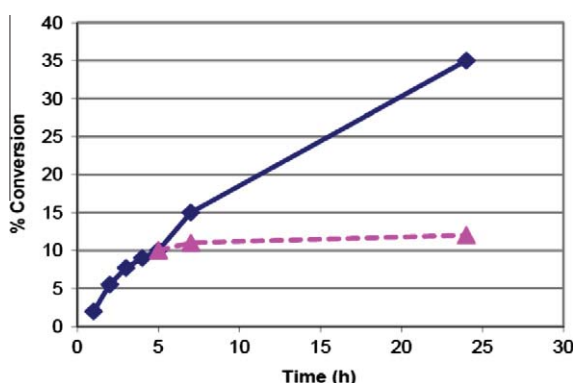


Fig. 13. Cyanosilylation of acetaldehyde in THF catalysed by **3**, $\blacklozenge$ with catalyst, $\blacktriangle$ without catalyst. (Color online.)

3. Thus, the catalyst (compound **3**) was filtered out after a reaction time of 5 h, corresponding to an acetaldehyde conversion of 10% (Fig. 13). Then, the filtrate was divided into two equal portions. The first one was stirred with fresh catalyst **3** while the other one was stirred without catalyst. For the filtrate without catalyst, the reaction does not proceed further, whereas the catalyst-containing suspension, the conversion of the substrate is observed, reaching 35% after 24 h (Fig. 13). Thus, the catalytic activity of Cu(II)-4,4'-bpy-carboxylato originates from the presence of the solid catalyst and is not due to molecular species that dissolve into the solution.

4. Conclusions

Three different coordination frameworks have been obtained through the combination of **4,4'-bpy** with distinct copper(II) salts and monocarboxylato co-ligands, namely $\{[\text{Cu}_3(\text{4,4'-bpy})_2(\mu\text{-OOCCH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2(\text{H}_2\text{O})_6\}_n$ (**1**), $\{[\text{Cu}(\text{4,4'-bpy})(\mu\text{-OOCCH}_3)(\text{NO}_3)]\}_n$ (**2**) and $\{[\text{Cu}_2(\text{4,4'-bpy})_2(\mu\text{-OOCCH}_3)_3](\text{PF}_6)(\text{H}_2\text{O})\}_n$ (**3**) 2D networks. Structural analysis of the three compounds suggests that both the nature of the anion employed (ClO_4^- , NO_3^- or PF_6^-) and the steric hindrance of the carboxylato co-ligand (formate or acetate) do affect a small changes in local geometries which lead to changes in the crystallographic symmetry with the (4,4) topology.

Furthermore, the catalytic activities of all copper(II)-4,4'-bpy-carboxylato compounds in the cyanosilylation of aldehydes have been investigated. The Lewis-acidic, heterogeneous catalysts are capable of generating 2-(methylsiloxy)propionitrile.

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Appendix A. Supplementary data

CCDC 870958, 804672 and 804673 contain the supplementary crystallographic data for **1**–**3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2012.04.014>.

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PUBLICATION PAPERS OF PART II

- 1) J. Boonmak, S. Youngme, N. Chaichit, G.A. van Albada, and J. Reedijk, "Series of copper(II) coordination polymers containing aminopyrazine and different carboxylato bridges: Syntheses, structures and magnetic properties", *Cryst. growth des.*, 2009, **9**, 3318-3326.
- 2) J. Boonmak, M. Nakano, N. Chaichit, C. Pakawatchai, and S. Youngme, "Water-induced reversible structural phase transformation with chromotropism in metal supramolecular frameworks containing aminopyrazine and sulfate anions", *Dalton Trans.*, 2010, **39**, 8161 – 8167.
- 3) J. Boonmak, M. Nakano, S. Youngme, "Structural diversity and magnetic properties in 1D and 2D azido-bridged cobalt(II) complexes with 1,2-bis(2-pyridyl)ethylene" *Dalton Trans.*, 2011, **40**, 1254-1260.
- 4) J. Boonmak, M. Nakano, N. Chaichit, C. Pakawatchai, S. Youngme, "Spin Canting and Metamagnetism in 2D and 3D Cobalt(II) Coordination Networks with Alternating Double End-On and Double End-to-End Azido Bridges" *Inorg. Chem.*, 2011, **50**, 7324-7333.

Series of Copper(II) Coordination Polymers Containing Aminopyrazine and Different Carboxylato Bridges: Syntheses, Structures and Magnetic Properties

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ABSTRACT: Five new copper(II) carboxylate compounds consisting of coordination networks with aminopyrazine (ampyz) spacer [Cu(ampyz)(O₂CH)₂]_n (**1**), [Cu₂(ampyz)(O₂C₂H₃)₄]_n (**2**), [Cu₂(ampyz)(O₂C₃H₅)₄]_n (**3**), [Cu₂(ampyz)(O₄C₄H₄)₂]_n·*n*H₂O (**4**), and [Cu(ampyz)(O₄C₃H₂)₂]_n·2*n*H₂O (**5**) were synthesized and structurally characterized by X-ray diffraction analyses together with electronic and EPR spectra. Compound **1** reveals a 2D wavy sheet structure. Both **2** and **3** consist of polymeric chains constructed from paddle-wheel (CuNO₄)₂ chromophores. The structure of **4** consists of a 2D layer built from double-stranded chain of paddle-wheel units connecting ampyz spacers. Compound **5** exhibits a 2D stairlike layer built from malonate anions and μ₂-ampyz. Besides the various coordinative modes of carboxylates, the ampyz spacer has an influence on the molecular structures either via the ditopic bridging mode or by other weaker interactions, such as hydrogen bonding and π–π stacking, which mainly contribute to the stabilization of the overall supramolecular structures.

Introduction

The field of coordination polymers has been extensively investigated over the past few decades with a focus on functional material research and crystal engineering. In material research, the coordination networks with interesting properties in areas such as molecular adsorption, catalysis, photoluminescence, magnetism, etc. are constructed for fine-tuning the properties and creating new functional materials.^{1–7} On the other hand, crystal engineering is attracting interest from both the synthetic routes and the art of structural design.^{8–14} One of the challenges in this field is to forecast the crystal structure from the building units. It is well-known that the chemistry of metal carboxylates shows various structural diversities beginning from simple mononuclear complexes to 3D frameworks with functional properties.^{15–18} This diversity results from the fact that the carboxylate groups can coordinate metal centers in various ways, such as monodentate, chelate, monatomic bridge, bridging bi- and tridentate, and also less common multiple bridges.^{18–21} Therefore, the combination of metal carboxylates and other coligands, either bridging or terminal coligands, has a large potential to construct novel coordination networks. Consequently, this field has become a popular research area in recent decades.^{15,22–24}

The short rigid rodlike spacer pyrazine (pyz) is an *N,N'*-ditopic diimine which is widely used for constructing many metal–organic frameworks.²⁵ It is well-known that the pyz spacer is a good electron transfer agent in the superexchange pathways between connected metal centers showing antiferromagnetic routes. Consequently, several compounds with mixed pyz spacer ligands and metal carboxylates exhibiting various structural topologies together with interesting magnetic phe-

nomena have been extensively investigated.^{26–31} With Cu(II), both pyz and carboxylates play a key role for building Cu coordination polymers, and interesting compounds have been observed. For instance, the 2D layered structure of [Cu(HCO₂)(NO₃)(pyz)]_n presents a long-range magnetic ordering below 3.7 K,²⁶ while [Cu₂(pyz)(O₄C₃H₂)₂]_n·2*n*H₂O (in which H₂C₃O₄^{2–} is the malonate anion) displays a unique 3D framework displaying metamagnetism.²⁷

The ligand 2-aminopyrazine (ampyz) is a substituted pyz containing an electron withdrawing amine group attached at the pyz ring, and it also effectively acts as an organic spacer in many metal–organic frameworks.³² However, no compounds containing both the ampyz spacer and bridging carboxylate groups have been reported as yet.

Consequently, the present work demonstrates the use of ampyz as a rigid ditopic spacer in combination with either mono- or dicarboxylate anions. Formate (HCO₂[–]), acetate (CH₃CO₂[–]), propionate (C₂H₅CO₂[–]), malonate (CH₂C₂O₄^{2–}), and succinate (C₂H₄C₂O₄^{2–}) anions have been used to construct a variety of Cu(II) coordination polymers. Herein, we report the syntheses, crystal structures, spectroscopic properties, and magnetism of five such new Cu(II) coordination networks containing both μ₂-ampyz and the bridging carboxylate anion, i.e. the 2D wavy sheet of [Cu(ampyz)(O₂CH)₂]_n (**1**), the polymeric chains of [Cu₂(ampyz)(O₂C₂H₃)₄]_n (**2**) and [Cu₂(ampyz)(O₂C₃H₅)₄]_n (**3**), the 2D layered structure of [Cu₂(ampyz)(O₄C₄H₄)₂]_n·*n*H₂O (**4**), and the 2D stairlike layer of [Cu(ampyz)(O₄C₃H₂)₂]_n·2*n*H₂O (**5**). All compounds emphasize the effect of the ampyz spacer in building the copper(II) networks and are compared with the same carboxylate coligands in the μ₂-pyz Cu(II) systems. The magnetic properties of all the compounds have also been investigated and will be briefly discussed.

Experimental Section

General. All chemicals were obtained from commercial sources and were used without further purification. Elemental analyses (C, H, N) were carried out with a Perkin-Elmer PE 2400 CHNS analyzer. IR

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Table 1. Crystallographic Data for Compounds 1–5

compound	1	2	3	4	5
formula	CuC ₆ H ₆ N ₃ O ₄	Cu ₂ C ₁₂ H ₁₆ N ₃ O ₈	Cu ₂ C ₁₆ H ₂₄ N ₃ O ₈	Cu ₂ C ₁₂ H ₁₂ N ₃ O ₉	Cu ₂ C ₁₄ H ₈ N ₆ O ₁₂
molecular weight	247.68	457.36	513.46	469.33	579.34
<i>T</i> (K)	293(2)	273(2)	273(2)	273(2)	273(2)
crystal system	monoclinic	triclinic	triclinic	triclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Pnma</i>
<i>a</i> (Å)	4.7807(4)	7.3107(3)	7.7508(2)	6.5942(3)	9.4050(4)
<i>b</i> (Å)	6.8558(6)	8.1323(3)	8.51420(10)	8.12840(10)	6.8579(3)
<i>c</i> (Å)	12.8809(11)	8.1761(2)	8.8762(2)	9.1655(3)	16.2248(4)
α (deg)	90	116.3860(10)	86.9880(10)	105.882(2)	90
β (deg)	90.438(2)	93.2830(10)	72.5300(10)	101.050(2)	90
γ (deg)	90	101.2350(10)	66.0330(10)	107.999(2)	90
<i>V</i> (Å ³)	422.17(6)	421.34(3)	508.94(2)	428.42(2)	1046.48(7)
<i>Z</i>	2	1	1	1	2
ρ_{calcd} (g cm ^{−3})	1.948	1.802	1.675	1.819	1.839
μ (Mo K α) (mm ^{−1})	2.578	2.570	2.137	2.534	2.109
data collected	2168	3188	2691	2261	5221
unique data (<i>R</i> _{int})	793 (0.0303)	2316 (0.0186)	2038 (0.0156)	1712 (0.0173)	1506 (0.0249)
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0391/0.0978	0.0315/0.0877	0.0406/0.0967	0.0438/0.1008	0.0357/0.0987
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [all data]	0.0408/0.0987	0.0347/0.0890	0.0563/0.1017	0.0767/0.1093	0.0488/0.1037
GOF	1.181	1.085	0.975	0.958	1.070
max/min electron density (e Å ^{−3})	0.972/−0.529	0.540/−0.748	0.530/−0.686	0.736/−0.473	0.616/−0.493

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = \{ \sum [w(|F_o| - |F_c|)]^2 / \sum [w|F_o|^2] \}^{1/2}.$$

spectra were obtained in KBr disks on a Perkin-Elmer Spectrum One FT-IR spectrophotometer in the 4000–450 cm^{−1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer, within the range 9000–25000 cm^{−1}. The X-ray powder diffraction (XRPD) data were collected on a Bruker D8 ADVANCE diffractometer using monochromatic Cu K α radiation, and the recording speed was 0.5 s/step over the 2 θ range of 5–50° at room temperature. X-band powder EPR spectra were obtained on a Bruker-EMXplus electron spin resonance spectrometer (field calibrated with DPPH (*g* = 2.0036)). Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Syntheses. [Cu(ampyz)(O₂CH₂)₂]_n (**1**). An ethanolic solution (5 mL) of ampyz (0.5 mmol, 48 mg) was carefully layered on an aqueous solution (5 mL) of Cu(HCO₂)₂ (0.5 mmol, 76 mg) with 0.1 mL (2.6 mmol) of formic acid in 20 mL of glass vial. This vial was sealed and allowed to stand undisturbed at room temperature. After four days, blue-green rod-shaped crystals of **1** were obtained. Yield: 84 mg (68%) based on copper salt. Anal. Calcd for CuC₆H₇N₃O₄: C, 28.98; H, 2.82; N, 16.90%. Found: C, 28.81; H, 2.91; N, 16.89%. IR (KBr, cm^{−1}): 3364w, 3127w, 1639m, 1587s, 1329m, 1236w, 1076w, 1030w, 811w, 572w. UV–vis (diffuse reflectance, cm^{−1}): 15 670.

[Cu₂(ampyz)(O₂C₂H₃)₄]_n (**2**). **2** was synthesized similarly to compound **1** using Cu(CH₃CO₂)₂ (0.5 mmol, 91 mg) instead of Cu(HCO₂)₂ with 0.1 mL (1.7 mmol) of acetic acid. After three days, green rod-shaped crystals of **2** were obtained. Yield: 190 mg (83%) based on copper salt. Anal. Calcd for Cu₂C₁₂H₁₇N₃O₈: C, 31.45; H, 3.71; N, 9.17%. Found: C, 31.33; H, 3.77; N, 9.18%. IR (KBr, cm^{−1}): 3387w, 3342w, 3224w, 1655m, 1608s, 1435m, 1349w, 1219w, 1017w, 685w, 628w. UV–vis (diffuse reflectance, cm^{−1}): 14 270.

[Cu₂(ampyz)(O₂C₃H₅)₄]_n (**3**). An ethanolic solution (5 mL) of ampyz (0.5 mmol, 48 mg) was added to a stirring 5 mL of aqueous solution containing Cu(OH)₂ (0.5 mmol, 49 mg) and propionic acid (1 mL, 13 mmol). The resulted solution was stirred at 50 °C for an hour, and then a small amount of precipitates was filtered off. The green filtrate was allowed to stand for four days at room temperature to yield green rod-shaped crystals of **3**. Yield: 132 mg (51%) based on copper salt. Anal. Calcd for Cu₂C₁₆H₂₅N₃O₈: C, 37.36; H, 4.86; N, 8.17%. Found: C, 37.13; H, 4.96; N, 8.17%. IR (KBr, cm^{−1}): 3427w, 3229w, 1645m, 1602s, 1541w, 1427m, 1381w, 1301w, 1217w, 1070w, 1018w, 813w. UV–vis (diffuse reflectance, cm^{−1}): 14 280.

[Cu₂(ampyz)(O₄C₄H₄)₂]_n·*n*H₂O (**4**). An ethanolic solution (3 mL) of ampyz (0.5 mmol, 48 mg) was carefully layered on a solution containing Cu(NO₃)₂·3H₂O (0.5 mmol, 121 mg) and succinic acid (0.5 mmol, 59 mg) in a mixture of water (4 mL) and ethanol (1 mL). The vial was sealed and allowed to stand undisturbed at room temperature.

After four days, blue-green rod-shaped crystals of **4** were obtained. Yield: 79 mg (34%) based on copper salt. Anal. Calcd for Cu₂C₁₂H₁₅N₃O₉: C, 30.52; H, 3.18; N, 8.90%. Found: C, 30.68; H, 3.32; N, 8.85%. IR (KBr, cm^{−1}): 3368br, 3172w, 1624s, 1544w, 1428s, 1403w, 1301w, 1219w, 1070w, 1021w, 577w. UV–vis (diffuse reflectance, cm^{−1}): 14 450.

[Cu(ampyz)(O₄C₃H₂)₂]_n·2*n*H₂O (**5**). **5** was synthesized similarly to compound **4** using disodium malonate monohydrate (0.5 mmol, 83 mg) instead of succinic acid. After four days, green rod-shaped crystals of **5** were obtained. Yield: 44 mg (15%) based on copper salt. Anal. Calcd for Cu₂C₁₄H₂₂N₆O₁₂: C, 28.34; H, 3.71; N, 14.17%. Found: C, 29.06; H, 3.02; N, 14.45%. The microanalysis is slightly deviated. Presumably this is from the loss of solvent. IR (KBr, cm^{−1}): 3342br, 3220w, 1665m, 1578s, 1547m, 1421m, 1362m, 1270w, 1229w, 1081w, 1031w, 810w, 744w. UV–vis (diffuse reflectance, cm^{−1}): 15 675.

X-ray Crystallography and Refinement Details. All reflection data were collected on a 1 K Bruker SMART CCD area-detector diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) using the SMART program.³³ Raw data frame integration was performed with SAINT,³⁴ which also applied correction for Lorentz and polarization effects. An empirical absorption correction by using the SADABS³⁵ program was applied. The structure was solved by direct methods and refined by full-matrix least-squares method on *F*² with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.1 software package.³⁶ All hydrogen atoms were placed in calculated positions and refined isotropically, with the exception of disordered C3 hydrogen atoms of **5** and hydrogen atoms on the unbound water molecules, which could not be located. All ampyz ligands lie across a mirror plane for **1** and **5** and on an inversion center for **2–4**, so the disordered amino group was refined with half occupancy. The disorder of ampyz is found to be similar to that known for methylpyrazine.³⁷ Therefore, there are two distinct hydrogen bonding networks present via the disordered amino group, and both are symmetry related in which changing one interaction has a knock-on effect. In **1**, the terminal formate group which lies across a mirror plane is disordered so the disordered conformer was refined with site occupancies of 0.35 and 0.15 for the A and B conformers, respectively. In **5**, the terminal oxygen and methylene group of the malonate ligand and one uncoordinated water molecule were refined with half occupancy. The details of crystal data, selected bond lengths and angles for compound **1–5** are listed in Tables 1 and 2.

Results and Discussion

General Observations. Reaction of copper(II) and carboxylate anion with ampyz in a mixture of ethanol and aqueous media gives various copper(II) coordination polymers containing ampyz spacer together with carboxylate bridges. The different

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1–5

Compound 1 ^a			
Cu1–O3A	1.953(6)	Cu1–O1	1.976(4)
Cu1–N1 ⁱ	2.039(4)	Cu1–N1	2.039(4)
Cu1–O2 ⁱⁱ	2.300(5)	N1 ⁱ –Cu1–N1	170.48(19)
Cu1···O2	2.718(5)	O3A–Cu1–N1 ⁱ	91.93(9)
O3A–Cu1–O1	169.8(2)	O3A–Cu1–O2 ⁱⁱ	78.4(3)
O1–Cu1–N1 ⁱ	88.87(9)	N1 ⁱ –Cu1–O2 ⁱⁱ	94.65(9)
O1–Cu1–O2 ⁱⁱ	91.4(2)		
Compound 2 ^b			
Cu1–O2 ⁱ	1.962(2)	Cu1–O3	1.965(2)
Cu1–O4	1.969(2)	Cu1–O1	1.973(2)
Cu1–N1	2.229(2)	Cu1···Cu1 ⁱ	2.6286(4)
O2 ⁱ –Cu1–O3	91.14(9)	O2 ⁱ –Cu1–O4	89.01(9)
O3–Cu1–O4	168.17(7)	O2 ⁱ –Cu1–O1	168.05(7)
O3–Cu1–O1	89.32(9)	O4–Cu1–O1	88.12(9)
O2 ⁱ –Cu1–N1	95.09(7)	O3–Cu1–N1	94.57(7)
O4–Cu1–N1	97.20(7)	O1–Cu1–N1	96.78(7)
Compound 3 ^c			
Cu1–O1	1.960(3)	Cu1–O3	1.963(3)
Cu1–O2 ⁱ	1.970(3)	Cu1–O4	1.970(3)
Cu1–N1	2.230(2)	Cu1···Cu1 ⁱ	2.6322(7)
O1–Cu1–O3	89.29(12)	O1–Cu1–O2 ⁱ	167.98(10)
O3–Cu1–O2 ⁱ	90.49(12)	O1–Cu1–O4	90.36(12)
O3–Cu1–O4	167.76(9)	O2 ⁱ –Cu1–O4	87.31(12)
O1–Cu1–N1	93.85(10)	O3–Cu1–N1	95.55(10)
O2 ⁱ –Cu1–N1	98.13(10)	O4–Cu1–N1	96.67(10)
Compound 4 ^d			
Cu1–O4 ⁱ	1.957(3)	Cu1–O2 ⁱⁱ	1.962(3)
Cu1–O3 ⁱⁱⁱ	1.967(3)	Cu1–O1	1.969(3)
Cu1–N1	2.206(3)	Cu1···Cu1 ⁱⁱ	2.6457(10)
O4 ⁱ –Cu1–O2 ⁱⁱ	89.07(15)	O4 ⁱ –Cu1–O3 ⁱⁱⁱ	167.60(12)
O2 ⁱⁱ –Cu1–O3 ⁱⁱⁱ	89.98(14)	O4 ⁱ –Cu1–O1	88.48(15)
O2 ⁱⁱ –Cu1–O1	167.58(12)	O3 ⁱⁱⁱ –Cu1–O1	89.82(14)
O4 ⁱ –Cu1–N1	96.34(15)	O2 ⁱⁱ –Cu1–N1	92.45(13)
O3 ⁱⁱⁱ –Cu1–N1	96.05(15)	O1–Cu1–N1	99.92(13)
Compound 5 ^e			
Cu1–O2	1.937(3)	Cu1–O3	1.954(2)
Cu1–N1 ⁱ	2.049(2)	Cu1–N1	2.049(2)
Cu1–O1	2.179(2)	Cu1···Cu1 ⁱⁱ	2.848(2)
O2–Cu1–N1 ⁱ	90.27(6)	O2–Cu1–O3	175.78(10)
O2–Cu1–N1	90.27(6)	N1 ⁱ –Cu1–N1	169.43(11)
O2–Cu1–O1	92.08(10)	O3–Cu1–N1	89.34(6)
N1–Cu1–O1	95.26(5)	O3–Cu1–O1	92.15(10)

^a Symmetry codes for **1**: (i) $x, 3/2 - y, z$; (ii) $1 + x, y, z$. ^b For **2**: (i) $-x, 1 - y, -z$. ^c For **3**: (i) $1 - x, -y, 1 - z$. ^d For **4**: (i) $1 + x, y, z$; (ii) $2 - x, -y, -z$; (iii) $1 - x, -y, -z$. ^e For **5**: (i) $x, 1/2 - y, z$; (ii) $1/2 + x, 1/2 - y, 3/2 - z$.

types of carboxylates can lead to structural diversities due to their coordination modes, steric effect, and flexibility. For the simplest carboxylate with the smallest steric effect, formate anion gives a 2D wavy sheet structure, whereas the larger sterically crowded carboxylates, acetate and propionate anions, give a polymeric chain, constructed from paddle-wheel CuNO_4 chromophores. On the other hand, the dicarboxylates can provide more opportunity to bind with metal centers, in particular the flexible dicarboxylates, such as malonate and succinate anions mostly constructing unpredictable crystal frameworks.³⁸ For this study, a 2D layer which contains the double-stranded chain of paddle-wheel units is built from succinate anions as well as 2D stairlike layer built from malonate anions. The description of the structures **1–5** is discussed below, together with the comparison with the bridging pyrazine spacer in the similar Cu(II) systems with their spectroscopic and magnetic properties.

Description of the Structures. $[\text{Cu}(\text{ampyz})(\text{O}_2\text{CH})_2]_n$ (**1**). The coordination environment of the Cu(II) center is shown in Figure

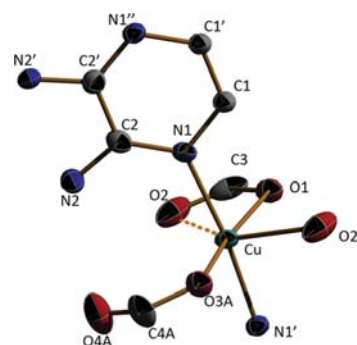


Figure 1. Asymmetric unit and atom labeling scheme of **1**. The ellipsoids are shown at 35% probability level, and the disordered O3B, C4B, O4B and hydrogen atoms are omitted for clarity. Both disordered positions of N2 are shown. The dashed line represents weak interaction in the off-the-axis position.

1. Each Cu^{2+} ion is five-coordinated showing a distorted square-pyramidal CuN_2O_3 chromophore with a τ value of 0.011 ($\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramid).³⁹ The equatorial plane around the copper atom is composed of two formate oxygen atoms (O1 and O3A) with average Cu–O distance of 1.965(5) Å and two ampyz-nitrogen atoms with Cu–N distances of 2.039(4) Å. The apical position is occupied by an oxygen from a formate bridge (Cu–O2' = 2.300(5) Å). The CuN_2O_2 square base is not perfectly planar with tetrahedral twists between the O1–Cu–N1 and O3A–Cu–N1' planes of 13.57°. The copper atoms are slightly shifted by 0.007 Å from the mean basal plane toward the apical position. This value is too small for the typically found square-pyramidal geometry, and which is attributed to the semicoordinated O2 atom of formate group weakly interacting to Cu center in off-the-axis position of an elongated octahedral geometry with the longest Cu–O2 distance of 2.718(5) Å.

The formate bridges exhibit a *syn,anti-η¹:η¹:μ₂* coordinative mode bridging between adjacent Cu(II) centers along the *a* axis with Cu···Cu separations of 4.7807(10) Å resulting a wavy polymeric chain structure as shown in Figure 2a. The ditopic ampyz spacers link the Cu–HCO₂–Cu wavy chains parallel to the *b* axis with Cu···Cu separation of 6.8558(6) Å via ampyz. The N1–Cu–N1' angle slightly deviates from linearity (9.5°). Consequently, the wavy 2D network is constructed from μ_2 -HCO₂[−] and μ_2 -ampyz with the square grid dimension of ca. 4.781×6.856 Å in the *ab* plane (Figure 2b). In addition, the layer of **1** is stabilized by hydrogen bonding and π – π stacking interactions within the layer. The intralayer hydrogen bonds are built from the amine hydrogen of ampyz and two formate oxygen atoms forming a rhomboid hydrogen bonding array throughout the layer [$\text{N2H} \cdots \text{O4A}^i = 2.25$ Å (124°), $\text{N2} \cdots \text{O4A}^i = 2.824(9)$ Å, (i) = $x, 3/2 - y, z$; $\text{N2H} \cdots \text{O3A}^i = 2.32$ Å (134°), $\text{N2} \cdots \text{O3A}^i = 2.979(9)$ Å, (i) = $-1 + x, y, z$]. The lattice is further stabilized by π – π stacking between adjacent ampyz ligands merely overlaying at the edges of the rings with the separation of 3.632(3) Å.⁴⁰ Interestingly, the crystal packing of these wavy sheets reveals the alternated ampyz arrangement in the *bc* plane (Figure 3), because of the 2₁-fold screw axis lined between the layers and the steric nature of ampyz ligands. Moreover, the interlayer hydrogen bonding between the hydrogen atoms of ampyz and the terminal formate oxygen atoms of the adjacent layer [$\text{N2H} \cdots \text{O4A}^i = 2.06$ Å (152°), $\text{N2} \cdots \text{O4A}^i = 2.848(10)$ Å, (i) = $-x, 1 - y, -z$] stabilizes the double sheet of **1** with the closest interlayer Cu···Cu separation of 6.7695(9) Å (inset of Figure 3).

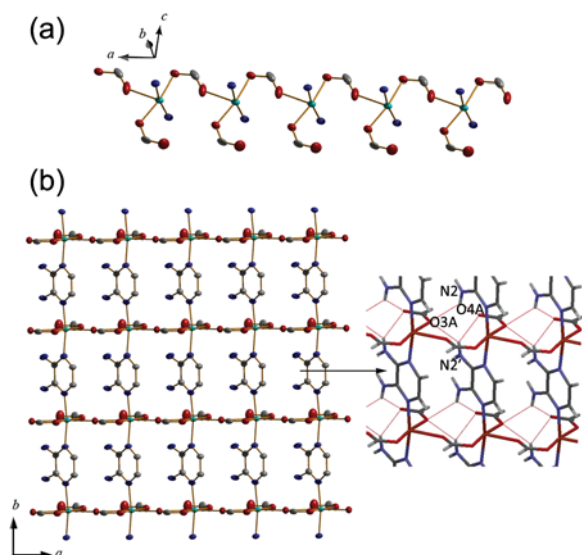


Figure 2. (a) Segment of a wavy polymeric chain in **1** constructed from *syn-anti* formate bridges along the *a* axis. Ampyz rings are omitted for the sake of clarity. (b) Two-dimensional sheet structure of **1** in the *ab* plane; the inset presents the intralayered hydrogen bonds. Both disordered positions of amino group are shown. Cu atoms are represented in green, N in blue, O in red, and C in gray.

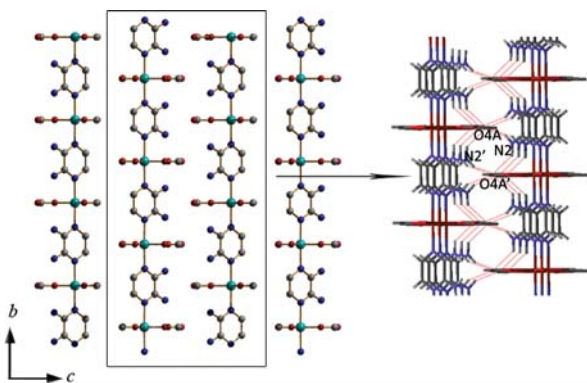


Figure 3. Packing diagram of the sheets in compound **1** showing the alternating ampyz ring arrangements in the *bc* plane. The inset shows hydrogen bonds stabilizing the double sheets of **1**. Both disordered positions of amino group are shown.

In comparison with mixed bridging pyz and formate in Cu(II) complexes, the structure of compound **1** is close to the 2D sheet of $[\text{Cu}(\text{HCO}_2)(\text{NO}_3)(\text{pyz})]_n$,²⁶ which crystallizes in the orthorhombic space group (*Pnma*) with the coordinated nitrate, whereas **1** crystallizes in the monoclinic space group (*P2₁/m*) with a monodentate formate instead of a nitrate group.

$[\text{Cu}_2(\text{ampyz})(\text{O}_2\text{C}_2\text{H}_3)_4]_n$ (**2**) and $[\text{Cu}_2(\text{ampyz})(\text{O}_2\text{C}_3\text{H}_5)_4]_n$ (**3**). Both compounds **2** and **3** consist of a polymeric chain structure built up from bridging ampyz spacers connecting the paddle-wheel units of $[\text{Cu}_2(\mu_2\text{-O}_2\text{C}_2\text{H}_3)_4]$ or $[\text{Cu}_2(\mu_2\text{-O}_2\text{C}_3\text{H}_5)_4]$ for **2** and **3**, respectively. Their structures with atom numbering scheme are shown in Figure 4. Each Cu^{2+} ion is five-coordinate showing a distorted square pyramidal CuNO_4 chromophore with $\tau = 0.002$ (for **2**) and 0.004 (for **3**). The basal position of the square pyramid is occupied by four oxygen atoms from four different carboxylate groups with mean distance of $1.967(2)$ and $1.966(3)$ Å for **2** and **3**, respectively. The apical position is occupied by a nitrogen atom from ampyz with $\text{Cu-N} = 2.229(2)$ and $2.230(2)$ Å for **2** and **3**, respectively. The basal plane is nonplanar with tetrahedral twist of 16.59° for **2** and

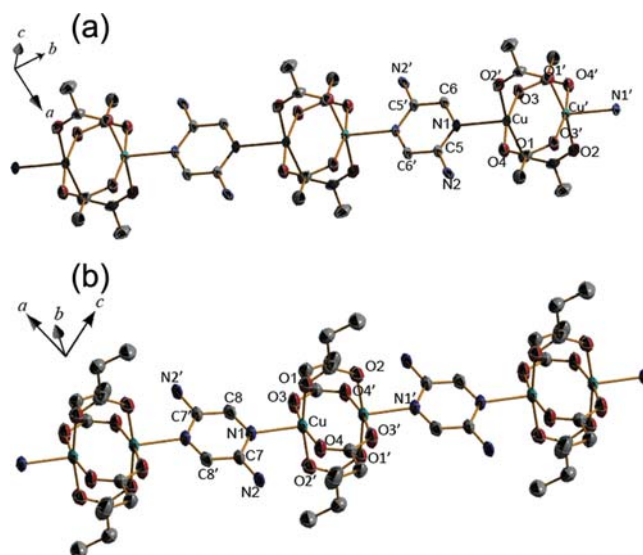


Figure 4. Part of a 1D chain structure of **2** (a) and **3** (b) with used atom labeling. The ellipsoids are shown at 35% probability level, and hydrogen atoms are omitted for clarity. Both disordered positions of N2 are shown.

16.89° for **3**. The copper atom lies 0.202 Å (for **2**) and 0.207 Å (for **3**) above the mean basal plane toward the axial site.

Both acetate and propionate anion acts as a bidentate bridge in *syn,syn-η¹:η¹;μ₂* coordinative mode bridging between Cu(II) centers forming a paddle-wheel secondary building unit (SBU). The $\text{Cu}\cdots\text{Cu}$ separation in each dinuclear unit is $2.6286(4)$ Å for **2** and $2.6322(7)$ Å for **3**, which indicates a metal-metal interaction, and it agrees well with those reported for Cu(II) paddle-wheel complexes of acetate and propionate.^{31,41,42} The paddle-wheel SBUs are connected by μ_2 -ampyz giving rise to the polymeric chain structure with $\text{Cu}\cdots\text{Cu}$ separation via ampyz of $7.2377(3)$ and $7.2498(5)$ Å for **2** and **3**, respectively. In the packing motif (Figure 5a), both 1D chains of **2** and **3** are assembled alternatively via hydrogen bonding between amine hydrogen of ampyz and a carboxylate oxygen [for **2**, $\text{N2H}\cdots\text{O4} = 1.96$ Å (159°), $\text{N2}\cdots\text{O4} = 2.774(4)$ Å; $\text{N2H}\cdots\text{O1}^i = 2.13$ Å (166°), $\text{N2}\cdots\text{O1}^i = 2.973(5)$ Å, (*i*) = $-x, 2 - y, 1 - z$; for **3**, $\text{N2H}\cdots\text{O4} = 2.12$ Å (146°), $\text{N2}\cdots\text{O4} = 2.875(6)$ Å; $\text{N2H}\cdots\text{O2}^i = 2.46$ Å (160°), $\text{N2}\cdots\text{O2}^i = 3.285(7)$ Å, (*i*) = $x, y, -1 + z$] to construct the 2D sheets with the closest $\text{Cu}\cdots\text{Cu}$ interchain distance of $6.3693(4)$ Å for **2** and $6.9001(7)$ Å for **3** corresponding to the steric size of carboxylate groups. These assembled sheets of **2** or **3** are alternately arranged in a zigzag jigsawlike motif to complete the overall solid-state structure, as shown in Figure 5b.

The copper paddle-wheel complexes have been investigated for a long time. The first 1D chain for the present system with a paddle-wheel SBU is $[\text{Cu}_2(\text{pyz})(\text{O}_2\text{C}_2\text{H}_3)_4]_n$,³¹ and was reported in 2006.⁴² The polymeric chain of **2** is almost the same as the previously reported structure. However, their crystal systems, space groups and packing motifs are dissimilar due to the amine groups appending on pyz moieties leading to the different arrangement in the solid-state structure. Contrary to **3**, the first mixed pyz and propionate in $[\text{Cu}_4(\text{pro})_4(\text{CH}_3\text{O})_4(\text{pyz})]_n$ ⁴³ gives rise to a 2D network. The distinctive structure is probably due to the higher steric effect of ampyz as compared to pyz. Therefore the paddle-wheel unit is possibly dominant leading to the 1D chain of **3**.

$[\text{Cu}_2(\text{ampyz})(\text{O}_4\text{C}_4\text{H}_4)_2]_n \cdot n\text{H}_2\text{O}$ (**4**). The structure of **4** with its atom labeling scheme is shown in Figure 6. Each Cu^{2+} ion

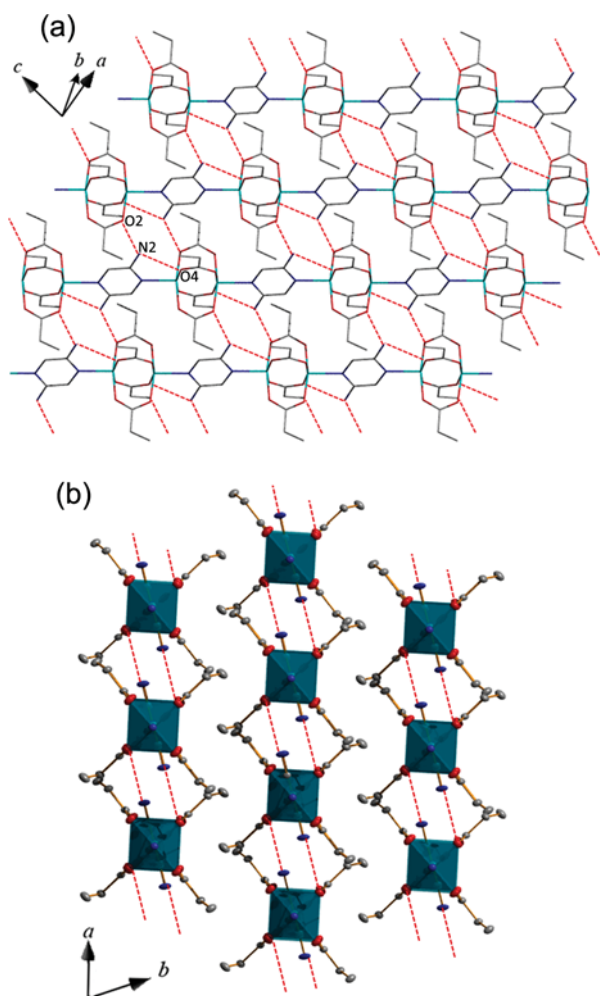


Figure 5. (a) The 2D sheet formed by hydrogen bonding between the chains of **3**. (b) Packing diagram of the 2D sheets in **3** showing zigzag arrangement of layers in *ab* plane. The hydrogen bonding between H-donors and H-acceptors are shown in red broken lines, and the blue pyramids represent CuNO_4 chromophores. Both disordered positions of amino group are shown.

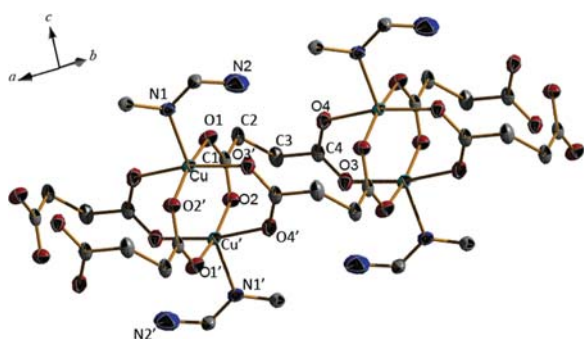


Figure 6. The double-stranded array of a paddle-wheel unit formed by four *syn-syn* succinate bridges of **4** with atom labels. The ellipsoids are shown at 35% probability level. The uncoordinated water molecule and the hydrogen atoms are omitted for clarity.

is five-coordinate showing distorted square pyramidal CuNO_4 chromophore with $\tau = 0.003$. The basal position of the square pyramid is occupied by four oxygen atoms from four different bridging succinate groups with average distance of 1.964(3) Å. The nitrogen of ampyz occupies the axial position of the square pyramid with a Cu–N distance of 2.206(3) Å. The basal plane

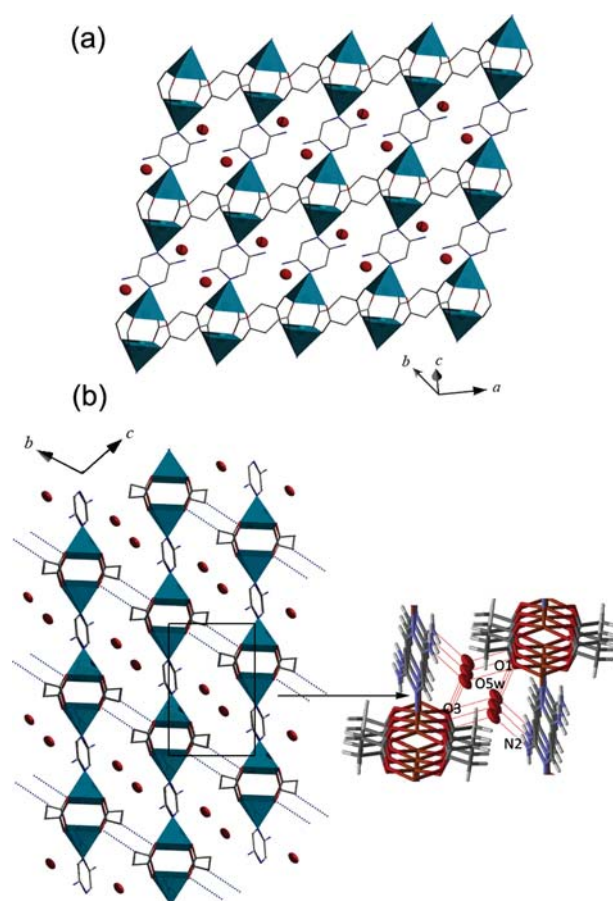


Figure 7. (a) 2D layer with uncoordinated water molecules filling up the windows of the sheet of **4**. (b) 3D packing structure of **4** formed by weak hydrogen bonding (blue dotted lines) between layers. The inset shows water molecules stabilizing the supramolecular network via hydrogen bonds. The blue pyramids are the CuNO_4 chromophores. Both disordered positions of amino group are shown.

is nonplanar with tetrahedral twist of 17.40°. The copper atom lies 0.212 Å above the mean basal plane toward the apical position.

Four succinate anions are bridging between the Cu(II) centers in a *syn,syn*- $\eta^1:\eta^1:\mu_2$ coordinative mode of carboxylate forming a Cu(II) paddle-wheel SBU. The Cu...Cu separation in each dinuclear unit is 2.6457(10) Å showing metal–metal bonding which is in good agreement with those reported for Cu(II) paddle-wheel complexes of succinate.⁴⁴ The succinate anion is a dicarboxylate containing two aliphatic carbons in the backbone. For **4**, the succinate acts as a tetradentate ligand connecting four adjacent Cu centers of the paddle-wheel SBU to form a double-stranded chain of a paddle-wheel unit, which reveals the repeating 14-membered ring of $\{\text{Cu}_2(\text{C}_2\text{O}_4)_2\}$ with the cavity's dimension of ca. 6.594×5.880 Å. The closest Cu...Cu separation among the paddle wheel SBUs is 6.5942(9) Å. The conformation of the succinate group in **4** exhibits the *syn-anti* mode²⁹ with a torsion angle of 69.88°, and the orientation of carboxylate moiety with respect to the carbon aliphatic backbone line generates angles of ca. 67.50° and 62.25°. Furthermore, these double-stranded chains are connected by ampyz spacers on an apical site of each paddle-wheel SBU with a Cu...Cu separation of 7.1951(6) Å via ampyz, giving rise to the 2D network together with uncoordinated water molecules filling on the upper and lower sites of the cavities (Figure 7a). The dimension of this cavity is about 6.594×7.195 Å. In the molecular packing motif, each 2D layer of **4** is assembled via

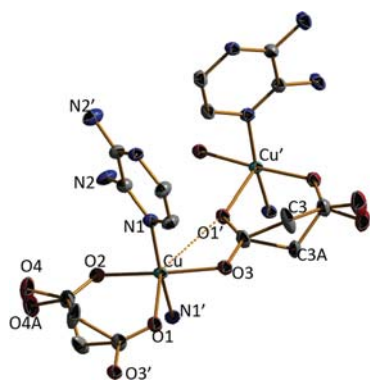


Figure 8. Asymmetric unit and the atom labeling scheme of **5** with 35% probability level. The two uncoordinated water molecules and the hydrogen atoms are omitted for clarity. Both disordered positions of N2 are shown. The dashed line represents weak interaction in the off-the-axis position.

intermolecular weak hydrogen bonding between an aliphatic hydrogen of succinate and a bridging succinato oxygen of the adjacent layer [$\text{C3H} \cdots \text{O3}^i = 2.57 \text{ \AA}$ (147°), $\text{C3} \cdots \text{O3}^i = 3.431(6) \text{ \AA}$, ($i = -x, -1 - y, -z$)] as shown in Figure 7b. Moreover, the uncoordinated water molecules play an important role to stabilize the whole packing structure via hydrogen bonding between amine hydrogen of ampyz and water oxygen [$\text{N2H} \cdots \text{O5w}^i = 1.94 \text{ \AA}$ (150°), $\text{N2} \cdots \text{O5w}^i = 2.715(15) \text{ \AA}$, ($i = 1 + x, y, z$)] and supposing via hydrogen bonding between succinato oxygen and water hydrogen with the $\text{O1} \cdots \text{O5w}$ and $\text{O3} \cdots \text{O5w}$ distances of $2.854(9) \text{ \AA}$ and $2.974(12) \text{ \AA}$, respectively. The neighboring $\text{O5w} \cdots \text{O5w}'$ distances are $2.972(16) \text{ \AA}$ indicative of normal hydrogen bonds. The closest $\text{Cu} \cdots \text{Cu}$ interlayer distance is $7.9690(8) \text{ \AA}$.

The comparison was made with known mixed bridging succinate–pyz complexes, like $[\text{Cd}_2(\text{O}_4\text{C}_4\text{H}_4)_2(\text{pyz})(\text{H}_2\text{O})]_n$,²⁹ which reveals a 2D infinite grid sheet containing a pentagonal bipyramidal chromophore. For the Cu(II) system, the compound $[\text{Cu}_2(\text{O}_4\text{C}_4\text{H}_4)_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ was obtained, being the first example of double-stranded chain motif.⁴⁴ The pyz only acts as the molecular template which is uncoordinated with Cu centers. In contrast, ampyz can incorporate in the network of **4** due to the maintenance of interlayer hydrogen bonding as well as the intralayer hydrogen bonding [$\text{N2H} \cdots \text{O3}^i = 2.00 \text{ \AA}$ (144°), $\text{N2} \cdots \text{O3}^i = 2.741(10) \text{ \AA}$, ($i = 1 - x, -y, -z$)] for stabilizing the 2D network of **4**.

[Cu(ampyz)(O₄C₃H₂)_n · 2nH₂O (5**)]**. The coordination environment of the Cu(II) center is shown in Figure 8. Each Cu^{2+} ion is five-coordinated, showing a distorted square pyramidal CuN_2O_3 chromophore with $\tau = 0.1058$. Two oxygen (O2 and O3) atoms from two different malonate groups and two ampyz nitrogen atoms occupy the equatorial plane of the square pyramidal geometry with average Cu–O and Cu–N distances of $1.945(3)$ and $2.049(2) \text{ \AA}$, respectively. The axial position is occupied by a malonate oxygen atom with Cu–O1 distance of $2.179(2) \text{ \AA}$. The copper atom is shifted by $0.130 \text{ \AA}$ from the mean basal plane toward the apical position.

Each malonate anion acts as tridentate ligand bridging two adjacent Cu(II) centers by use of a bidentate chelating mode through O2 and O1 toward Cu, forming a six-membered ring with the subtended angle at the copper atom being 92.08° . The bidentate triatomic bridge through O1 and O3' toward the adjacent Cu' resulting in a 1D zigzag chain along crystallographic *a* axis in *syn-anti* coordinative mode of malonate yields a $\text{Cu} \cdots \text{Cu}$ separation of $4.9881(6) \text{ \AA}$. The dihedral angle

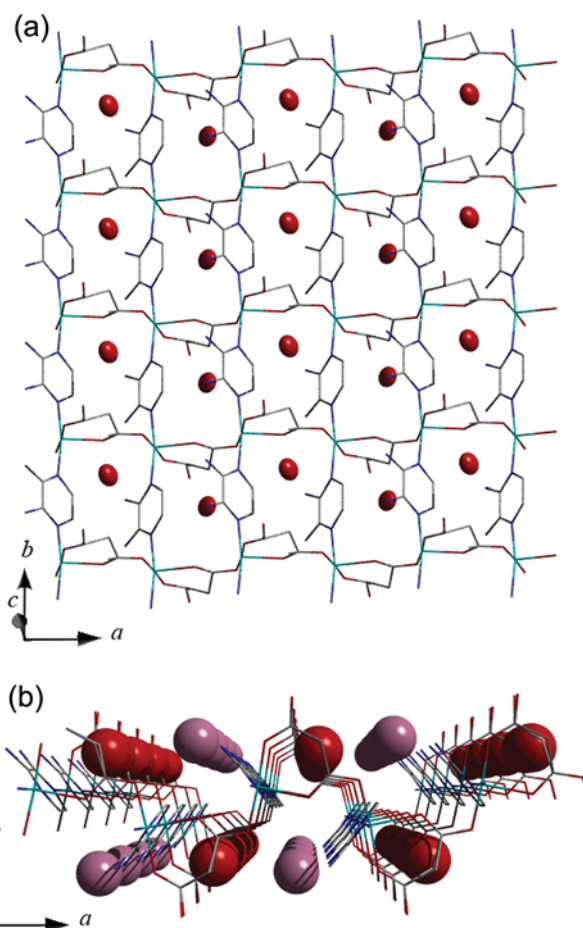


Figure 9. (a) View of the 2D layer of **5** containing nearly perpendicular orientation of ampyz spacers and uncoordinated water molecules filling up the windows. (b) Another view in the *ac* plane of a 2D stairlike layer showing the arrangement of two different groups of uncoordinated water molecules. The two sets of water molecules are represented in different colors in the space-filling model. Both disordered positions of amino group are shown.

between the basal planes of two adjacent copper atoms is 24.32° . The values of the bond lengths and angles of malonate ligand are comparable to those previously reported for malonate-bridged Cu(II) complexes.⁸ Furthermore, these 1D zigzag chains are connected by ditopic ampyz spacer along the *b* axis leading to 2D layered structure with the unbound water molecules filling up the windows (Figure 9a). The $\text{Cu} \cdots \text{Cu}$ separation via ampyz is $6.8579(3) \text{ \AA}$. Interestingly, the layers of **5** contain two sets of guest water molecules, as shown in Figure 9b. The former set is filled in the cavities of the layer in zigzag fashion spreading along the *ab* plane where the hydrogen bonding stabilizes this water set via uncoordinated malonate oxygen of adjacent layer with $\text{O4}' \cdots \text{O6w}$ separations of $2.913(11) \text{ \AA}$. The dimension of the grid cavity is about $6.858 \times 4.988 \text{ \AA}$. Another set of water molecules is filled among the layers which is stabilized by hydrogen bonding between the amine hydrogen of ampyz spacer and the water oxygen atom [$\text{N2H}_4 \cdots \text{O5w} = 1.98 \text{ \AA}$ (137°), $\text{N2} \cdots \text{O5w} = 2.671(6) \text{ \AA}$] and also by a hydrogen bond from the bridging malonate oxygen of the adjacent layer with $\text{O3}' \cdots \text{O5w}$ separations of $2.850(6) \text{ \AA}$. The filling of the different positions of water molecules causes the arrangement of ampyz rings in the layers of **5** that are twisted nearly perpendicular one another with the dihedral angle between adjacent ampyz aromatic rings being 73.52° (Figure 9a). This structural feature contributes to the stairlike layered structure (Figure 10). In the

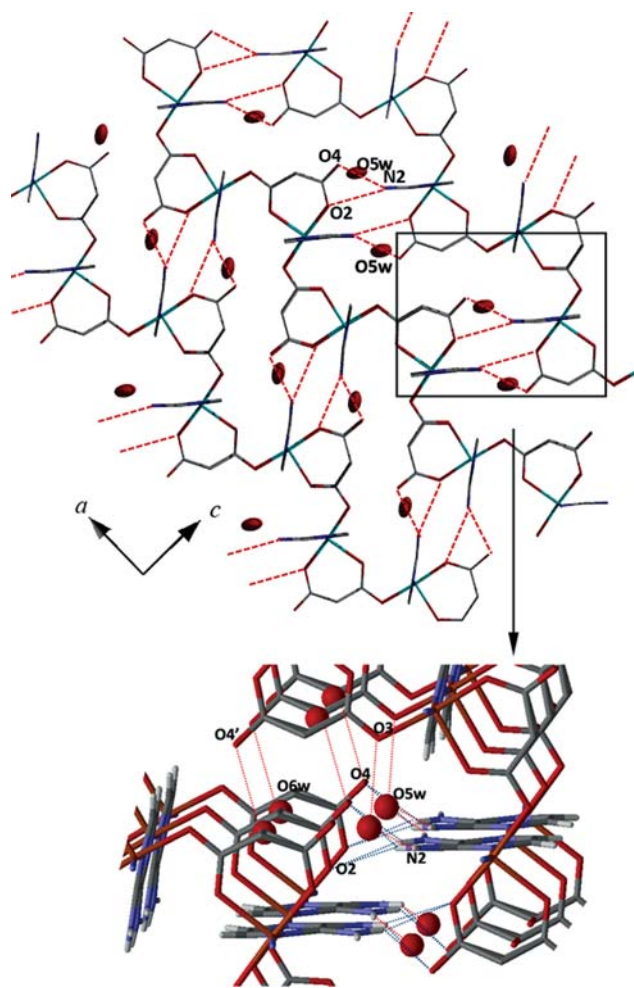


Figure 10. The 3D packing structure of **5** viewed along the *b* axis formed by the hydrogen bonding between stairlike layers. The inset presents the hydrogen bonds from uncoordinated water molecules stabilizing the supramolecular assembly.

packing motif, each 2D stairlike layer of **5** is assembled via hydrogen bonding between amine hydrogen and malonate oxygen atom [$\text{N2H}_6 \cdots \text{O2}^i = 2.45 \text{ \AA}$ (160°), $\text{N2} \cdots \text{O2}^i = 3.274(5) \text{ \AA}$, ($i = 1 - x, -1/2 + y, -z$) and $\text{N2H}_6 \cdots \text{O4}^i = 2.11 \text{ \AA}$ (135°), $\text{N2} \cdots \text{O4}^i = 2.783(7) \text{ \AA}$, ($i = -x, -y, 1 - z$)] together with the uncoordinated water molecules stabilizing the layers which completely results to the overall 3D structure of **5** as shown in the inset of Figure 10.

A comparison was made with the mixed bridging malonate–pyz Cu(II) complexes, like $[\text{Cu}_2(\text{pyz})(\text{O}_4\text{C}_3\text{H}_2)_2]_n \cdot 2n\text{H}_2\text{O}$,²⁷ which was reported to exhibit a unique 3D network constructed from bridging tetradentate malonate groups and μ_2 -pyz. Our compound **5** reveals a 2D stairlike network that may be attributed from the higher steric effect of ampyz spacer which causes malonate only acting as a tridentate connector with a terminal oxygen atom.

IR and UV–Visible Spectroscopy. The solid-state IR spectra of **1–5** in the region $4000\text{--}450 \text{ cm}^{-1}$ exhibit characteristic bands for carboxylates and ampyz ligand. Compounds **1–3** show two narrow weak bands in the regions $3400\text{--}3300 \text{ cm}^{-1}$ and $3100\text{--}3200 \text{ cm}^{-1}$, which can be assigned to asymmetric and symmetric stretching of the primary amine in the ampyz ligand. Compounds **4** and **5** show broad bands in the region $3100\text{--}3400 \text{ cm}^{-1}$ due to the bands overlapping the $\nu(\text{O–H})$ of water molecule. The NH_2 scissoring mode shows medium bands

around $1640\text{--}1660 \text{ cm}^{-1}$ which overlap with the $\nu_{\text{as}}(\text{OCO})$ of carboxylate appearing strong bands in the range of $1620\text{--}1570 \text{ cm}^{-1}$. The $\nu_{\text{s}}(\text{OCO})$ shows medium bands in the region $1320\text{--}1430 \text{ cm}^{-1}$. The weak, sharp band around $1070\text{--}1080 \text{ cm}^{-1}$ can be assigned to the $\nu(\text{C–N})$ of ampyz.

The solid-state UV–visible–NIR diffuse reflectance spectra all show a single broadband around $14\,270$ to $14\,450 \text{ cm}^{-1}$ for compounds **2–4**, which are in agreement with those of common Cu(II) paddle-wheel complexes with a square-pyramidal geometry.⁴¹ Compounds **1** and **5** show a single broadband at a higher energy, i.e. around $15\,670 \text{ cm}^{-1}$, corresponding to the further structural distortion toward an elongated octahedral geometry with the sixth off-the-axis weakly interacting to Cu center. In fact these values of the transition energy ($14\,270$ to $15\,670 \text{ cm}^{-1}$) are all in the range usually found for the distorted square-pyramidal geometry of Cu(II).⁴⁵

EPR and Magnetic Measurements. The X-band EPR was measured on polycrystalline samples at RT and 77 K for all five compounds. Compounds **2** and **4** showed in principle the same spectrum at 77 K, while at RT the intensities of particular features differed somewhat between them (see Supporting Information Figures S1–S3). In particular, at 77 K, where the triplet ($S = 1$) state is the only significantly populated excited state, two peaks are visible at around 250 and 4700 G, which are assigned to the turning points in the triplet powder pattern with $H_{\parallel}$ and $H_{\perp}$, respectively. Other expected turning points are either outside the available magnetic field range, or not observable in X-band because the value of D approaches that of the microwave quantum. The recorded spectra are indeed typical for a triplet state with a sizable zero-field splitting, such as that well-known for the classical paddle-wheel type dicopper tetracarboxylates.⁴⁶ In compound **3**, an additional feature is the hyperfine structure appearing on the parallel turning point of the spectrum at 77 K. The occurrence of the several additional peaks in the $700\text{--}4000$ gauss range in the RT EPR spectra of complexes **2–4** is in all likelihood caused by higher excited states ($S \geq 2$) being populated at elevated temperatures.^{46e} The peak at around 3200 G is an $S = 1/2$ signal of a mononuclear Cu(II) impurity and is ignored in the analysis. The spin Hamiltonian parameters optimized to simulate the experimental triplet EPR spectra at 77 K are $S = 1$, $g_{\parallel} = 2.00$, $g_{\perp} = 2.05$ and $|D| = 0.336 \text{ cm}^{-1}$ for **2** and **4**. Complex **3** is characterized by an almost identical set of parameters, with the addition of two copper ($I = 3/2$) nuclei interacting with the $S = 1$ electron spin, with the $A_{\parallel}$ component of the hyperfine tensor equal to $4 \times 10^{-3} \text{ cm}^{-1}$ (120 MHz), and $A_{\perp}$ unresolved. The appearance of triplet EPR spectra in compounds **2–4** is in accordance with the magnetic susceptibility observations and the fact that these three complexes all have very short $\text{Cu} \cdots \text{Cu}$ distances. Compounds **1** and **5**, which have different structures and both have a very long $\text{Cu} \cdots \text{Cu}$ distance, only show a broad isotropic $S = 1/2$ signal with $g = 2.12$ both at 77 K and RT.

The magnetic susceptibility of powdered sample of all five compounds was measured from 5 to 300 K under a constant magnetic field of 0.1 T. The magnetic properties of compounds **2**, **3** and **4** are, in accordance with the earlier EPR observations, the same. A sample is depicted in Supporting Information Figure S4 in the form of $\chi_{\text{M}}T$ vs T for one Cu(II) ion. At 300 K the $\chi_{\text{M}}T$ product is almost diamagnetic and has a value at around $0.08 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is much lower than the value expected for one uncorrelated Cu(II) ion ($0.375 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for $g = 2$). The $\chi_{\text{M}}T$ product gradually decreased as the temperature was lowered and reached a value of $0.0 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at around 100 K, staying

constant until 2 K. This magnetic behavior agrees with a very strong antiferromagnetic interaction ($J < -500 \text{ cm}^{-1}$).

The magnetic properties of compounds **1** and **5** are mutually the same, also in accordance with the earlier EPR observations. A sample is depicted in Supporting Information Figure S5 in the form of $\chi_M T$ vs T for one Cu(II) ion. At 300 K the $\chi_M T$ product has a value at around $0.40 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is near the value expected for uncorrelated Cu(II) ions ($0.375 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for $g = 2$). The $\chi_M T$ product stayed constant until around 40 K, where it decreased gradually as the temperature was lowered and reached a value around $0.15 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at around 2 K. This magnetic behavior agrees with a very weak antiferromagnetic interaction, which has not been explored in detail.

Conclusions

The introduction of the amine group to the pyz ring in Cu(II) carboxylate systems contributes to the structural networks mostly by amending from higher dimension to lower dimension when comparing with pyz spacer, as found in $\text{Cu}(\text{HCO}_2)_2(\text{pyz})^{28}$ revealing a 3D framework, whereas compound **1** shows a 2D wavy network. The structure is attributed to the more pronounced steric effect in ampyz which possibly causes the carboxylate group to organize itself to reduce the steric effect, as found in **5**. Here malonate acts as tridentate ligand bridging between Cu centers to build a 2D stairlike layer, instead of acting as tetradentate bridging three Cu centers to build 3D framework, like in the pyz system.²⁷ However, the ampyz spacer in addition provides other weaker interactions, such as hydrogen bonding and π - π stacking in which it is not only stabilizing within the coordination network but also contributing the stability of whole supramolecular lattice structure. For instance, compound **4** reveals a 2D sheet which is composed of double-stranded chains acting as SBU, connected by ampyz spacers, whereas it is not found in those of the Cu-pyz systems. For **2** and **3**, the structures exhibit a 2D sheet stabilized via the hydrogen bonding between polymeric chains.

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Supporting Information Available: X-ray crystallographic information files (CIF), EPR spectra, figures of the magnetic susceptibility, and the simulated and experimental powder XRD patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>. In addition, crystallographic data of the structures **1**–**5** were deposited with the following Cambridge Crystallographic Data Centre codes: 709739–709743.

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Water-induced reversible structural phase transformation with chromotropism in metal supramolecular frameworks containing aminopyrazine and sulfate anions†

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Three new supramolecular metal-coordination architectures

$[M(H_2O)_4(ampyz)_2][M(H_2O)_6](SO_4)_2(H_2O)_2$ ($M = Co$ (**1**), Fe (**2**), and mixed Co/Fe (**3**); $ampyz = 2$ -aminopyrazine) and a $Cd(II)$ coordination polymer $[Cd(ampyz)(H_2O)_2(SO_4)]_n(H_2O)_n$ (**4**) were synthesized by layered diffusion and structurally characterized. Compounds **1–3** are isomorphous. Monomeric complex units $[M(H_2O)_4(ampyz)_2]^{2+}$ are assembled by intermolecular hydrogen bonding and π – π stacking *via* $ampyz$ moieties to build 2D sheets. These layers are linked by intermolecular hydrogen bonding *via* $ampyz$ ligand, $[M(H_2O)_6]^{2+}$ unit, sulfate anion and lattice and coordinated water molecules to stabilize 3D supramolecular structure. Compound **4** shows a 2D coordination network where the sulfato connector and the bridging $ampyz$ link $Cd(II)$ ions. Lattice water molecules are filled in between the layers *via* the hydrogen bonds stabilizing 3D supramolecular network of **4**. Interestingly, compounds **1–3** exhibit water-induced reversible crystal-to-amorphous transformations with chromotropism and compound **4** also shows water-induced reversible structural phase transformation confirmed by spectroscopic techniques, elemental analyses, TGA, and XRPD. These results demonstrate the significant role between coordination bridges and weaker intermolecular interactions for the structural conversion even though **1–3** lack coordination bridges for the maintenance of their structures, however, the weak intermolecular interactions, especially hydrogen bonding, play a key role to the recovery of the crystalline phase.

Introduction

Flexible and dynamic molecular solids have recently received great attention because of their fascinating architectures with promising functional properties. Particularly, the guest removal and re-adsorption in metal–organic frameworks are of interest for many potential applications especially in the areas of gas storage and sensors.¹ The guest-induced crystalline-to-amorphous transformation and the guest-induced backward transformation are characteristic of the third generation compounds which are typically found in the flexible coordination frameworks supported by weak molecular interactions, such as hydrogen bonds, π – π stacking, van der Waals forces and others.^{1a,b} Whereas such reversible structural

transformations in non-coordination supramolecular systems are not common² since the structural destruction accompanying with the guest removal is too severe to recover the crystallinity after re-adsorption, this is not the case for flexible coordination polymers which contain the bridging spacers maintaining the skeleton of the whole structures. Within the field of inorganic–organic supramolecular chemistry, the utilization of transition metal ions and organic spacers can form a number of extended frameworks through either coordination or weak intermolecular interactions.³ It is known that the metal sulfate is a good candidate for constructing the open-framework materials along with other organic spacers, especially *N,N'*-ditopic spacers, yielding various supramolecular architectures because sulfate anion (SO_4^{2-}) can behave as a versatile connector playing the role of monodentate ligand, bridging ligand, and good hydrogen acceptor.⁴ For examples, $[Co_2(bipy)_3(SO_4)_2(H_2O)_2](bipy)(CH_3OH)^{4b}$ and $[Co(SO_4)(H_2O)_3(bipy)](H_2O)_2^{4c}$ ($bipy = 4,4'$ -bipyridine) show distinctive structures supported by sulfate ions. Likewise, structural diversity was also observed in $Cu(II)$ pyrazine complexes containing a sulfato ligand.^{4d,e}

In this study the 2-aminopyrazine ($ampyz$) was used as an *N,N'*-ditopic spacer which contains many interaction sites; coordination sites at N atoms on pyrazine ring, hydrogen donor site at amino group, and the intermolecular π – π stacking site through aromatic moieties, as found in many coordination polymers.⁵ We herein reported a series of metal(II) supramolecular structures containing 2-aminopyrazines and sulfate anions, which exhibit significant

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† Electronic supplementary information (ESI) available: Tables S1–S2: selected bond lengths and angles, and the intermolecular hydrogen bonds, far-IR spectra; Fig. S1–S8: crystal structures, packing diagram, XRPD patterns, IR and UV-vis spectra. CCDC reference numbers 752993–752996. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c002556a

chromotropism associated with reversible water-induced crystal-to-amorphous phase transformations.

Experimental

Materials and physical measurements

All chemicals were obtained from commercial sources and were used without further purification. IR spectra ($4000\text{--}450\text{ cm}^{-1}$) were obtained in KBr disks on a JASCO FT/IR-300E spectrometer. Far-IR spectra ($500\text{--}50\text{ cm}^{-1}$) were recorded on a BioRad FTS-60V spectrometer in polyethylene pellets. Resolution of the experiments was equal to 2 cm^{-1} . Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a JASCO V-570 UV/VIS/NIR spectrophotometer, within the range of $250\text{--}1100\text{ nm}$. Elemental analyses were carried out at the Laboratory for Instrumental Analysis, Graduate School of Engineering, Osaka University. Thermogravimetric analyses (TGA) were performed using a TG-DTA 2010S MAC apparatus between $25\text{--}500\text{ }^{\circ}\text{C}$ in N_2 atmosphere with heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. X-Ray powder diffraction (XRPD) data were collected on a Rigaku RINT Inplane/ultrax18SAXS-IP diffractometer using monochromatic $\text{Cu-K}\alpha$ radiation generated at 40 kV , 200 mA and the recording speed was $1^{\circ}/\text{min}$ over the 2θ range of $5\text{--}40^{\circ}$ at room temperature.

Synthesis of $[\text{Co}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ (1)

An ethanolic solution (5 mL) of ampyz (1.0 mmol , 96 mg) was carefully layered on an aqueous solution (5 mL) of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.5 mmol , 141 mg) in a glass vial (20 mL). This vial was sealed and allowed to stand undisturbed at room temperature. After four days, orange crystals of **1** were obtained. Yield 92 mg (26%) based on metal salt. Anal. Calcd for $\text{Co}_2\text{C}_8\text{H}_{34}\text{N}_6\text{O}_{20}\text{S}_2$: C, 13.41 ; H, 4.78 ; N, 11.73% . Found: C, 13.48 ; H, 4.39 ; N, 11.79% . IR (KBr, cm^{-1}): 3450 s , 3335 s , 3257 s , 1644 m , 1603 w , 1540 m , 1444 m , 1216 w , 1108 s , 1074 s , 1022 m , 983 w , 825 w , 642 m . UV-vis (diffuse reflectance, cm^{-1}): $31\,000$, $22\,300$, $19\,800$, less than 9000 .

Synthesis of $[\text{Fe}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ (2)

Compound **2** was synthesized in a similar manner to that of compound **1** by using $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (0.5 mmol , 139 mg) instead. After four days, yellow crystals of **2** were obtained. Yield 80 mg (23%) based on metal salt. Anal. Calcd for $\text{Fe}_2\text{C}_8\text{H}_{34}\text{N}_6\text{O}_{20}\text{S}_2$: C, 13.53 ; H, 4.83 ; N, 11.83% . Found: C, 13.49 ; H, 4.41 ; N, 11.84% . IR (KBr, cm^{-1}): 3451 s , 3335 s , 3255 s , 1645 m , 1602 w , 1540 m , 1444 m , 1216 w , 1107 s , 1074 s , 1021 m , 982 w , 825 w , 655 m . UV-vis (diffuse reflectance, cm^{-1}): $29\,000$, $24\,500\text{ sh}$, $11\,700$.

Synthesis of $[\text{Co}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Fe}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ (3)

Compound **3** was synthesized in a similar manner to that of compound **1** by using $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.25 mmol , 70 mg) and $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (0.25 mmol , 70 mg) instead. After four days, yellowish orange crystals of **3** were obtained. Yield 72 mg (20%) based on metal salt. Anal. Calcd for $\text{CoFeC}_8\text{H}_{34}\text{N}_6\text{O}_{20}\text{S}_2$: C, 13.47 ; H, 4.80 ; N, 11.78% . Found: C, 13.48 ; H, 4.28 ; N, 11.80% . IR (KBr, cm^{-1}): 3450 s , 3337 s , 3257 s , 1644 m , 1540 m , 1444 w ,

1216 w , 1109 s , 1075 s , 1022 m , 982 w , 824 w , 655 m . UV-vis (diffuse reflectance, cm^{-1}): $31\,600$, $24\,300\text{ sh}$, $19\,200\text{ sh}$, $11\,100\text{ br}$.

Synthesis of $[\text{Cd}(\text{ampyz})(\text{H}_2\text{O})_2(\text{SO}_4)]_n(\text{H}_2\text{O})_n$ (4)

Compound **4** was synthesized in a similar manner to that of compound **1** by using $\text{CdSO}_4\cdot 8/3\text{H}_2\text{O}$ (0.5 mmol , 385 mg) instead. After four days, colorless crystals of **4** were obtained. Yield 90 mg (53%) based on metal salt. Anal. Calcd for $\text{CdC}_4\text{H}_{10}\text{N}_3\text{O}_6\text{S}$: C, 14.10 ; H, 2.96 ; N, 12.34% . Found: C, 14.09 ; H, 2.34 ; N, 12.33% . IR (KBr, cm^{-1}): 3426 m , 3328 m , 3223 m , 1634 m , 1542 m , 1474 w , 1444 m , 1360 w , 1327 w , 1218 m , 1114 s , 1075 m , 1017 m , 814 w , 617 s . UV-vis (diffuse reflectance, cm^{-1}): $27\,700$.

X-Ray crystallography†

All reflection data were collected on a 1 K Bruker SMART CCD area-detector diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) using the SMART program.⁶ Raw data frame integration was performed with SAINT,⁷ which also applied correction for Lorentz and polarization effects. An empirical absorption correction by using the SADABS⁸ program was applied. The structure was solved by direct methods and refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.1 software package.⁹ Hydrogen atoms bound to carbon and nitrogen atoms were placed in calculated positions and refined isotropically with a riding model. The hydrogen atoms of all water molecules in **1–3** were found *via* Fourier difference maps, then restrained at fixed positions and refined isotropically whereas those of all water molecules of **4** could not be located. Ampyz ligands in **4** lie across a mirror plane so the disordered amino group was refined with half occupancy. The disorder of ampyz is found to be similar to that known for methylpyrazine¹⁰ and aminopyrazine complexes.^{5a} The details of crystal data, selected bond lengths and angles, and the intermolecular hydrogen bonds for compounds **1–4** are listed in Table 1 and Tables S1–S2,† respectively.

Results and discussion

Syntheses and spectroscopic characterizations

The layering diffusion reaction of metal(II) sulfate with ampyz in $1:2$ molar ratio in a mixture of ethanolic and aqueous media yielded high purity single-crystals of **1–4**. The IR spectra of four compounds show strong bands in the region $3400\text{--}3100\text{ cm}^{-1}$ which can be assigned to the stretching $\nu(\text{N-H})$ of the primary amine in the ampyz ligand overlapping with $\nu(\text{O-H})$ of water molecule. The NH_2 scissoring mode¹¹ shows medium bands around $1660\text{--}1640\text{ cm}^{-1}$ and the strongest bands due to SO_4^{2-} stretching vibrations are observed around 1100 cm^{-1} .¹² The solid-state UV-vis diffuse reflectance spectrum of **1** agrees with the typical d–d transition of high-spin Co(II) in octahedral geometry with two observed bands at $22\,000\text{--}19\,500$ and less than 9000 cm^{-1} , which are assigned to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ transitions, respectively. For compound **2**, the broad band around $11\,700\text{ cm}^{-1}$ is attributed to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transition for high-spin Fe(II) in octahedral geometry.¹³ The bands which appear higher than $24\,000\text{ cm}^{-1}$ are due to charge transfer transition and internal transition within ampyz. Compound **3** is a heterometallic complex,

Table 1 Crystallographic data for compounds **1–4**

	1	2	3	4
Formula	Co ₂ C ₈ H ₃₄ N ₆ O ₂₀ S ₂	Fe ₂ C ₈ H ₃₄ N ₆ O ₂₀ S ₂	CoFeC ₈ H ₃₄ N ₆ O ₂₀ S ₂	CdC ₄ H ₁₀ N ₃ O ₆ S
Formula weight	716.39	710.23	713.31	340.61
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>m</i>
<i>a</i> /Å	6.5697(4)	6.5698(13)	6.5742(4)	19.4038(4)
<i>b</i> /Å	8.3236(5)	8.3974(17)	8.3548(5)	7.3913(4)
<i>c</i> /Å	13.2130(8)	13.212(3)	13.2410(8)	6.6216(3)
α /°	75.832(1)	75.65(3)	75.676(1)	90
β /°	78.614(1)	78.33(3)	78.502(1)	106.719(1)
γ /°	78.829(1)	78.79(3)	78.814(1)	90
<i>V</i> /Å ³	678.68(7)	683.5(2)	682.46(7)	909.52(7)
<i>Z</i>	1	1	1	4
ρ_c /g cm ^{−3}	1.753	1.725	1.736	2.487
μ (Mo–K α)/mm ^{−1}	1.468	1.306	1.384	2.647
Data collected	3734	9392	4208	1729
Unique data (<i>R</i> _{int})	2531 (0.0127)	3013 (0.0208)	3016 (0.0129)	859 (0.0207)
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0277/0.0788	0.0269/0.0716	0.0276/0.0794	0.0334/0.1106
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [all data]	0.0309/0.0806	0.0302/0.0733	0.0294/0.0862	0.0336/0.1109
GOF	1.069	1.052	1.075	1.264
Max/min electron density/e Å ^{−3}	0.309/−0.475	0.347/−0.266	0.448/−0.599	0.750/−0.663

$$^a R = \sum \|F_o| - |F_c|\| / \sum |F_o|. \quad ^b R_w = \{\sum [w(|F_o| - |F_c|)]^2 / \sum [w|F_o|^2]\}^{1/2}.$$

so the spectrum of **3** shows the overlaying transitions between Co(II) and Fe(II) in octahedral geometries (Fig. S1†), resulting in a yellowish orange color which is between the orange crystal of **1** and the yellow crystal of **2**. Besides the crystallographic data, the positions of Co(II) and Fe(II) chromophores in **3** were further verified by far-IR spectra (500–50 cm^{−1}) which yield the information of M–O and M–N vibrations in compounds **1–3** (see the detail in the ESI†).

Crystal structures

[Co(H₂O)₄(ampyz)₂][Co(H₂O)₆](SO₄)₂(H₂O)₂ (**1**). Single-crystal X-ray diffraction analyses revealed that compounds **1–3** are not only isostructural frameworks, but also form a beautiful isomorphous series, and the structure of **1** is described in detail here.

Complex **1** contains two crystallographically independent Co(II) ions (Co1 and Co2) in [Co(H₂O)₄(ampyz)₂]²⁺ and [Co(H₂O)₆]²⁺ cationic units, as shown in Fig. 1. Both Co²⁺ ions are 6-coordinated

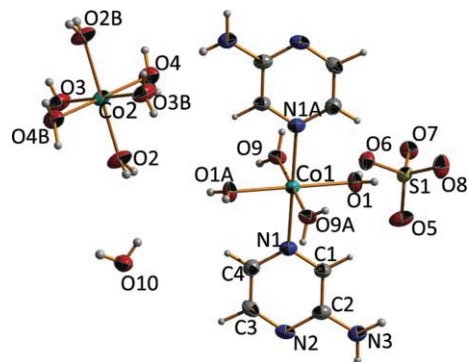


Fig. 1 Crystal structure and atom labeling scheme of **1**. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A” and “B” are symmetry-generated equivalents, (A) $-x, 1 - y, 1 - z$; (B) $-x, 2 - y, -z$.

and lie on independent inversion centers. Co1 shows elongated octahedral geometry comprised of four oxygen atoms from water molecules at equatorial positions with the average Co1–O distance of 2.0702(13) Å, and two nitrogen atoms from ampyz ligands at axial sites with Co1–N1 distance of 2.2071(16) Å. Co2 shows slightly compressed octahedron, surrounded by six water molecules with the average Co2–O bond length at equatorial plane of 2.1072(15) Å and the Co2–O3 distance at apical position of 2.0691(14) Å. The bond angles around octahedron are in the range of 87.33–180°, which are close to ideal octahedral geometry.

[Co(H₂O)₄(ampyz)₂]²⁺ units are assembled by intermolecular hydrogen bonding between pyrazine nitrogen and hydrogen of coordination water along *b*-axis [O9–H...N2ⁱ = 1.86 Å (173°), O9...N2ⁱ = 2.792(2) Å, (i) = *x*, 1 + *y*, *z*], and π – π stacking interaction among adjacent ampyz moieties along *a*-axis with the separation of 3.417–3.557 Å, giving rise to 2D layer substructure in *ab* plane with the closest intermolecular Co...Co separation of 6.5697(4) Å (Fig. 2). Moreover, these layers are supported by electrostatic forces and the intermolecular hydrogen bonds involving sulfate anions (O5–O8), amine moieties on ampyz (N3), coordination waters in [Co(H₂O)₆]²⁺ unit (O2–O4), and lattice water molecules (O10), to provide an entire 3D supramolecular structure of **1** as shown in Fig. 3. Details of hydrogen bonds are summarized in Table S2† and crystal structures of **2–3** are depicted in Fig. S2–S3.†

[Cd(ampyz)(H₂O)₂(SO₄)₂](H₂O)_n (**4**). The coordination environment of the Cd(II) center is shown in Fig. 4. The Cd1 atom, sulfate atoms S1, O1, O2 and the water oxygen O4 all lie on a mirror plane in this structure. Each Cd²⁺ ion is five-coordinated showing a distorted square-pyramidal CdN₂O₃ chromophore with $\tau = 0.04$.¹⁴ The basal plane around the cadmium atom is comprised of one oxygen atom from coordination water (O4) and one oxygen atom from a μ_2 -sulfato bridge (O2A) with the Cd–O distance of 2.303(6) and 2.297(5) Å, respectively and two ampyz-nitrogen atoms with

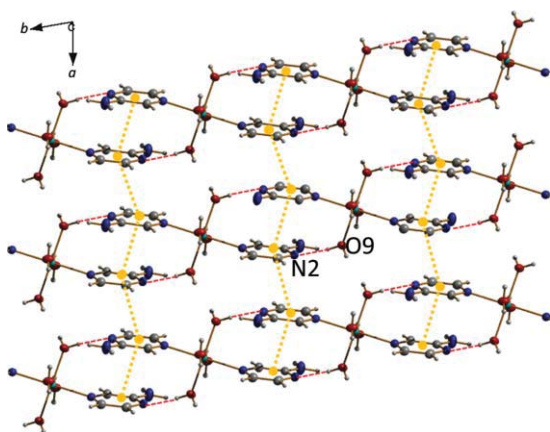


Fig. 2 2D sheet structure of **1** in the *ab* plane, assembled via the intermolecular π - π stacking and hydrogen bonding interaction which are represented in yellow and red broken lines, respectively.

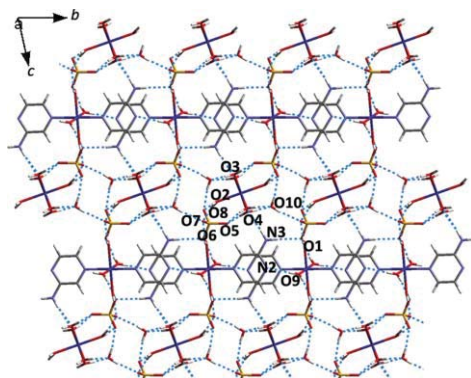


Fig. 3 3D packing structure of **1** in *bc* plane formed by intermolecular hydrogen bonding (blue dotted lines) among layers through ampyz, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ unit, sulfate anion, lattice and coordination water molecules.

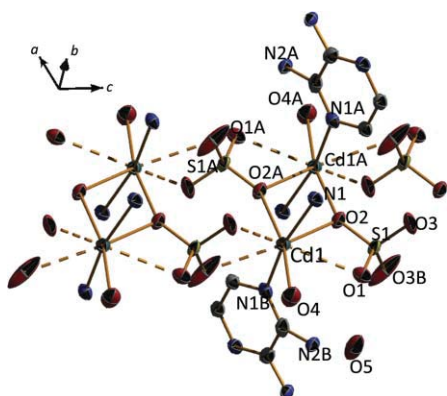


Fig. 4 Expanded asymmetric unit and atom labeling scheme of **4**. The ellipsoids are shown at 35% probability level. Atoms labeled with the notation "A" and "B" are symmetry-generated equivalents, (A) $1 - x, y, 1 - z$; (B) $x, -y, z$. Both disordered positions of N2 are shown. The dashed lines represent the weak coordinative bonds between sulfate oxygen atoms and Cd(II) ions.

the Cd–N distances of 2.315(4) Å. The apical position is occupied by a μ_2 -sulfato oxygen (O2) with Cd–O2 length of 2.587(5) Å. The bond angles between axial shared with a neighboring square pyramid and square corners are remarkably deviated from 90°

and rather distorted from regular square pyramidal geometry of Cd(II).¹⁵ It is possibly attributed to three sulfato oxygen atoms excluded from μ_2 -bridges, weakly interacting with adjacent Cd(II) centers with Cd $\cdots$ O3 and Cd $\cdots$ O1 distances of 2.754(6) and 2.765(6) Å, respectively, forming the semi-eight coordination. The weak secondary bonds of Cd $\cdots$ O are also reported in other Cd(II) complexes.¹⁶

The sulfato ligand acting as a monoatomic bridge connects Cd(II) centers in *ac* plane, yielding the Cd(II) dimer with the separation of 4.0359(5) Å. These Cd(II) dimers are linked by the ditopic ampyz spacers along *b*-axis leading to 1D ladder chain structure with Cd $\cdots$ Cd separation via ampyz of 7.3913(4) Å (see Fig. 5(b)). Moreover, when above-mentioned weak coordination bonds are considered, the inorganic double-stranded chain of metal sulfate^{4a} is observed, which is comprised by CdN_2O_6 polyhedra and SO_4 tetrahedral units, as shown in Fig. 5(a). The monoatomic sulfato bridge connects Cd(II) ions, leading to edge-sharing CdN_2O_6 polyhedra that further share edges with tetradentate bridges of SO_4 tetrahedra to form a four-member ring ladder along *c*-axis. In addition this chain is linked by the ampyz spacers along *b*-axis, giving rise to the 2D layer structure of **4** as shown in Fig. 5(b). The lattice water molecules (O5) are filled in between 2D sheets, which effectively provide the intermolecular hydrogen bonds with amine nitrogen of ampyz (N2), sulfato oxygen (O1, O3) and coordination water (O4), contributing to the stabilization of the overall 3D supramolecular structure as shown in Fig. 6. Details of hydrogen bonds are summarized in Table S2.†

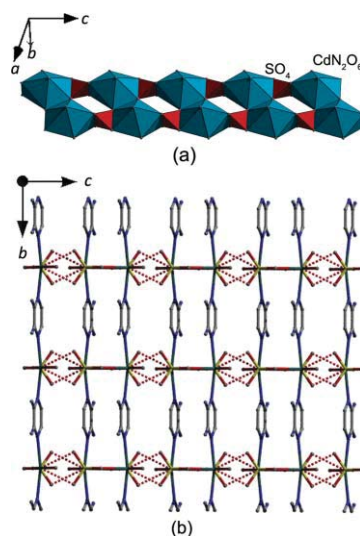


Fig. 5 (a) Double-stranded chain of $[\text{Cd}(\text{ampyz})(\text{H}_2\text{O})_2(\text{SO}_4)]_n$. (b) View of the 2D layer of **4** in *bc* plane. The red broken lines represent the weak coordinative bonds between sulfate oxygen atoms and Cd(II) ions.

Thermogravimetric analyses

To examine the thermal stabilities of compounds **1–4**, the TGA were performed in the temperature range 25–500 °C, as shown in Fig. 7. The TGA profiles of **1–3** indicate that the releases of all twelve water molecules including coordinated and lattice water molecules occur at the first step of weight loss in the temperature range 55–180 °C (found, 31.46%; Anal. Calcd, 30.15% for **1**;

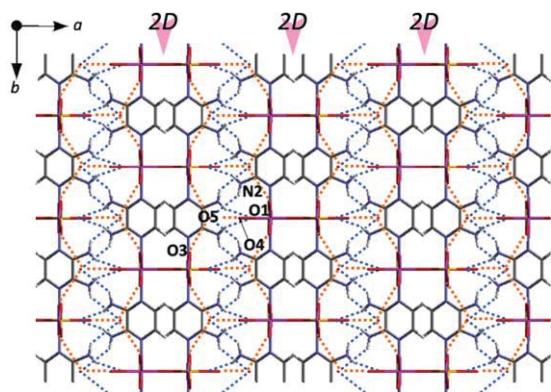


Fig. 6 3D packing structure of **4** in *ab* plane formed by intermolecular hydrogen bonding between layers and lattice water molecules. The blue and orange dotted lines represent the N2–H···O(1, 5) and O5···O(4, 3) intermolecular hydrogen bonds, respectively.

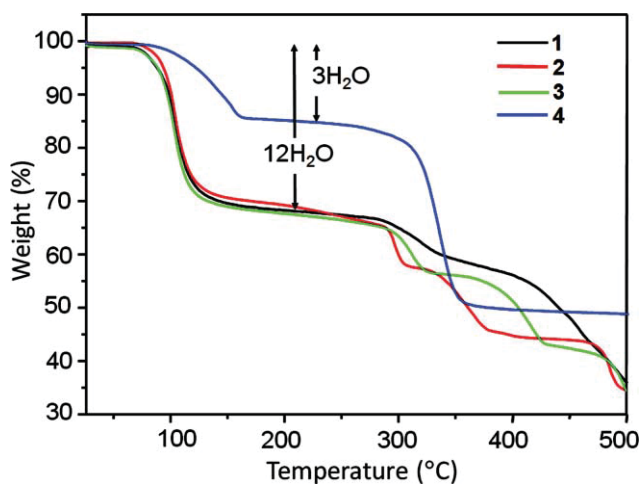


Fig. 7 TGA curves of compounds **1–4**.

found, 29.44%; Anal. Calcd, 30.41% for **2**; found, 31.48%; Anal. Calcd, 30.28% for **3**), resulting to the dehydrated forms of $[M_2(\text{ampyz})_2(\text{SO}_4)_2]$ (**1A–3A**), which are stable up to $\approx 240^\circ\text{C}$ and then the structures gradually decompose to the unidentified products. The TGA profile of **4** shows two steps of weight loss. The first step ($75\text{--}180^\circ\text{C}$) corresponds to the loss of all three water molecules (found, 15.20%; Anal. Calcd, 15.86%), resulting in the dehydrated forms of $[\text{Cd}(\text{ampyz})(\text{SO}_4)]$ (**4A**), which are stable up to $\approx 250^\circ\text{C}$. The second step ($250\text{--}420^\circ\text{C}$) gives a mixture of the CdO and CdS as main products.

Water-induced reversible structural phase transformation with chromotropism

Aforementioned all compounds contain both lattice and coordination water molecules and the stable dehydrated forms of **1A–4A** were clarified by TGA profiles. The dynamic structural behaviors of **1–4** relating to their dehydration and rehydration processes are studied by elemental analyses, XRPD, and spectroscopic techniques.

When the single-crystals of **1–4** were heated to 220°C in air for 30 min, these crystals suddenly lose the crystallinity and the colors changed from orange to purple for **1**; yellow to

orange for **2**; yellowish orange to brown for **3**; and no color changes was observed in colorless compound **4**. Then these non-crystalline solids were exposed to the laboratory air for 8 h and the colors of solids **1A–3A** returned to their original crystalline ones. Consequently, the bulk samples of **1–4** were used to study in detail. The dehydrated forms of **1A–4A** were obtained by heating the bulk samples at 220°C in air for 4 h and the re-hydrated forms of **1'–4'** were obtained by exposing the dehydrated samples to water vapor for 2 days at room temperature without condensation. The XRPD pattern of **1** is shown in Fig. 8. The TGA, elemental analysis of **1A** (Anal. Calcd: C, 19.21; H, 2.02; N, 16.80%. Found: C, 18.51; H, 2.10; N, 16.18%), and XRPD results indicate that the dehydrated $[\text{Co}_2(\text{ampyz})_2(\text{SO}_4)_2]$ (**1A**) is in an amorphous phase which is formed by the collapse of supramolecular structure of **1** accompanied with the destruction of hydrogen bonding networks when all water molecules are removed. The original crystalline phase $[\text{Co}(\text{H}_2\text{O})_4(\text{ampyz})_2][\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2(\text{H}_2\text{O})_2$ (**1'**) can be restored from the amorphous phase of **1A** after rehydration process which confirmed by the elemental analysis (Anal. Calcd: C, 13.41; H, 4.78; N, 11.73%. Found: C, 13.39; H, 4.29; N, 11.72%), and the XRPD pattern. These results suggest the crystalline-to-amorphous and amorphous-to-crystalline transformations in supramolecular network of **1** triggered by the hydration control. Furthermore, this structural change of bulk sample is accompanied with a remarkable color change as confirmed by the solid-state UV-vis diffuse reflectance spectra in Fig. 9 for **1**. The spectra clearly show that the bands observed in **1** and **1'** correspond very well to the identical transitions causing the same color of bulk products, and evidence that **1** and **1'** have the same Co(II) environments. Whereas the amorphous phase **1A** shows the different d–d transition with a lower-energy broad band centered around 550 nm, giving the distinctive purple color. The chromotropic behaviors of **1** are principally ascribed to the changes of the d-orbital energy level, induced by the drastic change in the coordination environments around metal center during dehydration and rehydration processes.^{4b,17} In addition, these results agree with the reversible change of the sulfate vibrational band in IR spectra (Fig. 10) where the different splitting peaks at ~ 1100 (ν_3) and ~ 630 cm^{-1} (ν_4) are observed for the amorphous phase, indicating that site symmetry at sulfate ions is lowered.¹² By contrast, these

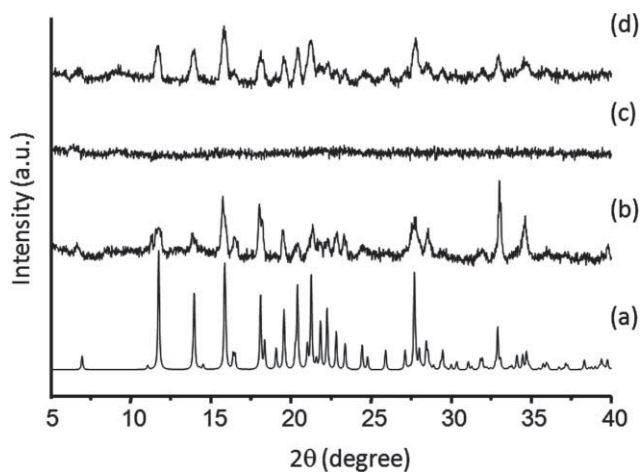


Fig. 8 XRPD patterns: (a) simulated from single-crystal X-ray data; (b) as-synthesize **1**; (c) the dehydrated form **1A**; (d) the rehydrated form **1'**.

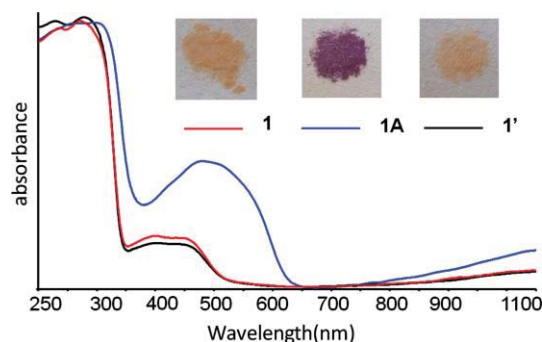


Fig. 9 The UV-vis diffuse reflectance spectra of as-synthesize **1** (red line), the dehydrated form **1A** (blue line), and the rehydrated form **1'** (black line), representing together with the chromatic changes in bulk samples.

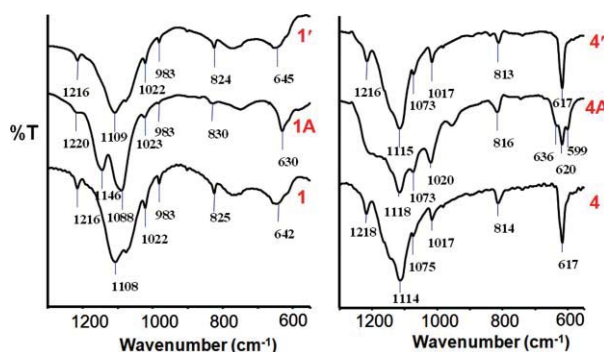


Fig. 10 IR spectra: (left) for as-synthesize **1**, the dehydrated form **1A** and the rehydrated form **1'**; (right) for compound **4**.

splits are removed in the IR spectra of the rehydrated form, which are identical to those of the as-synthesized one. All of these results confirm the water-induced reversible crystalline-to-amorphous phase transformation with chromotropism in the supramolecular network of **1**. This phenomenon is also observed in the isostructural **2** and **3**. On the other hand, the coordination network **4** exhibits the structural phase change in the dehydrated phase, [Cd(ampyz)(SO₄)] (**4A**) which reveals the different XRPD pattern comparing with as-synthesized **4** (Fig. 11). Interestingly, this crystalline phase is converted to the same structure as the original one (**4'**) by rehydration process, which can be confirmed by the XRPD, IR-spectra, and elemental analysis (for **4'**: Anal. Calcd: C, 14.10; H, 2.96; N, 12.34%. Found: C, 14.11; H, 2.39; N,

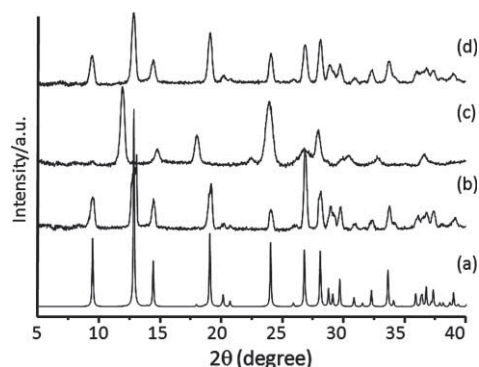


Fig. 11 XRPD patterns: (a) simulated from single-crystal X-ray data; (b) as-synthesize **4**; (c) the dehydrated form **4A**; (d) the rehydrated form **4'**.

12.37%). These results confirm the water-induced structural phase transformation in coordination network **4**. The XRPD patterns, and UV-vis spectra of **2–3** are given in Fig. S4–S8.†

When the lattice and coordination water molecules are removed, the supramolecular networks **1–3** collapse due to the destruction of the hydrogen bonding networks while the coordination polymer **4** does not collapse but exhibits another crystalline phase. This result indicates that the coordination bridges *via* ampyz spacer and sulfato ligand play an important role for supporting the structural skeleton in **4**. Remarkably, all compounds recover original crystalline phases after the exposure to water vapor, indicating that the significant role of hydrogen bonding through water molecules can trigger the reformation of other weak intermolecular interactions such as π - π stacking among ampyz moieties in **1–3** and other hydrogen bonds through sulfate ions in **1–4**. This structurally dynamic process supports the idea that hydrogen-bonded networks have great potential for utility in the world of material chemistry.

Conclusions

By using the versatile ampyz ligand, three metal supramolecular assemblies with a lack of coordination bridges **1–3** and a Cd(II) coordination polymer **4** were successfully synthesized. The Cd(II) ion has a larger accessible space for arranging the bridging ampyz and bridging sulfato group leading to the 2D coordination network. In contrast, the smaller Co(II) and Fe(II) ions give isostructural assemblies of monomeric complexes which contain intermolecular π - π stacking and hydrogen bonding interactions stabilizing the whole structures. The water desorption/resorption processes trigger the reversible crystal-to-amorphous transformation with chromotropism for compounds **1–3**. Although the lack of coordination bridge maintaining the skeleton of the framework structures in **1–3**, the original crystalline phases are recovered from collapsed amorphous structures by the restoration of water molecules. On the other hand, the coordination bridges in **4** play an important role for preserving the crystallinity in dehydrated phase thus the reversible structural phase transformation in **4** is observed. This work is also beneficial in expanding the field of crystal engineering by controlling the weak interaction of coordination moieties.

Acknowledgements

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Structural diversity and magnetic properties in 1D and 2D azido-bridged cobalt(II) complexes with 1,2-bis(2-pyridyl)ethylene†

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By utilizing a flexible co-ligand 1,2-bis(2-pyridyl)ethylene (2,2'-bpe), two new azido-bridged cobalt(II) complexes with the formulae $[\text{Co}_3(\text{N}_3)_6(\text{OH}_2)_2(2,2'\text{-bpe})_2]_n(2,2'\text{-bpe})_n$ (**1**) and $[\text{Co}(\text{N}_3)_2(2,2'\text{-bpe})_2]_n$ (**2**) have been synthesized and structurally characterized. Compound **1** shows an uncommon 1D chain comprised of double EO azido bridged five- and six-coordinated Co^{II} geometries in a unique $(-5-5-6-)_n$ sequence of the coordination number. The 2,2'-bpe acts as a terminal co-ligand and an uncoordinated molecule in the crystal lattice. Moreover the adjacent 1D chain is assembled by $\text{C-H}\cdots\pi$ interactions and the intermolecular hydrogen bonding between uncoordinated 2,2'-bpe and coordinated water molecules building a 2D layer. Whereas, compound **2** is a 2D coordination network containing the alternating double EO and double EE bridging modes of azides and ditopic 2,2'-bpe bridges. The magnetic investigation of **1** reveals dominant intra-chain ferromagnetic interactions, with the double EO azide-bridge and weak inter-chain antiferromagnetic interactions, with overall metamagnetic behaviour, having magnetic ordering at 6 K. The magnetic behaviour of **2** shows spin-canted antiferromagnetism below a T_{N} of 12 K.

Introduction

Molecule-based magnetic materials involving azido bridges have incessantly attracted much attention because of their diverse architectures with interesting physical properties, such as single molecule magnet, single chain magnet and long-range magnetic ordering behaviours.¹⁻⁵ The crystal engineering of molecular magnetism aims to control the spins in molecules and molecular assemblies.^{6,7} As an excellent ligand, containing several pairs of electrons, azido can readily bridge two or more spin carriers. It can provide many bridging modes [μ_2 -1,3 (end-to-end, EE), μ_2 -1,1 (end-on, EO), μ_3 -1,1,1 and other bridges] and effectively mediate either ferromagnetic or antiferromagnetic coupling, normally through EO and EE modes, respectively.¹⁻⁵ It is known that one of the interesting structural aspects of working with the cobalt ion is the wide range of geometries, octahedral, tetrahedral, square-pyramidal, trigonal-bipyramidal and square-planar, that are stable.¹ Consequently, when the azide ion and co-ligands are coupled with cobalt(II) ions, which accommodate four-,

five- and six-coordination depending on the situation, various low-dimensional structures are expected along with interesting magnetism.⁸⁻¹³ The versatile *N,N'*-ditopic bridging spacer 1,2-bis(4-pyridyl)ethylene and its derivatives have been used as co-ligands widely in organic-inorganic hybrid materials including azido complexes and they usually give unexpected structures with interesting magnetic orders.¹⁴⁻¹⁷ However, the *trans*-1,2-bis(2-pyridyl)ethylene (2,2'-bpe) has not yet been reported in any azido complexes. Herein we show that 2,2'-bpe can act as both terminal (*endo*) and bridging (*exo*) co-ligands in a Co^{II} azido system, which effectively support either blocking the metal's coordination sites or extending the structural dimensions. The syntheses, structures and magnetic studies of two novel cobalt(II) azido complexes were reported. The $[\text{Co}_3(\text{N}_3)_6(\text{OH}_2)_2(2,2'\text{-bpe})_2]_n(2,2'\text{-bpe})_n$ (**1**) shows a remarkable 1D chain, comprised of alternating distinctive cobalt(II) geometries in a unique $[-5-5-6-]_n$ sequence of coordination number, which is ferromagnetically bridged by the double EO modes of the azide. Another product, $[\text{Co}(\text{N}_3)_2(2,2'\text{-bpe})_2]_n$ (**2**) has 2D wavy layers, containing the alternating double EE and double EO cobalt(II) azido chains bundled together by 2,2'-bpe bridges, which shows weak ferromagnetism due to spin canting.

Experimental

Materials and physical measurements

All chemicals were obtained from commercial sources, 1,2-bis(2-pyridyl)ethylene was from Tokyo Chemical Industry (TCI)

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† Electronic supplementary information (ESI) available: Single-crystal X-ray crystallographic information files (CIF) for **1** and **2**, Fig. S1–S5: IR and UV-vis spectra, XRPD patterns, and additional magnetic data. CCDC reference numbers 766434 and 766435. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00853b

and they were used without further purification. IR spectra (4000–450 cm⁻¹) were obtained in KBr disks on a JASCO FT/IR-300E spectrometer. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer, within the range of 450–1100 nm. Elemental analyses were carried out at the Laboratory for Instrumental Analysis, Graduate School of Engineering, Osaka University. The X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT Inplane/ultrax18SAXS-IP diffractometer using monochromatic Cu-K α radiation generated at 40 kV, 200 mA and the recording speed was 1° min⁻¹ over the 2 θ range of 5–40° at room temperature. All magnetic measurements were performed on polycrystalline samples, which were mounted in calibrated gelatin capsules held at the centre of a polypropylene straw fixed to the end of the sample rod. The *dc* magnetic measurements were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer equipped with reciprocating sample option (RSO). The *ac* magnetic measurements were carried out on a Quantum Design MPMS-2 SQUID magnetometer. Magnetic data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Caution! Although not encountered in our experiments, azido compounds are potentially explosive and should be manipulated with care and used only in small quantities.

Synthesis of [Co₃(N₃)₆(OH₂)₂(2,2′-bpe)₂]_n(2,2′-bpe)_n (**1**) and [Co(N₃)₂(2,2′-bpe)₂]_n (**2**)

A solution containing CoCl₂·6H₂O (0.5 mmol, 119 mg) and 2,2′-bpe (0.5 mmol, 91 mg) in a mixture of water (2 mL) and ethanol (2 mL) was carefully layered on an aqueous solution (2 mL) of NaN₃ (1 mmol, 65 mg) in an 18 mL glass vial. The vial was sealed and allowed to stand undisturbed at room temperature. After 5 days, long blue rod-shaped crystals of **1** and small pink square-shaped crystals of **2** were obtained. These crystals were manually separated, washed with water and dried in air. Yield for **1**: 26 mg (5%) based on metal salt. Anal. calcd for Co₃C₃₆H₃₄N₂₄O₂: C 42.74, H 3.39, N 33.23%. Found: C 42.49, H 3.10, N 32.98%. IR (KBr, cm⁻¹): 3200 br, 2089 vs, 2050 m, 1592 m, 1479 m, 1296 m, 1158 w, 974 m, 780 m. UV-vis (diffuse reflectance, cm⁻¹): 18500 sh, 16500, 12500 sh, 9800. Yield for **2**: 56 mg (34%) based on metal salt. Anal. calcd for CoC₁₂H₁₀N₈: C 44.32, H 3.10, N 34.46%. Found: C 44.04, H 2.98, N 34.51%. IR (KBr, cm⁻¹): 3397 w, 3091 w, 2097 vs, 2072 vs, 1599 m, 1480 m, 1298 w, 1160 m, 970 m, 779 m, 743 m, 542 w. UV-vis (diffuse reflectance, cm⁻¹): 18000, 16500, less than 9000. The single-crystals of **2** were prepared in a U-shaped tube. An aqueous solution (2 mL) of NaN₃ (1 mmol) was filled into one branch of a U-tube that contained distilled water 1 mL. Another branch was filled with a solution containing CoCl₂·6H₂O (0.5 mmol) and 2,2′-bpe (0.5 mmol) in a mixture of water (1 mL) and ethanol (2 mL). After one week, suitable single-crystals of **2** for X-ray diffraction study were obtained.

X-Ray crystallography

The reflection data were collected on a Rigaku RAXIS RAPID imaging-plate area detector with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). Data collection and cell refinement

were performed with the *PROCESS-AUTO*.¹⁸ An absorption correction was performed by using the *ABSCOR*.¹⁹ Data reduction by the *CrystalStructure*²⁰ program was applied. The structure was solved by direct methods and refined by full-matrix least-squares method on *F*² with anisotropic thermal parameters for all non-hydrogen atoms using the *SHELXTL-PC V6.1*²¹ software package. Hydrogen atoms bound to a carbon atom were placed in calculated positions and refined isotropically with a riding model. The hydrogen atoms of water molecules in **1–2** were found *via* Fourier difference maps, then restrained at fixed positions and refined isotropically.

Results and discussion

Syntheses and characterizations

The layered diffusion reaction of CoCl₂·6H₂O, 2,2′-bpe and NaN₃ in a 1 : 1 : 2 molar ratio in water and ethanol media yielded the mixture of blue rod-shaped crystals of **1** and pink square-shaped crystals of **2**. The crystals were manually separated because of the visible difference in the colour and shape of the crystals. Then the physical purities of the crystalline phase of the bulk products were confirmed by XRPD technique comparing with their simulated XRD patterns from the single-crystal data (Fig. S1, ESI†). An attempt has been made to find the optimal conditions for preparing a single phase of **1** or **2**, based on molar ratios and solvents, without success. The IR spectrum of **1** with end-on mode of azide shows a very strong band at 2089 cm⁻¹ $\nu_{as}(\text{N}_3^-)$ with a shoulder peak and medium band at 1296 cm⁻¹ $\nu_s(\text{N}_3^-)$. Complex **2** containing both μ_2 -1,1 and μ_2 -1,3 bridging azides shows two very strong bands due to $\nu_{as}(\text{N}_3^-)$ mode at 2097 and 2072 cm⁻¹ and medium band at 1296 cm⁻¹ $\nu_s(\text{N}_3^-)$. The electronic spectra show the overlapped bands of the d-d transitions arising from the penta-coordination and octahedral geometries of the high-spin Co^{II} ions for **1** and exhibit the typical d-d transitions of octahedral geometry for **2** (Fig. S3, ESI†).

Crystal Structures

[Co₃(N₃)₆(OH₂)₂(2,2′-bpe)₂]_n(2,2′-bpe)_n (**1**). Single-crystal X-ray analysis revealed that compound **1** contains two crystallographically independent Co1 and Co2 ions bridged by three independent EO azido ligands, as shown in Fig. 1(a). Co1 is placed in an intermediate 5-coordination geometry, slightly distorted toward trigonal bipyramid with a τ value²² of 0.55, where the metal atom is coordinated by four N atoms from four EO azide anions and a N atom from a monodentate 2,2′-bpe. Co2 has a CoN₄O₂ compressed octahedral geometry, which is located on the crystallographic inversion centre and it is coordinated by four N atoms from EO azido ligands in the equatorial positions and two water molecules in the axial sites. The crystallographic data is shown in Table 1 and selected bond lengths and bond angles are given in Table 2.

The adjacent Co^{II} centres are connected by an azide in the double-EO mode along the *a* axis associated with the inversion centre, to build a 1D zigzag chain with the rare [–5–5–6–]_n sequence of cobalt(II) coordination numbers (Fig. 1(b)). The bond angles of Co–N–Co are in the range between 97.09(12)° and 100.37(12)° and the intrachain Co···Co separations through the double EO

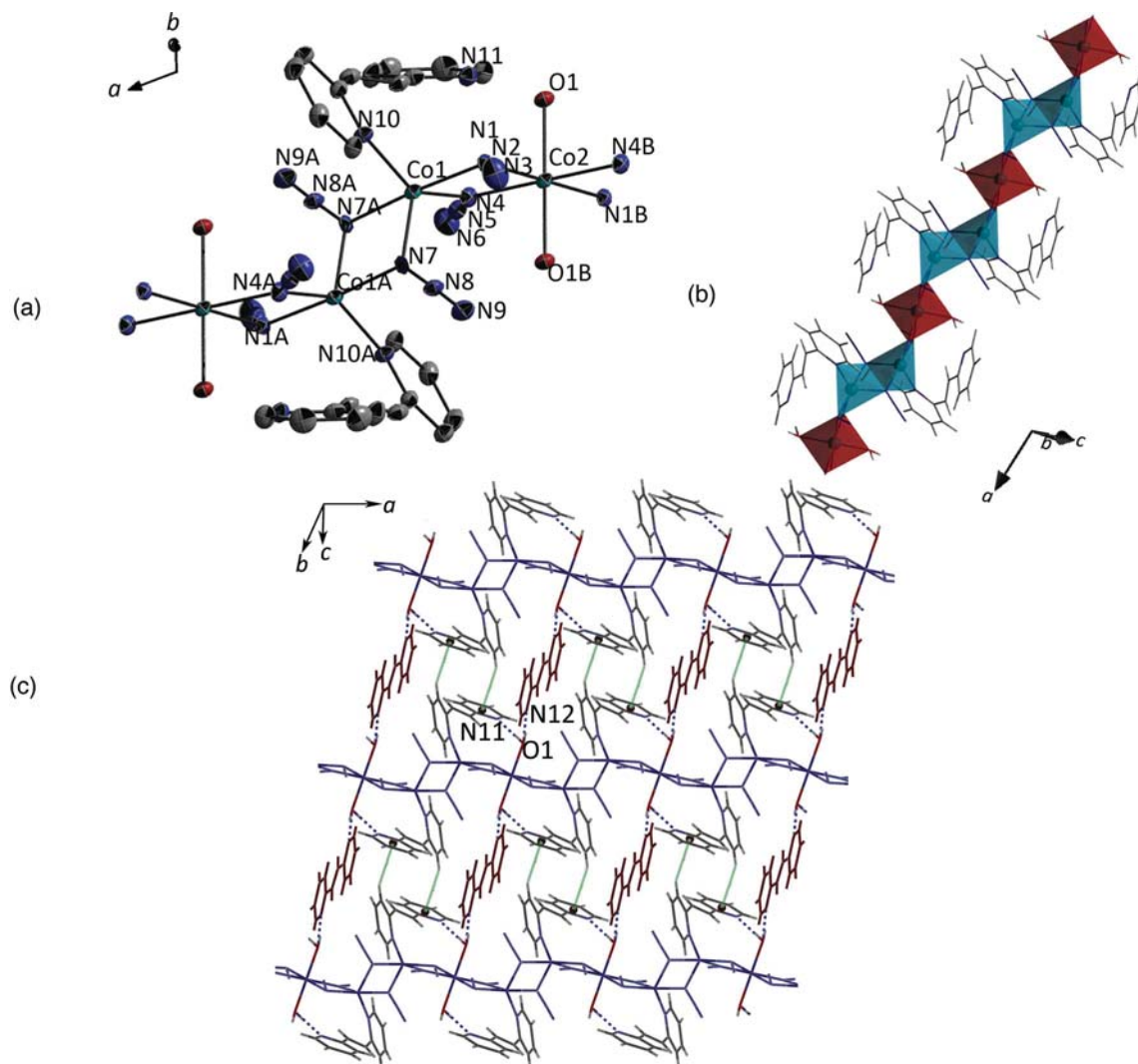


Fig. 1 (a) The crystal structure and atom labelling scheme of **1**. The ellipsoids are shown at 50% probability level. Atoms labelled with the notation “A” and “B” are symmetry-generated equivalents, (A) $1-x, -y, 1-z$; (B) $-x, -y, 1-z$. (b) The 1D chain of **1** is running along the a axis with octahedra and hexahedra of Co^{II} ions. The free 2,2'-bpe and H atoms are omitted for clarity. (c) The formation of the 2D sheet of **1** in the ab plane, formed by $\text{C-H}\cdots\pi$ interactions and hydrogen bonds between the neighbouring chains. The dotted lines represent the intramolecular $\text{O1-H}\cdots\text{N11}$ hydrogen bond and the intermolecular $\text{O1-H}\cdots\text{N12}$ hydrogen bond and $\text{C-H}\cdots\pi$ interaction.

azido bridges are $3.174(1)$ Å for $\text{Co1}\cdots\text{Co1}^i$ ($i = 1-x, -y, 1-z$), and $3.207(1)$ Å for $\text{Co1}\cdots\text{Co2}$, as usually observed for this kind of bridging in cobalt(II) azido compounds.⁸ The coordinated 2,2'-bpe acts as a terminal co-ligand because the intrachain hydrogen bonding between the N atom on the terminal pyridine of the coordinated 2,2'-bpe and the H atom of the coordinated water [$\text{O1H}\cdots\text{N11} = 1.89$ Å (172°), $\text{O1}\cdots\text{N11} = 2.811(4)$ Å] causes the arrangement of the 2,2'-bpe in *cis* position, with a dihedral angle between the two pyridine rings of $55.65(1)^\circ$. In addition, the chains are assembled *via* $\text{C-H}\cdots\pi$ interactions and the intermolecular hydrogen bonds between uncoordinated 2,2'-bpe and the coordinated water along the b axis [$\text{O1H}\cdots\text{N12} = 1.80$ Å (172°), $\text{O1}\cdots\text{N12} = 2.750(4)$ Å], yielding a 2D structure of **1**, as shown in Fig. 1(c). The interchain $\text{C-H}\cdots\pi$ interactions involve C4-H interacting with the centroid of the terminal pyridine ring of an adjacent coordinated 2,2'-bpe, with the distance of $2.876(4)$ Å and a $\text{C4-H}\cdots\pi$ angle of 133° .

[Co(N₃)₂(2,2'-bpe)₂]_n (2). The crystal structure of **2** is depicted in Fig. 2. Compound **2** has a 2D wavy layer structure, which consists of an azido- Co^{II} neutral chain with alternating double EE and double EO azido bridges along the a axis and ditopic 2,2'-bpe bridging the Co^{II} ions along the b axis. There is only one crystallographically independent Co^{II} ion, which has an elongated octahedral geometry, comprised of two N atoms from bridging 2,2'-bpe in the axial sites and four N atoms from two EE and two EO azide ions located in the equatorial positions. The crystallographic data is shown in Table 1 and selected bond lengths and bond angles are given in Table 3. The adjacent Co^{II} ions in a chain are related by inversion centres and are linked alternately by double-EE and double-EO azido bridges, with $\text{Co}\cdots\text{Co}$ distances of $5.052(2)$ Å and $3.314(1)$ Å, respectively. These bridging modes of the azide are widely found in the polymeric chain complexes containing additional chelating ligands.^{16,23–29} In the double EO bridged $\text{Co}(\text{N}_3)_2\text{Co}$ moiety, the Co1-N3-Co1A-N3A ring is

Table 1 Crystallographic data for compounds **1** and **2**

Compound	1	2
Formula	Co ₃ C ₃₆ H ₃₄ N ₂₄ O ₂	CoC ₁₂ H ₁₀ N ₈
Molecular weight	1011.66	325.21
<i>T</i> /K	123(2)	273(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	8.8038(18)	8.2902(17)
<i>b</i> /Å	11.541(2)	8.3224(17)
<i>c</i> /Å	12.422(3)	10.284(2)
α /°	117.61(3)	87.99(3)
β /°	100.91(3)	67.88(3)
γ /°	96.17(3)	79.07(3)
<i>V</i> /Å ³	1070.2(4)	644.9(2)
<i>Z</i>	1	2
ρ_c /g cm ⁻³	1.570	1.675
μ (Mo-K α)/mm ⁻¹	1.215	1.337
Data collected	10327	6371
Unique data	3817	2188
$R_i^a/wR_2^b[I > 2\sigma(I)]$	0.0479/0.1153	0.0393/0.0771
R_i^a/wR_2^b [all data]	0.0651/0.1560	0.0723/0.1317
GOF	1.184	1.263
Max/min electron density/e Å ⁻³	0.920/−1.743	1.164/−1.334

^a $R = \sum \|F_o| - |F_c|\| / \sum |F_o|$; ^b $R_w = \{ \sum [w(|F_o| - |F_c|)]^2 / \sum [w|F_o|^2] \}^{1/2}$

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Compound 1 ^a			
Co1–N4	2.025(3)	Co2–O1 ⁱⁱ	2.068(3)
Co1–N7	2.034(3)	Co2–O1	2.068(3)
Co1–N10	2.098(3)	Co2–N1 ⁱⁱ	2.133(3)
Co1–N7 ⁱ	2.138(3)	Co2–N1	2.133(3)
Co1–N1	2.146(3)	Co2–N4	2.149(3)
N4–Co1–N7	112.86(13)	Co2–N4 ⁱⁱ	2.149(3)
N4–Co1–N10	142.28(12)	O1 ⁱⁱ –Co2–N1	87.50(11)
N7–Co1–N10	104.78(12)	O1–Co2–N1	92.50(11)
N4–Co1–N7 ⁱ	93.85(12)	N1 ⁱⁱ –Co2–N1	180
N7–Co1–N7 ⁱ	80.94(13)	O1 ⁱⁱ –Co2–N4	89.10(12)
N10–Co1–N7 ⁱ	94.38(12)	O1–Co2–N4	90.90(12)
N4–Co1–N1	82.00(12)	N1 ⁱⁱ –Co2–N4	100.50(11)
N7–Co1–N1	98.66(12)	N1–Co2–N4	79.50(11)
N10–Co1–N1	90.22(12)	O1 ⁱⁱ –Co2–N4 ⁱⁱ	90.90(12)
N7–Co1–N1	175.34(11)	O1–Co2–N4 ⁱⁱ	89.10(12)
O1 ⁱⁱ –Co2–O1	180	N1 ⁱⁱ –Co2–N4 ⁱⁱ	79.50(11)
O1 ⁱⁱ –Co2–N1 ⁱⁱ	92.50(11)	N1–Co2–N4 ⁱⁱ	100.50(11)
O1–Co2–N1 ⁱⁱ	87.50(11)	N4–Co2–N4 ⁱⁱ	180
Co2–N1–Co1	97.09(12)	Co1–N7–Co1 ⁱ	99.06(13)
Co1–N4–Co2	100.37(12)		

^a Symmetry codes: (i) 1 – *x*, –*y*, 1 – *z*; (ii) –*x*, –*y*, 1 – *z*.

strictly planar due to the existence of the inversion centre with a Co1–N3–Co1A angle of 102.25(14)°. For the double-EE mode, the EE bridges adopt a chair conformation for the Co–(N₃)₂–Co unit with a dihedral angle between the N7N6N8BN8N6BN7B plane and the CoN8N7 plane of 33.8(1)°. The 2,2′-bpe acts as a ditopic connector in the *trans* position, bridging the cobalt(II) azido neutral chains along the *b* axis and building the 2D wavy sheet of **2** (Fig. 2(b)). The Co···Co separation *via* the 2,2′-bpe spacer is 8.322(2) Å.

Magnetic measurements

The magnetic susceptibility of a polycrystalline sample of **1** at 2–310 K is shown in Fig. 3. At 310 K, the $\chi_m T$ value is 11.16

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Compound 2 ^a			
Co1–N7	2.122(3)	Co1–N8	2.138(4)
Co1–N3 ⁱ	2.122(3)	Co1–N2 ⁱⁱ	2.236(3)
Co1–N3	2.135(3)	Co1–N1	2.296(4)
N7–Co1–N3 ⁱ	173.83(14)	N7–Co1–N1	87.64(13)
N7–Co1–N3	96.15(14)	N3 ⁱ –Co1–N1	93.68(13)
N3 ⁱ –Co1–N3	77.75(14)	N3–Co1–N1	94.16(13)
N7–Co1–N8	93.39(14)	N8–Co1–N1	85.28(14)
N3 ⁱ –Co1–N8	92.72(14)	N2 ⁱⁱ –Co1–N1	173.62(12)
N3–Co1–N8	170.41(13)	N3–Co1–N2 ⁱⁱ	88.51(13)
N7–Co1–N2 ⁱⁱ	86.32(13)	N8–Co1–N2 ⁱⁱ	93.05(14)
N3 ⁱ –Co1–N2 ⁱⁱ	92.55(12)	Co1 ⁱ –N3–Co1	102.25(14)

^a Symmetry codes: (i) 1 – *x*, 1 – *y*, 1 – *z*; (ii) *x*, 1 + *y*, *z*.

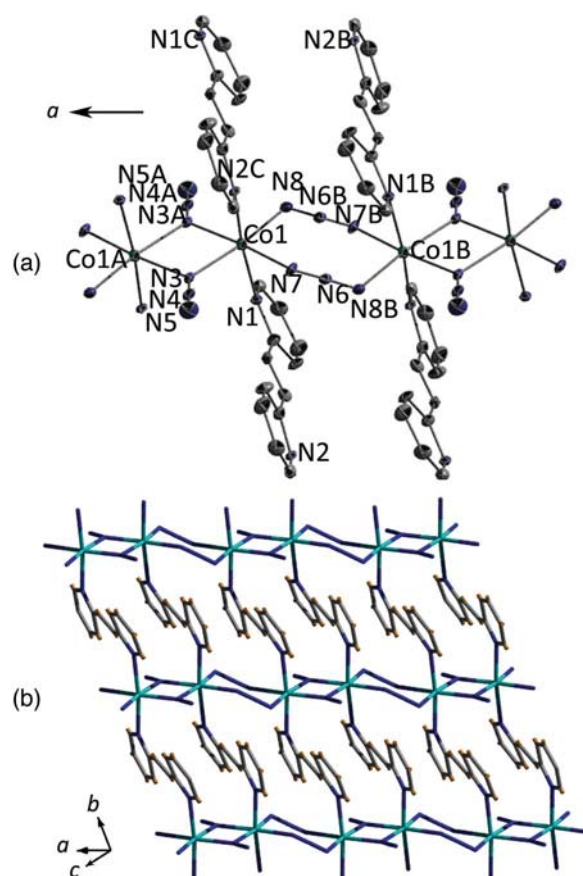


Fig. 2 (a) The expanded asymmetric unit and atom labelling scheme of **2**. The ellipsoids are shown at 50% probability level. Atoms labelled with the notation “A”, “B” and “C” are symmetry-generated equivalents, (A) 1 – *x*, 1 – *y*, 1 – *z*; (B) –*x*, 1 – *y*, 1 – *z*; (C) *x*, 1 + *y*, *z*. All H atoms are omitted for clarity. (b) The 2D wavy coordination network of **2**.

cm³ K mol⁻¹ per Co₃ unit, which is significantly higher than the spin-only value of 5.62 cm³ K mol⁻¹ expected for three uncoupled *S* = 3/2 ions, this is owing to ferromagnetic interactions and the significant orbital contribution of high-spin Co^{II} in an octahedral surrounding. The $\chi_m T$ value increases gradually upon cooling to *ca.* 50 K. Below this temperature, $\chi_m T$ increases abruptly to a maximum value of 48.75 cm³ K mol⁻¹ at 15 K because of rapidly increasing ferromagnetic coupling between adjacent spin carriers. Upon cooling to 2 K, $\chi_m T$ decreases quickly to 8.32 cm³ K mol⁻¹

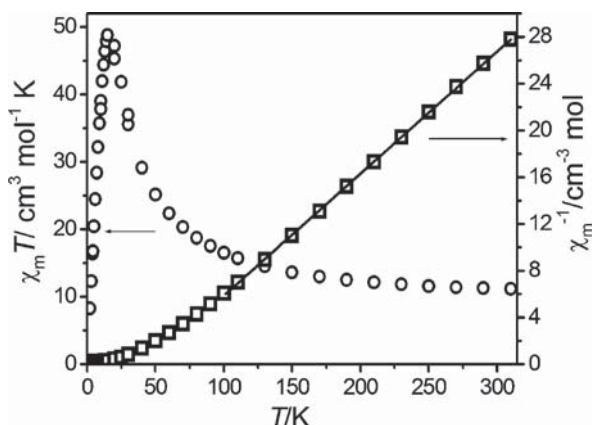


Fig. 3 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **1** at $H = 10$ kOe from 2 to 310 K. The solid line represents the best fit to the Curie–Weiss law.

because of magnetization saturation and possible interchain antiferromagnetic interactions. Similar behaviour has been observed in other related complexes containing a 1D double EO azido bridge, such as $[\text{Co}(2,2'\text{-bithiazoline})(\text{N}_3)_2]_n$,⁸ $[\text{Mn}(\text{N}_3)_2(\text{pyz})]_n$ ³⁰ (pyz = pyrazine) and $[\text{Ni}(\text{en})(\text{N}_3)_2]_n$ ³¹ (en = ethylenediamine). The χ_m^{-1} values above 100 K were fitted with the Curie–Weiss law $\chi = C/(T - \theta)$ with a Curie constant $C = 9.59(3) \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = +43.7(5) \text{ K}$, indicating dominant ferromagnetic coupling between the Co^{II} ions *via* double EO azido bridges. Owing to the lack of a theoretical model for the complicated chain composed by octahedral Co^{II} and non-octahedral Co^{II} ions, the exchange parameters could not be estimated.

In addition, the dominant ferromagnetic coupling was confirmed by magnetization measurements performed at 1.8 K in an external field of 0–5 T, as shown in Fig. 4. The molar magnetization curve exhibits a rapid increase, reaching about 80% of M_s at 1 kOe, which appears to show a soft ferromagnet because coercivity was not observed. At higher field, the saturation magnetization, $M_s = 8.81 \text{ N}\beta$, agrees with there being three ferromagnetically coupled Co^{II} ions with an expectation value of $M_s = 6\text{--}9 \text{ N}\beta$.^{32,33} A comparison with the Brillouin function for three isolated $S = 3/2$ spins stresses the remarkable cooperativity in this system, consistent with the ferromagnetic interaction.

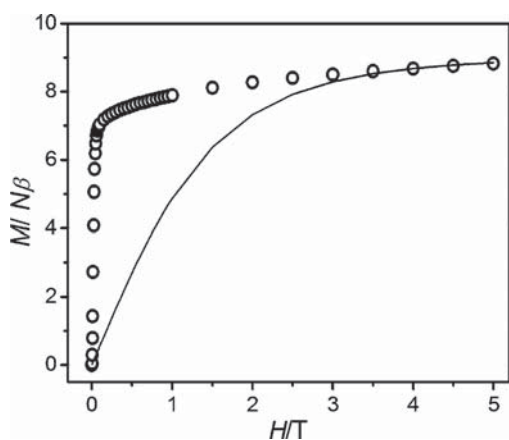


Fig. 4 Field dependence of magnetization of **1** at 1.8 K. The continuous line corresponds to the Brillouin function for three Co^{II} ions, $S = 3/2$ with $g = 2.0$.

All evidence points to the long-range magnetic ordering, which is likely to be due to interchain coupling through the extensive hydrogen bonds and $\text{C-H}\cdots\pi$ contacts. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization plot under a field of 50 Oe (Fig. 5, inset) showed a disagreement below 6 K and presented a swell at around 6 K, suggesting the onset of long-range antiferromagnetic ordering among the ferromagnetic chains. However, the ZFC–FC plot under a field of 1000 Oe shows no maximum, tends to saturate at lower temperature and did not show the irreversibility, thus indicating that the weak interchain antiferromagnetic interaction is overcome by the external field. These features are indicative of a metamagnet built of ferromagnetic chains. The temperature dependence of *ac* susceptibility was also measured at zero *dc* field (Fig. S4, ESI†). The χ' signal shows a peak at 6 K confirming the occurrence of phase transition and the nonzero χ'' signal below 6 K is consistent with the ferromagnetic order. No frequency dependence of the *ac* signals was observed among 25–997 Hz. The metamagnetic behaviour was further confirmed by the hysteresis loop measurements, as given in Fig. 5, which revealed that **1** is a metamagnet with a typical crossover magnetic hysteresis in the slightly sigmoid shape of the $M(H)$ curve.^{34–36} The critical field H_c is ≈ 70 Oe, estimated as the field at which a maximum $\delta M/\delta H$ value is reached. This metamagnetic-like transition results from the presence of weak interchain antiferromagnetic interactions among the strongly ferromagnetic chains. At low temperature, the antiferromagnetic coupling of the ferromagnetic chains leads to an antiferromagnetic ground state. With an increase in the external magnetic field ($H_c > 70$ Oe), the ferromagnetic chains tend to align parallel, resulting in ferromagnetic ordering. This behaviour is characteristic of a metamagnet built of ferromagnetic chains.^{31,34–42} However, because of the strong spin–orbit coupling of Co^{II} ions, the magnetic interaction might be more complicated.^{1,35} This similar metamagnetic-like transition was also observed in other polymeric chain systems containing ferromagnetic 1D double EO azido bridges with weak interchain antiferromagnetic interactions.^{31,34,36,41} For instance, the previous related compound $[\text{Mn}(\text{tptz})(\text{N}_3)_2]_n$ ³⁶ (tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine), which contains similar double EO azide-bridged 1D chains that are assembled by face-to-face π – π and $\text{C-H}\cdots\pi$ interactions, revealed overall metamagnetic behaviour

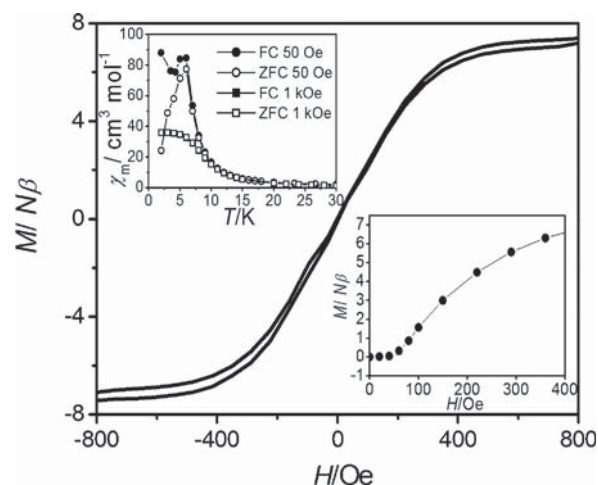


Fig. 5 Hysteresis curve for **1** at 1.8 K. The insets show the initial plot in a low field (right) and the ZFC–FC plots of **1** at 50 Oe and 1 kOe (left).

below 2.7 K with a very small H_c of approximately 80 Oe. This reported value of H_c is very close to that of this work.

The magnetic susceptibility of **2** is depicted in Fig. 6. The $\chi_m T$ value of *ca.* 3.01 cm³ K mol⁻¹ at 310 K is much higher than the spin-only value of a high-spin d⁷ ion (1.87 cm³ K mol⁻¹), owing to ferromagnetic interactions *via* μ_2 -1,1 N₃⁻ bridges and the significant orbital contributions of the octahedral Co^{II} ions. Upon cooling, the $\chi_m T$ decreases gradually down to 0.04 cm³ K mol⁻¹ at 2 K, indicating the dominant antiferromagnetic coupling *via* μ_2 -1,3 N₃⁻ bridges. The plot of χ_m vs. T (Fig. 6, inset) exhibits an abrupt increase below about 17 K to a maximum value of 0.02 cm³ mol⁻¹ at 2 K, which can probably be attributed to paramagnetic impurity or possible spin canting. The data above 150 K obey the Curie–Weiss law, with a Curie constant $C = 3.58(3)$ cm³ K mol⁻¹ and a Weiss constant $\theta = -58(2)$ K. The negative θ suggests antiferromagnetic coupling between the Co^{II} ions.

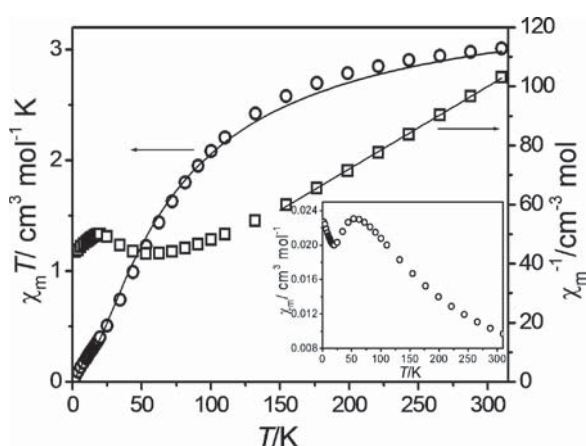


Fig. 6 Temperature dependence of $\chi_m T$ and χ_m^{-1} of **2** from 2 to 310 K. The solid lines correspond to the best fit (see the text). Inset: plot of χ_m vs. T for **2**.

To estimate both magnetic exchange interactions and the spin–orbit coupling effect in the temperature range of 2–310 K for low-dimensional Co^{II} systems, we used the simple phenomenological equation given by Rueff *et al.*^{43,44}

$$\chi_m T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$$

$A + B$ equals the Curie constant (≈ 2.8 – 3.4 cm³ K mol⁻¹ for octahedral Co^{II}) and E_1 and E_2 represent the activation energies corresponding to the spin–orbit coupling and the antiferromagnetic exchange interaction, respectively. The fitted parameters are $A + B = 3.58$ cm³ K mol⁻¹, equivalent to the Curie constant obtained from the Curie–Weiss law in the high temperature range; $E_1/k = +61(2)$ K, which is consistent with those reported for 1D and 2D cobalt(II) systems.^{32,43–45} For the value found for the antiferromagnetic exchange interaction, E_2/k equals to $+4.1(2)$ K, corresponding to $J = -8.2$ K, according to the Ising chain approximation, $\chi_m T \propto \exp(+J/2kT)$.

It can be seen from the abrupt increase of the plot of χ_m vs. T below about 17 K and from the other reported complexes containing chains of alternating double EO and double EE bridging modes of azides that these complexes frequently exhibit weak ferromagnetism due to spin canting,^{23,25–28} thus the magnetic behaviour of **2** was further clarified. The temperature dependencies

of the ZFC and the FC magnetization were measured at a low field of 20 Oe, as shown in Fig. 7(inset). The obvious divergence of the ZFC and FC plots below 12 K indicates hysteretic long-range magnetic order, which is compatible with the maxima in χ' and the nonzero χ'' signal around 12 K in the *ac* susceptibility at 997 Hz (Fig. S5, ESI†). The isothermal magnetization with the field up to 5 T at 1.8 K is depicted in Fig. 7. The initial increase of magnetization shows a slight positive curvature and is not linear with the field up to 7 kOe, and then it becomes almost linear up to 0.146 N β at 5 T, far from the theoretical saturation magnetization of the Co^{II} ion, suggesting that overall there is antiferromagnetic coupling between Co^{II} ions. A hysteresis loop of **2** is clearly observed when the field is less than 10 kOe, giving a coercive field of ≈ 300 Oe and remanent magnetization of ≈ 0.002 N β . These results indicate that the spin-canting effect between overall antiferromagnetically coupled Co^{II} ions leads to residual spins. The extrapolation of the high field linear part of magnetization to zero field (M_w) gives a value of 0.013 N β , and the canting angle (α)^{6,9,13,46,47} is estimated to be about 0.3° ($\alpha = \sin^{-1} M_w/M_s$, theoretical saturation magnetization (M_s) = $g'SN\beta = 2.16$ N β , $S' = 1/2$, $g' = 4.33$ for octahedral Co^{II} at 1.8 K).^{6,7} Complex **2** exhibits hard ferromagnetism whereas **1** shows soft ferromagnetism, which may be attributed to the difference between the parallel anisotropy axes in **2** and the almost orthogonal trigonal bipyramidal and octahedral axes in **1**. It is well known that two mechanisms lead to spin canting: (i) magnetic anisotropy and (ii) antisymmetric exchange.^{6,7} However, the spin canted structure is not compatible with the crystal structure of **2** because of the presence of an inversion centre between the bridged Co^{II} sites, which forbids the occurrence of antisymmetric interactions. The observation of the spin canting in **2** should be attributed to the great single-ion anisotropy of the octahedral cobalt(II) ions or a possible structure phase transition at low temperature,^{23,25–28} which will provide merit for future investigations. The weak ferromagnetism due to spin canting in the presence of an inversion centre between metal sites has also been observed in other complexes containing the same bridging mode of azide, such as [Co(dpa)(N₃)₂]_n (dpa = 2,2'-dipyridylamine),²⁷ [Mn(dpq)(N₃)₂]_n (dpq = dipyrdo-(3,2-*d'*:2',3'-*f*)quinoxaline)²⁶ and [Mn(TaiEt)(N₃)₂]_n (TaiEt = 1-ethy-2-(*p*-tolylazo) imidazole).²³

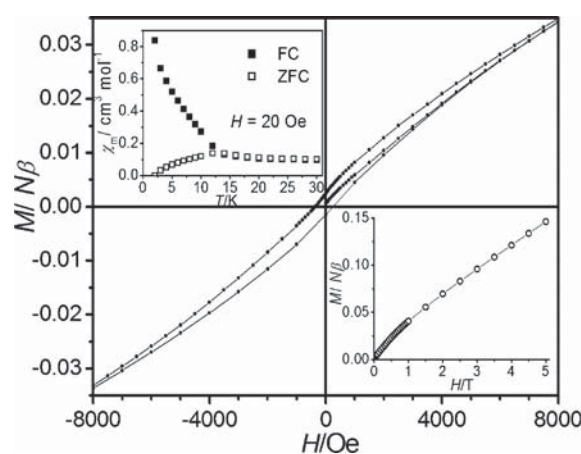


Fig. 7 The hysteresis loop of **2** at 1.8 K. The insets show the ZFC and FC magnetization at $H = 20$ Oe from 2 to 30 K. (left) and the field dependence of magnetization at 1.8 K (right).

Conclusions

Two novel cobalt(II) azido inorganic–organic hybrid materials containing 2,2′-bpe have been obtained. The 2,2′-bpe can serve as either a terminal co-ligand in monodentate coordination, as in **1**, or as a ditopic bridging spacer in the *trans* position as in **2**, with which molecular magnets of different lattice dimensionalities were developed. The 1D chain of **1** contains the rare mixed geometries of the Co^{II} ions, in a unique [–5–5–6]_n sequence of coordination number, bridged by the double EO mode of azide. The adjacent chains are assembled by C–H⋯ π interactions and intermolecular hydrogen bonds, stabilizing the 2D sheet of **1**. The magnetic behaviour of **1** reveals a metamagnetic transition, which may be due to the presence of weak interchain antiferromagnetic interactions among the strong ferromagnetism of the double EO Co^{II}–azido chains. In contrast, compound **2** is a 2D wavy coordination polymer, containing the alternating double EO and double EE bridging modes of azide and exhibits a weak ferromagnetism due to spin canting.

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Spin Canting and Metamagnetism in 2D and 3D Cobalt(II) Coordination Networks with Alternating Double End-On and Double End-to-End Azido Bridges

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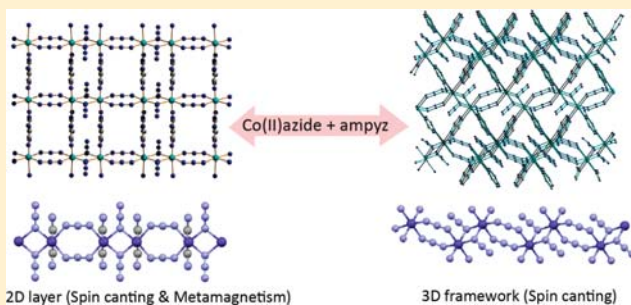
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S Supporting Information

ABSTRACT: By employing an *N,N'*-ditopic spacer 2-aminopyrazine (ampyz), two-dimensional (2D) (**1**) and three-dimensional (3D) (**2**) azido-bridged cobalt(II) coordination networks with the identical formula $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ have been synthesized and characterized structurally and magnetically. Compound **1** was prepared by the layer diffusion method in ambient temperature and crystallized in the high symmetric space group *Immm*. The 2D square-grid structure of **1** contains the perfect symmetric linear of alternating double end-on (EO) and double end-to-end (EE) azido-bridged Co^{II} chains which are linked together by an ampyz spacer in *trans*-arrangement. The intra-layer π – π stacking interactions among ampyz spacers additionally stabilize this layer. The adjacent 2D layers are assembled by the intermolecular hydrogen bonding between the NH_2 of the ampyz and the EE azido ligands building a 3D structure. Compound **2** was prepared by a hydrothermal technique and shows a 3D framework containing a zigzag chain of similarly alternating double EO and double EE azido-bridged Co^{II} center. In contrast, this chain is linked by two ampyz spacers in *cis*-fashion giving rise to a 3D structure. The magnetic investigation of **1** shows the coexistence of a big spin canting angle and metamagnetism having magnetic ordering at 10 K, whereas the magnetic behavior of **2** simply exhibits spin-canted antiferromagnetism below T_N of 16 K.



INTRODUCTION

The crystal engineering and magnetism of molecule-based coordination frameworks with low- or high dimensional structures have been of great interest in recent years with the intention of understanding the fundamental magneto-structural correlations within the structure and controlling the spins in molecules and molecular assemblies for conceiving practical functional molecule-based materials.^{1–5} To rationally design magnetic molecular assemblies, it is important to select the appropriate bridging ligands that effectively transmit the exchange interactions between the spin carriers together with the aspects of diverse topologies. An excellent azido ligand is the one of the extensively used bridging ligands in the construction of magnetic molecular materials because it can provide a short bridge with the extremely versatile coordination modes and effectively mediates either ferromagnetic or antiferromagnetic coupling generally through μ_2 -1,1 (end-on, EO) and μ_2 -1,3 (end-to-end, EE) modes, respectively. In addition the different combinations of EO and EE azido bridging modes may exist in the same structure, leading to several

topologies as well as competing magnetic interactions in sign according to a certain EO and EE azido bridging sequence.^{6–12} Consequently, the fascinating magnetic phenomena have been recognized in many azido-bridged coordination polymers which have been an active research area so far.^{6,13–15} Likewise, the organic coligands are very significant to the formation of some particular architectures and to their structural modification. It is well-known that the *N,N'*-ditopic diimine spacer pyrazine (pyz) is a long bridge for magnetic systems and effectively transfers electrons in the antiferromagnetic superexchange pathways between metal centers. With pyz and derivatives of pyz ligands, the azido complexes usually exhibit various structural topologies together with interesting magnetic properties.^{16–20} For instance, the 2D layer of $[\text{Fe}(\text{N}_3)_2(\text{pyz})]_n$ showed metamagnetism arising from the competition of ferromagnetically coupled EO azido chains and 2D antiferromagnetically coupling via pyz.¹⁸ In

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contrast with the lack of local anisotropic ions, this metamagnetic feature for the Mn^{II} and Cu^{II} analogues was not observed.^{19,20}

In this report, we are interested in the versatile 2-aminopyrazine (ampyz) spacer as organic coligand in a magnetic azido complex system. The ampyz spacer contains many interaction sites; coordination sites at the N atoms on the pyrazine ring, hydrogen donor sites at the amino group, and the intermolecular π – π stacking site through aromatic moieties, which has been used for constructing many coordination polymers.^{21–25} Without the spin carriers, the structural diversity of zinc(II) azido complexes with ampyz has been recently obtained depending on the molar ratio of the starting components.²⁴ With this in mind, herein we show that the ampyz spacer accommodates well in the magnetic anisotropic Co^{II} azido system. Remarkably, new 2D layer (**1**) and 3D framework (**2**) of azido-bridged Co^{II} coordination networks with the identical molar ratio $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ were well prepared in different preparative techniques and characterized structurally and magnetically. In addition both complexes similarly contain the 1D chain of alternately double EO and double EE azido-bridged Co^{II} ions, whereas the ampyz spacers in **1** and **2** are in dissimilar arrangements, *trans*- and *cis*-positions in octahedral Co^{II} ions for **1** and **2**, respectively. To our knowledge, only two azido Co^{II} chains with alternating double EE and double EO bridges have been reported in the literature.^{26,27} Although **1** and **2** are similar in local coordination environments, they are somewhat different in structural symmetries, dimensionalities, and bridging parameters; consequently, their magnetic behaviors at low temperature reveal the significant disparities. Complex **1** exhibits complex magnetic behaviors combining a big spin canting angle and metamagnetism while **2** simply displays the canted antiferromagnetism with a smaller canting angle. These behaviors allow us to perform the magnetic investigation and discussion.

■ EXPERIMENTAL SECTION

Materials and Physical Measurements. All chemicals were obtained from commercial sources, and they were used without further purification. IR spectra (4000 – 450 cm^{-1}) were obtained in KBr disks on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer, within the range of 450 – 1100 nm . Elemental analyses were carried out at the Laboratory for Instrumental Analysis, Graduate School of Engineering, Osaka University. The X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT Inplane/ultrax18SAXS-IP diffractometer using monochromatic $\text{CuK}\alpha$ radiation generated at 40 kV , 200 mA , and the recording speed was $1^\circ/\text{min}$ over the 2θ range of 5 – 40° at room temperature. All magnetic measurements were performed on polycrystalline samples which were mounted in calibrated gelatin capsules held at the center of a polypropylene straw fixed to the end of the sample rod. The direct current (dc) magnetic measurements were carried out on a Quantum Design MPMS-XLS SQUID magnetometer equipped with reciprocating sample option (RSO). The alternating current (ac) magnetic measurements were carried out on a Quantum Design MPMS-2 SQUID magnetometer. Magnetic data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.²⁸

Caution! Although not encountered in our experiments, azido compounds are potentially explosive and should be manipulated with special care and used only in small quantities. If possible the hydrothermal method for azido complexes with organic ligands should be avoided.

Synthesis of 2D Layer of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (1**).** A mixture solution of water (1 mL) and ethanol (2 mL) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

(0.5 mmol, 145 mg) was carefully layered on an aqueous solution (3 mL) of NaN_3 (1 mmol, 65 mg) in a glass vial (20 mL). Then an ethanolic solution (3 mL) of ampyz (1 mmol, 95 mg) was layered on this mixture. The vial was sealed and allowed to stand undisturbed at room temperature. After one week, orange rectangular crystals of **1** were obtained and then washed with water and filtered. It should be mentioned that **1** was obtained in low yield because many small crystals of **1** were eluted with an unidentified pink powder during washing process. Yield 36 mg (30%) based on metal salt. Anal. Calcd for $\text{CoC}_4\text{H}_5\text{N}_9$: C, 20.18; H, 2.12; N, 52.95%. Found: C, 20.62; H, 2.05; N, 53.27%. IR (KBr, cm^{-1}): 3407 m, 3326 m, 2100vs, 2080vs, 1629 m, 1541 m, 1443 m, 1354w, 1298w, 1220 m, 1079w, 1025 m, 804 m. UV–vis (diffuse reflectance, cm^{-1}): 18400, less than 9000. The single-crystals of **1** were prepared in a U-shaped tube. An ethanolic solution (1 mL) of ampyz (1 mmol) was filled into the one branch of the U-tube that contains distilled water (1 mL). Another branch was filled with an aqueous solution (1 mL) containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and NaN_3 (1 mmol). After one week, the suitable single-crystals of **1** for X-ray diffraction study were obtained.

Synthesis of 3D Framework of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (2**).** A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 145 mg), NaN_3 (1 mmol, 65 mg), and ampyz (1 mmol, 95 mg) in water (2 mL) and ethanol (2 mL) was sealed in a Pyrex tube (7 mL), then heated to 90°C (temperature increase rate of $18^\circ\text{C}/\text{min}$), allowed to stay for 24 h, and cooled to 30°C (temperature decrease rate of $0.04^\circ\text{C}/\text{min}$). The red-orange polygonal crystals of **2** were obtained in a major phase together with unidentified purple powder phase. The crystals were washed with water and filtered to give pure crystals of **2**. Yield 53 mg (45%) based on metal salt. Anal. Calcd for $\text{CoC}_4\text{H}_5\text{N}_9$: C, 20.18; H, 2.12; N, 52.95%. Found: C, 19.80; H, 2.15; N, 52.00%. IR (KBr, cm^{-1}): 3415 m, 3307 m, 2105vs, 2068vs, 1624 m, 1540 m, 1438 m, 1322w, 1298w, 1218 m, 1026w, 821w. UV–vis (diffuse reflectance, cm^{-1}): 18400, 9300.

X-ray Crystallography and Refinement Details. All Reflection data were collected on a 1 K Bruker SMART CCD area-detector diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) using the SMART program.²⁹ Raw data frame integration was performed with SAINT,³⁰ which also applied correction for Lorentz and polarization effects. An empirical absorption correction by using the SADABS program³¹ was applied. The structure was solved by direct methods and refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.1 software package.³² Hydrogen atoms bound to carbon and nitrogen atoms were placed in calculated positions and refined isotropically with a riding model. Ampyz ligand in **1** lies across two mirror planes so the disordered amino group (N2) was refined with quarter occupancy. The disorder of ampyz is found to be similar to that known for aminopyrazine complexes.^{21,22} Therefore, there are many distinct hydrogen bonding networks present via the disordered amino group, and all are symmetry related in which changing one interaction has a knock-on effect. In **1**, the terminal N atoms of EO azido-bridge (N4 and N5) which lie above a mirror plane are disordered, so those atoms were refined with half occupancies. The details of crystal data, selected bond lengths and angles for compounds **1** and **2** are listed in Table 1–3.

■ RESULTS AND DISCUSSION

Syntheses and Characterizations. The different preparative methods of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, azide anion and ampyz in a 1:2:2 molar ratio in a mixture of ethanol and aqueous media yielded two cobalt(II) coordination polymers containing the ampyz spacer together with the alternating double EO and double EE azido bridging mode which show the different dimensionalities. The layered diffusion reaction in ambient temperature gave the orange rectangular crystals of **1** showing the high symmetric 2D square-grid structure of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ whereas the hydrothermal

Table 1. Crystallographic Data for Compounds 1 and 2

	1	2
formula	CoC ₄ H ₅ N ₉	CoC ₄ H ₅ N ₉
molecular weight	238.10	238.10
T (K)	293(2)	293(2)
crystal system	orthorhombic	monoclinic
space group	<i>Immm</i>	<i>P2₁/n</i>
a (Å)	8.440(2)	7.3754(15)
b (Å)	7.1808(12)	14.095(3)
c (Å)	13.845(2)	7.9773(16)
α (deg)	90.00	90.00
β (deg)	90.00	97.03(3)
γ (deg)	90.00	90.00
V (Å ³)	839.1(3)	823.1(3)
Z	4	4
ρ _{calcd} (g cm ⁻³)	1.885	1.921
μ (Mo Kα) (mm ⁻¹)	2.019	2.058
data collected	2202	9368
unique data	565	1901
R ₁ ^a /wR ₂ ^b [I > 2σ(I)]	0.0397/0.1291	0.0285/0.0815
R ₁ ^a /wR ₂ ^b [all data]	0.0493/0.1314	0.0296/0.0822
GOF	1.285	1.118
max/min electron density (e Å ⁻³)	0.527/−0.758	1.053/−0.330

^a R = Σ||F_o| − |F_c||/Σ|F_o|. ^b R_w = {Σ[w(|F_o| − |F_c||)²]/Σ[w|F_o|²]}^{1/2}.

reaction at 90 °C for 1 day yielded the red-orange polygonal crystals of **2** showing 3D framework of [Co(N₃)₂(ampyz)]_n. These experiments do not only demonstrate the significant role of the primary units, the excellent azido bridges, and versatile ampyz spacer for building both structures but also demonstrate the important influence of the reaction's conditions on the structural topologies and dimensionalities. The physical purities of crystalline phase of bulk products were confirmed by XRPD technique comparing with their simulated XRD patterns from the single-crystal data (see Supporting Information, Figures S1). The IR spectra of both complexes are quite similar. Complexes **1** and **2** containing both μ₂-1,1 and μ₂-1,3 bridging azides, show two very strong bands due to ν_{as}(N₃[−]) modes at 2100 and 2080 cm^{−1} for **1** and 2105 and 2068 cm^{−1} for **2** indicating the presence of two different azido groups. The weak band at 1322 cm^{−1} is ν_s(N₃[−]) for the EO bridge. This band is not active for the symmetrical EE bridge.⁸ Two narrow weak bands in the regions 3400–3300 cm^{−1} can be assigned to ν(N–H) of the primary amine in the ampyz ligand. The solid-state UV–vis diffuse reflectance spectra of both complexes agree with the typical d-d transition of high-spin Co^{II} in octahedral geometry with two observed bands at 20000–18000 and less than 9500 cm^{−1}, which are assigned to the ⁴T_{1g} → ⁴T_{1g}(P) and ⁴T_{1g} → ⁴T_{2g} transitions, respectively. The weak band at about 15000 cm^{−1} which is assigned to the ⁴T_{1g} → ⁴A_{2g} transition is not well resolved. The growing bands which appear higher than 22000 cm^{−1} are due to charge transfer transition and internal transition within ampyz³³ (see Supporting Information, Figures S2 and S3).

Description of the Structures. *2D Layer of [Co(N₃)₂(ampyz)]_n (1).* Compound **1** was crystallized in the orthorhombic crystal system with high centrosymmetric space group, *Immm*. The crystallographic data is shown in Table 1. The coordination environment of the Co^{II} center is shown in Figure 1a. The Co1 atom, EE azido

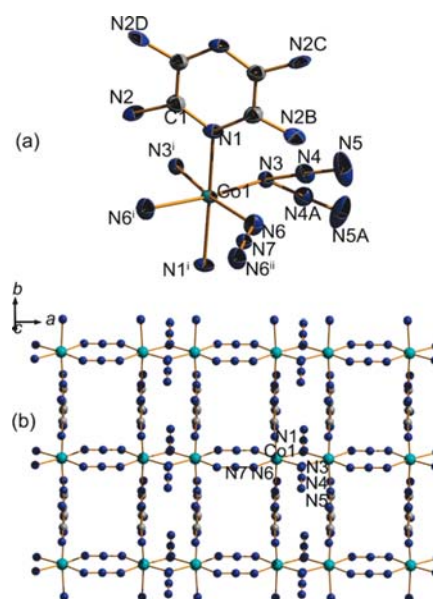


Figure 1. (a) Crystal structure and atom labeling scheme of **1**, (i) *x*, *−y*, 2−*z*; (ii) *−x*, *−y*, *z*. The ellipsoids are shown at 50% probability level. All disordered positions of amino group and N atoms of EO-azide are shown. (b) 2D layer of **1** in the *ab* plane. All H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 1

Compound 1 ^a			
Co1–N3	2.116(4)	Co1–N6	2.141(5)
Co1–N3 ⁱ	2.116(4)	Co1–N1 ⁱⁱⁱ	2.193(4)
Co1–N6 ⁱⁱ	2.141(5)	Co1–N1	2.193(4)
N3–Co1–N3 ⁱ	78.3(3)	N6 ⁱⁱ –Co1–N1 ⁱⁱⁱ	88.10(8)
N3–Co1–N6 ⁱⁱ	170.35(19)	N6–Co1–N1 ⁱⁱⁱ	88.10(8)
N3 ⁱ –Co1–N6 ⁱⁱ	92.10(19)	N3–Co1–N1	92.24(9)
N3–Co1–N6	92.10(19)	N3 ⁱ –Co1–N1	92.24(9)
N3 ⁱ –Co1–N6	170.35(19)	N6 ⁱⁱ –Co1–N1	88.10(8)
N6 ⁱⁱ –Co1–N6	97.5(3)	N6–Co1–N1	88.10(8)
N3–Co1–N1 ⁱⁱⁱ	92.24(9)	N1 ⁱⁱⁱ –Co1–N1	174.2(2)
N3 ⁱ –Co1–N1 ⁱⁱⁱ	92.24(9)	N6–N7–N6 ^{iv}	176.2(8)
Co1–N3–Co1 ⁱ	101.7(3)	N5–N4–N3	178.1(13)
N7–N6–Co1	129.3(5)		

^a Symmetry codes: (i) 1−*x*, *−y*, 2−*z*; (ii) *x*, *y*, 2−*z*; (iii) *x*, *−y*, 2−*z*; (iv) *−x*, *−y*, *z*.

atoms N6, N7 and EO azido N3 atom all lie on a crystallographically *ac* mirror plane. In addition there are three other vertical mirror planes. The first *bc* mirror plane lies on EO azido N3, N4, and N5 atoms. Second is another *bc* mirror plane lying on the EE azido atom N7 and the third is the *ab* mirror plane lying on pyrazine N1 and Co1 atoms. There is only one crystallographically independent Co^{II} ion, which has a slightly elongated octahedron composed of two N atoms from bridging ampyz in the axial sites (2.193(4) Å) and four N atoms from two EE and two EO azide ions located in the equatorial positions (2.141(5)–2.116(4) Å). The selected bond lengths and bond angles are given in Table 2. The adjacent Co^{II} ions are related by those crystallographic mirror planes and inversion center and linked alternately by double EE

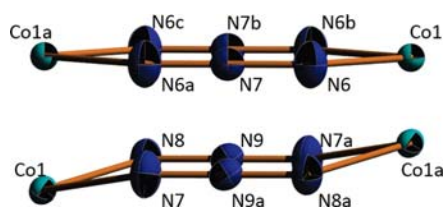


Figure 2. Different conformations of the double EE azido bridged $\text{Co}(\mu_2-1,3 \text{N}_3)_2\text{Co}$ ring, complete planarity in **1** (top) and chair conformation in **2** (bottom).

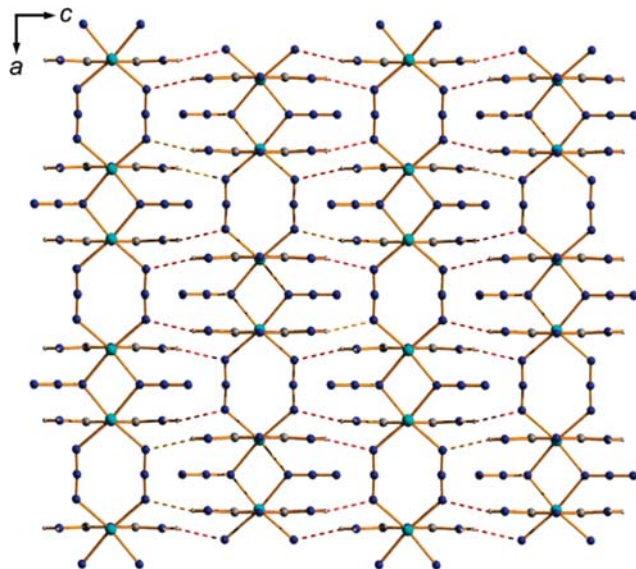


Figure 3. Formation of a 3D framework of **1** in the ac plane formed by hydrogen bonds between the neighboring layers. The dotted line represents the interlayer $\text{N2}-\text{H2B}\cdots\text{N6}$ hydrogen bond.

and double EO azido bridges, giving rise to a neutral 1D perfect linear chain along the a axis with the $\text{Co}\cdots\text{Co}$ separations of 5.157(2) and 3.283(1) Å, respectively, where the sum of these values equals to the crystallographic a parameter of 8.440(2) Å. In double EO bridged $\text{Co}(\mu_2-1,1 \text{N}_3)_2\text{Co}$ moiety, the $\text{Co1}-\text{N3}-\text{Co1A}-\text{N3A}$ ring is strictly planar because of the existence of the inversion center and mirror planes with the $\text{Co1}-\text{N3}-\text{Co1A}$ angle of $101.7(3)^\circ$, as is usually observed for this kind of azido bridge.³⁴ The disordered EO azido bridge, which is nearly linear ($\angle \text{N3}-\text{N4}-\text{N5} = 178.1^\circ$), slightly deviates (up and down) from that plane. For double EE mode, the $\text{Co}(\mu_2-1,3 \text{N}_3)_2\text{Co}$ moiety forms the perfect planarity because the crystallographic ac mirror plane is placed on this ring. As a result, a dihedral angle δ between the N6N7N6aN6cN7bN6b mean plane and the CoN6N6b plane is 0° , as shown in Figure 2. The symmetric $\text{Co1}-\text{N6}-\text{N7}$ angle is $129.3(5)^\circ$. It is the uncommon observation of the complete planar for the $\text{M}(\mu_2-1,3 \text{N}_3)_2\text{M}$ moiety in the alternating chain of double EE and double EO azido bridges, where the chair conformation is usually observed.^{35,36} To our knowledge, the lowest δ value is 1.82° which is found in $[\text{Mn}(\text{TaiEt})(\text{N}_3)_2]_n$ ($\text{TaiEt} = 1\text{-ethyl-2-}(\rho\text{-tolylazo})\text{imidazole}$).³⁶ The ampyz acts as a N,N' -ditopic connector in *trans* position, bridging this neutral azido cobalt(II) chain along the b axis and building the 2D square-grid sheet of **1**, as shown in Figure 1b. The intralayer $\pi-\pi$ stacking interactions among ampyz spacers stabilize the layer of **1** with the separations of

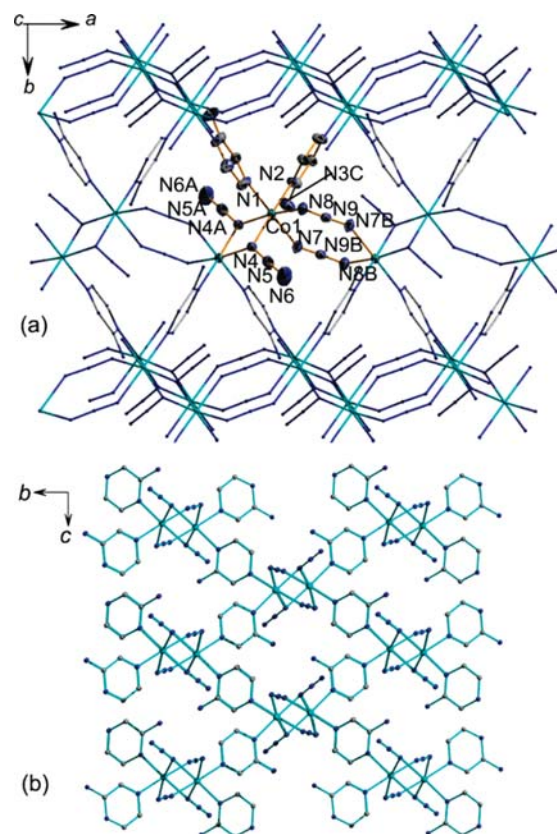


Figure 4. (a) 3D framework with atom labeling scheme of **2** in the ab plane. The ellipsoids are shown at 50% probability level. Atoms labeled with the notation “A”, “B”, and “C” are symmetry-generated equivalents, (A) $-x, 1-y, 1-z$; (B) $1-x, 1-y, 1-z$; (C) $1/2+x, 1/2-y, 1/2+z$. (b) Another view of 3D structure of **2** in the bc plane.

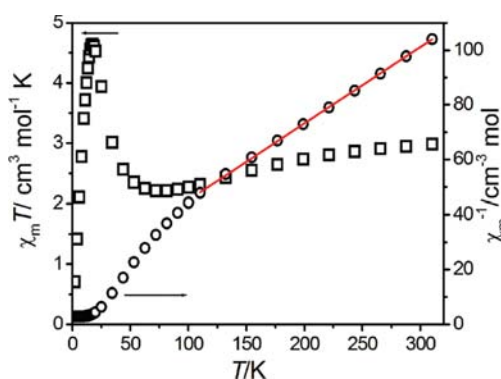
3.502(4) and 4.938(4) Å. The $\text{Co}\cdots\text{Co}$ separation via the ampyz spacer equals to the crystallographic b parameter of 7.1808(12) Å. Moreover, the adjacent 2D sheets of **1** are assembled by interlayer hydrogen bonding between the amine H of ampyz and the N6 atom of the EE azido bridge [$\text{N2H}\cdots\text{N6}^i = 2.39$ Å (157°), $\text{N2}\cdots\text{N6}^i = 3.205(14)$ Å, (i) $= 1/2-x, 1/2-y, 1/2+z$], yielding a 3D framework of **1** with the closest interlayer $\text{Co}\cdots\text{Co}$ separation of 7.8453(9) Å, as shown in Figure 3.

3D Framework of $[\text{Co}(\text{N}_3)_2(\text{ampyz})]_n$ (2**).** The crystal structure of **2** is depicted in Figure 4a. Compound **2** shows a 3D framework which is isostructural to the reported zinc(II) compound $[\text{Zn}(\text{N}_3)_2(\text{ampyz})]_n$.²⁴ There is one crystallographically independent Co^{II} ion, which is an octahedral CoN_6 chromophore composed of two N atoms from two bridging ampyz ligands in *cis*-position and four N atoms from two EE and two EO bridging azide ions. The selected bond lengths and bond angles are given in Table 3. The 3D framework of **2** also consists of an azido cobalt(II) neutral zigzag chain with the alternating double EE and double EO azido bridges along the a axis, but N,N' -ditopic ampyz spacers link adjacent Co^{II} ions in *cis*-arrangement. The angle of $\text{Co}\cdots\text{Co}\cdots\text{Co}$ in the zigzag chain is $116.62(8)^\circ$, and the $\text{Co}\cdots\text{Co}$ separations via ampyz spacers are 7.1119(14) and 7.6013(14) Å. The hydrogen bonds between the amine H of *cis*-ampyz spacers and N atoms of azido bridges additionally stabilize the entire framework [$\text{N3H}\cdots\text{N4}^i = 2.48$ Å (138°), $\text{N3}\cdots\text{N4}^i = 3.174(3)$ Å; $\text{N3H}\cdots\text{N7}^{ii} = 2.57$ Å (124°), $\text{N3}\cdots\text{N4}^{ii} = 3.130(3)$ Å; and

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 2

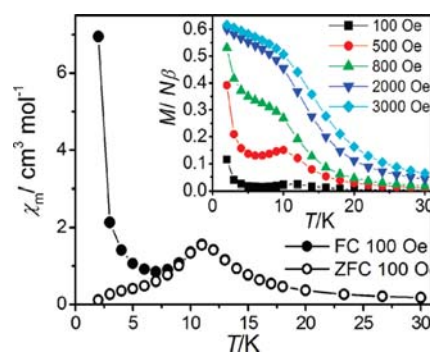
Compound 2 ^a			
Co1–N4 ⁱ	2.0986(18)	Co1–N4	2.1698(17)
Co1–N8	2.139(2)	Co1–N7	2.1704(19)
Co1–N2	2.1591(17)	Co1–N1	2.1773(17)
N4 ⁱ –Co1–N8	169.60(7)	N4–Co1–N7	87.36(8)
N4 ⁱ –Co1–N2	98.55(7)	N4 ⁱ –Co1–N1	93.31(7)
N8–Co1–N2	91.82(7)	N8–Co1–N1	87.36(7)
N4 ⁱ –Co1–N4	81.10(7)	N2–Co1–N1	90.94(7)
N8–Co1–N4	88.51(7)	N4–Co1–N1	91.47(7)
N2–Co1–N4	177.58(6)	N7–Co1–N1	177.70(7)
N4 ⁱ –Co1–N7	88.47(7)	N6–N5–N4	178.1(3)
N8–Co1–N7	90.63(7)	N7 ⁱⁱ –N9–N8	176.8(2)
N2–Co1–N7	90.23(8)	Co1 ⁱ –N4–Co1	98.90(7)

^a Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$.

**Figure 5.** Temperature dependence of $\chi_m T$ (□) and χ_m^{-1} (○) of **1** from 2 to 310 K at $H = 10$ kOe. The solid lines correspond to the best fit to the Curie–Weiss law.

$N3H \cdots N8^{iii} = 2.31$ Å (171°), $N3 \cdots N8^{iii} = 3.165(3)$ Å, (i) = $1/2+x, 1/2-y, -1/2+z$, (ii) = $1/2-x, -1/2+y, 1/2-z$, (iii) = $-1/2+x, 1/2-y, 1/2+z$. The adjacent Co^{II} ions in an azido chain are related by inversion centers and linked alternately by double EE and double EO azido bridges with the $Co \cdots Co$ distances of 5.3279(10) Å and 3.2438(6) Å, respectively. In double EO bridging mode, the Co1–N4–Co1A–N4A ring is strictly planar because of the existence of the inversion center with the Co1–N4–Co1A angle of $98.90(7)^\circ$. The EO azido bridge is nearly linear ($\angle N4-N5-N6 = 178.1(3)^\circ$) and deviates up and down 43.8° from the plane of Co_2N_2 . For double EE bridging mode, the EE bridges adopt a chair conformation for the $Co(\mu_2-1,3-N_3)_2Co$ unit with the dihedral angle δ of $12.57(6)^\circ$, as shown in Figure 2. The Co1–N8–N9 and Co1–N7–N9B angles are $124.3(2)^\circ$ and $139.3(2)^\circ$, respectively.

Magnetic Properties. The magnetic susceptibility of a polycrystalline sample of **1** at 2–310 K is shown in Figure 5. At 310 K, the $\chi_m T$ value is 2.98 cm³ K mol^{−1}, which is significantly higher than the spin-only value of 1.87 cm³ K mol^{−1} expected for an $S = 3/2$ ion, owing to the significant orbital contribution of high-spin Co^{II} in an octahedral surrounding. Upon cooling, the $\chi_m T$ value decreases slowly, attains a minimum value of 2.21 cm³ K mol^{−1} at 70 K, and then shows an abrupt increase to a maximum value of 4.64 cm³ K mol^{−1} at 18 K. This behavior indicates that a

**Figure 6.** ZFC and FC magnetization of **1** at $H = 100$ Oe from 2 to 30 K. The inset shows the FC magnetization plot of **1** below 30 K at various fields.

small spontaneous magnetization emerges in an antiferromagnetic system, owing to spin canting in which the predominantly antiferromagnetic coupled spins from different sublattices are not perfectly antiparallel, but canting to each other, and the resulting net moments are correlated in a weak ferromagnetic fashion.^{3,37,38} Upon further cooling to 2 K, $\chi_m T$ decreases gradually down to 0.70 cm³ K mol^{−1}, suggesting antiferromagnetic interactions among the neighboring azido Co^{II} chains or the magnetization saturation. The χ_m^{-1} values above 100 K were fitted with the Curie–Weiss law $\chi = C/(T - \theta)$ with a Curie constant $C = 3.58(2)$ cm³ K mol^{−1} and a Weiss constant $\theta = -61.8(13)$ K. The C is in the usual range of octahedral high-spin Co^{II} ions.^{3,38,39} The negative θ value can be attributed to both significant spin–orbit coupling of the octahedral Co^{II} ions with a $^4T_{1g}$ ground term and the presence of antiferromagnetic coupling between the Co^{II} centers through the $\mu_{1,3}$ -azido bridging ligands. Owing to the lack of a theoretical model for the alternating chain of exchange interactions of octahedral Co^{II} with large spin–orbit coupling effects, the exchange parameters could not be estimated.

To characterize the low-temperature behaviors of **1**, the temperature dependencies of field-cooled (FC) and zero-field-cooled (ZFC) magnetization were performed under a field of 100 Oe upon warming from 2 K, as shown in Figure 6. The ZFC and FC plots present a cusp at around 11 K and show a disagreement below 10 K, suggesting the onset of long-range antiferromagnetic ordering and hysteretic long-range magnetic order, respectively. The temperature dependence of the ac susceptibility measured in a field of 3 Oe shows the same features (Supporting Information, Figures S4). The maximum of χ' observed at 11 K, in agreement with the above results, confirms the occurrence of a phase transition. The absence of an out-of-phase signal (χ'') around this temperature points to a long-range antiferromagnetic order. However, the χ'' value shows a nonzero signal below 10 K which is the signature of a magnetized state, thus indicating that a partly canted antiferromagnetic structure exists below this temperature.^{40–42} The temperature dependence of the FC magnetization of **1** at various fields is depicted in Figure 6, inset. The application of different magnetic fields in the range of 100–3000 Oe showed a strong field dependence of the magnetic susceptibility below T_N . For applying fields below 500 Oe, the curves show a swell at around 11 K, indicating the antiferromagnetic ordered state. In the lower temperature region, the magnetizations increase because of small spontaneous magnetization of canted antiferromagnetism. However, applying a magnetic field above 800 Oe is sufficient to

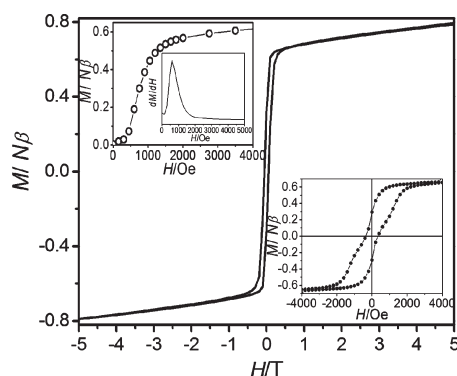


Figure 7. Field dependence of the magnetization for **1** at 2 K. The insets show the initial plot in a low field (left) and the hysteresis loop (right).

overcome these interactions. The cusp disappears, and the magnetization tends to saturate at higher field. These trends suggest a field-induced magnetic phase transition from an antiferromagnetic to a ferromagnetic-like state.^{43–45} In addition, the spin canting and metamagnetic-like behaviors were confirmed by the hysteresis loop measurements at 2 K in an external field of 0–5 T, as given in Figure 7. The initial $M(H)$ plot shows a characteristic sigmoidal form (Figure 7, inset), which is a typical feature of a metamagnetic behavior.^{18,43–45} The critical field H_c is ≈ 600 Oe, estimated as the field at which a maximum $\partial M/\partial H$ value is reached. At $H < 600$ Oe, a linear increase in $M(H)$ is associated with antiferromagnetic interactions, and then above the critical field, the magnetization is drastically increased to $H = 5$ T without saturation and exhibits a magnetization value of $0.79 N\beta$, that is far from the theoretical saturation magnetization of Co^{II} ion ($M_s = 2.16 N\beta$, $S' = 1/2$, $g' = 4.33$ for octahedral Co^{II} at 2 K),^{1,28} suggesting the overall antiferromagnetic coupling between Co^{II} ions. Clearly, a higher field is required to reach saturation to a ferromagnetic phase. Upon decreasing the applied field, the magnetization curve decreases along a different route and exhibits a slightly sigmoid-shaped hysteresis loop with coercive field of ≈ 350 Oe and remanent magnetization M_r of $\approx 0.29 N\beta$. These behaviors confirm the occurrence of spontaneous magnetization of **1** which is in agreement with the observed coexistence of spin-canted antiferromagnetism and metamagnetism. The canting angle (α)^{1,5} is estimated to be about 7.7° based on the equation $\alpha = \sin^{-1} M_r/M_s$, where M_s the theoretical saturation magnetization of Co^{II} ion at 2 K. This value is among the big canting angles reported for weak ferromagnets.⁵ [$\text{Co}(\text{N}_3)_2(\text{bpg})_2$]³⁴ ($\alpha = 5.2^\circ$), [$\text{Co}(\text{N}_3)_2(\text{btzb})$]³⁷ ($\alpha = 6.4^\circ$), [$\text{Co}(\text{N}_3)_2(\text{btze})_2$]³⁷ ($\alpha = 9.9^\circ$), [$\text{Co}_2(\text{N}_3)_4(\text{hmta})(\text{H}_2\text{O})$]³⁸ ($\alpha = 7.2^\circ$), [$\text{Co}(\text{N}_3)_2(4\text{-acetylpyridine})_2$]⁴⁶ ($\alpha = 15^\circ$), [$\text{Fe}(\text{N}_3)_2(4,4'\text{-bpy})$]⁴⁷ ($\alpha = 7\text{--}8^\circ$), [$\text{Co}(\text{pyrimidine})_2(\text{X})_2$] ($\text{X} = \text{Cl}, \text{Br}$)⁴⁸ ($\alpha = 9^\circ$) and [$\text{Fe}(\text{pyrimidine})_2\text{Cl}_2$]⁴⁹ ($\alpha = 14^\circ$).

Temperature dependence of the magnetic susceptibility of **2** at 2–310 K under the field of 10 kOe is presented in Figure 8. The $\chi_m T$ value of $2.86 \text{ cm}^3 \text{ K mol}^{-1}$ at 310 K is much higher than the spin-only value of high-spin Co^{II} ions, owing to the orbital contributions of octahedral Co^{II} ions. Upon cooling the temperature, the $\chi_m T$ values decrease gradually and show the cusp around 15 K with the $\chi_m T$ value of $0.57 \text{ cm}^3 \text{ K mol}^{-1}$, after that the $\chi_m T$ values drop sharply down to $0.09 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The plot of $\chi_m T$ vs T at small fields in the temperature range of 2–30 K is depicted in Figure 8, inset. Below 16 K, the abrupt increases in $\chi_m T$ values are observed under the field below

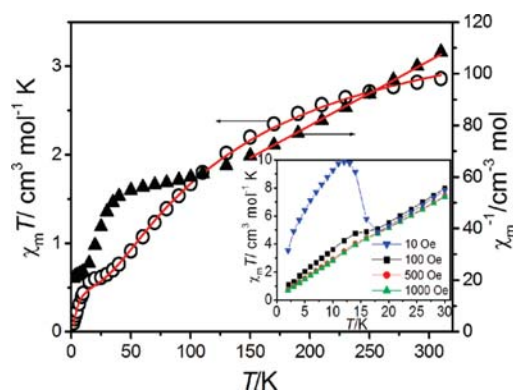


Figure 8. Temperature dependence of $\chi_m T$ (○) and χ_m^{-1} (▲) of **2** from 2 to 310 K at $H = 10$ kOe. The solid lines correspond to the best fit (see the text). The inset shows the $\chi_m T$ vs T plot of **2** below 30 K at small fields.

100 Oe; the susceptibility becomes field dependent. At a small field of 10 Oe, $\chi_m T$ shows an abrupt increase to a maximum value of $9.86 \text{ cm}^3 \text{ K mol}^{-1}$ at 12 K before decreasing in the lowest temperature region. The upturn of $\chi_m T$ below 16 K suggests uncompensated magnetic moments of the system arising from spin canting of the antiferromagnetically coupled Co^{II} ions.^{26,36} The data above 150 K obeys the Curie–Weiss law with a Curie constant $C = 3.99(6) \text{ cm}^3 \text{ K mol}^{-1}$ and a Weiss constant $\theta = -119(5) \text{ K}$. The C is much larger than the expected spin-only value, which indicates the significant orbital contribution of Co^{II} in an octahedral surrounding.⁵⁰ The large negative θ value suggests the strong spin–orbital coupling of Co^{II} ions in an octahedral field and the antiferromagnetic coupling between Co^{II} ions within 3D framework of **2**. Because of the spin–orbit coupling contribution of Co^{II} ions, it is difficult to find an accurate analytical expression to describe the temperature dependence of the magnetic susceptibility for the polymeric chains of the Co^{II} ions. However, Rueff et al.^{51–53} have proposed a very successful phenomenological approach for a low-dimensional antiferromagnetic Co^{II} system that allows an estimation of the strength of the antiferromagnetic exchange interactions and also the effects of spin–orbit coupling. They postulate the phenomenological equation:

$$\chi_m T = A \exp(-E_1/kT) + B \exp(-E_2/kT)$$

$A + B$ equals the Curie constant and E_1 and E_2 represent the activation energies corresponding to the spin–orbit coupling parameter and the antiferromagnetic exchange interaction, respectively, where E_2 is related to the magnetic coupling constant J according to the Ising chain approximation, $\chi_m T \propto \exp(+J/2kT)$. This equation adequately describes the spin–orbit coupling, which results in a splitting between discrete levels and the exponential low-temperature divergence of the susceptibility. The reasonable values for magnetic coupling and spin–orbit interaction have been reported in several studies of 1D and 2D Co^{II} networks.^{51,52,54–56} The fitted parameters are $A + B = 3.90 \text{ cm}^3 \text{ K mol}^{-1}$, practically equivalent to the Curie constant obtained from the Curie–Weiss law in the high temperature range, $3.99 \text{ cm}^3 \text{ K mol}^{-1}$. The E_1/k is $+112(8) \text{ K}$ which is of the same magnitude as those reported for Co^{II} complexes (the order of $+100 \text{ K}$).^{51,52,54–56}

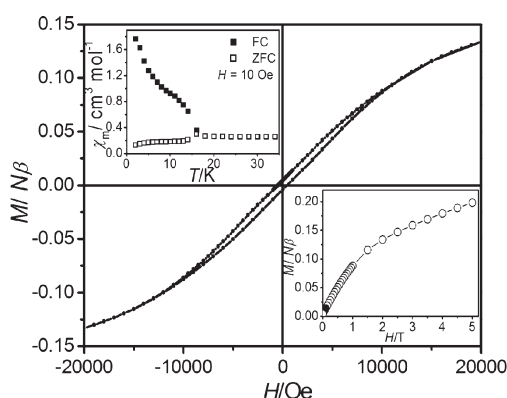


Figure 9. Hysteresis curve of **2** at 2 K. The insets show the field dependence of initial magnetization (right) and the ZFC-FC plots of **2** at 10 Oe (left).

For the antiferromagnetic coupling $E_2/k = +4.4(2)$ K, corresponding to $J = -8.8$ K, according to the Ising chain approximation, $\chi_m T \propto \exp(+J/2kT)$. It is noticeable that the small E_2/k value is very close to those reported values for the 2D layer of $[\text{Co}(2,2'\text{-bpe})(\text{N}_3)_2]_n$ ($E_2/k = +4.1(2)$ K)²⁷ which contains the same alternating double EO and double EE azido- Co^{II} chain. It is an indication of the overall antiferromagnetic coupling within the 1D azido- Co^{II} chain. However, the E_1/k value of **2** is much higher than that of $[\text{Co}(2,2'\text{-bpe})(\text{N}_3)_2]_n$ ($E_1/k = +61(2)$ K),²⁷ implying that **2** presents the stronger spin–orbit coupling of Co^{II} ions in an octahedral field, corresponding to the observation of higher Curie and Weiss constants of **2**.

As a further proof for the presence of the spin canting, the temperature dependencies of the ZFC and the FC magnetization were measured at a low field of 10 Oe, as shown in Figure 9, inset. The obvious divergence of the ZFC and FC plots below 16 K indicates the onset of a magnetized state, which is compatible with the maxima in χ' and the nonzero χ'' signal at 16 K in the ac susceptibility at 997 Hz, indicative of a long-range magnetic ordering (Supporting Information, Figures S5). The isothermal magnetization with a field up to 5 T at 2 K is depicted in Figure 9. The initial increase of magnetization shows a positive curvature to 0.198 $N\beta$ at 5 T, far from the theoretical saturation magnetization of Co^{II} ion, and no saturation is observed, which is indicative of the overall antiferromagnetic coupling between Co^{II} ions. A hysteresis loop of **2** is clearly observed when the field is less than 1 T, giving a coercive field of ≈ 450 Oe and remanent magnetization of $\approx 0.004 N\beta$. These results indicate that the spin canting effect between overall antiferromagnetically coupled Co^{II} ions leads to residual spins. The canting angle (α) is estimated to be about 0.11° based on the equation $\alpha = \sin^{-1} M_r/M_s$ ($M_s = 2.16 N\beta$ for octahedral Co^{II} at 2 K).

Remarkably, the 2D layer of complex **1** exhibits the coexistence of big canting angle and metamagnetic phenomena whereas the 3D framework of complex **2** only displays the canted antiferromagnetism with a smaller canting angle. As we know that two mechanisms lead to spin canting behavior: (i) single-ion magnetic anisotropy and (ii) antisymmetric exchange interaction.^{1,28} However, the spin canted structures are not compatible with both crystal structures of **1** and **2** because of the presence of an inversion center between the bridged Co^{II} sites, which forbids the occurrence of

antisymmetric interactions. It is noticeable that the canted antiferromagnets in the presence of an inversion center between metal sites have been often observed in corresponding complexes that contain the 1D chain of alternating double EO and double EE azido-bridged metal(II) ions, as summarized in Table 4. Generally, these complexes were crystallized in low crystal systems (monoclinic and triclinic lattices) and display an inversion center between metal sites. The 1D chain complexes with *cis*-bidentate chelating coligands are widely found in this magnetic system while the 2D layer and 3D framework structures are rarely observed. The isotropic Mn^{II} complexes usually exhibit the overall antiferromagnetic interaction within the 1D alternating ferromagnetic and antiferromagnetic chains, and their magnetostructural correlations have been investigated entirely.^{8,35,36,57} Whereas the metamagnetism and weak ferromagnetism due to canted antiferromagnetic system are usually observed in anisotropic ones (Co^{II} , Fe^{II} , and Ni^{II} complexes).^{7,26,27} However some spin canting of 1D Mn^{II} complexes were also reported, which are due to the possible distortion in the crystal structure at low temperature.^{36,57,58}

Consequently, the observation of spin canting for **1** and **2** should be attributed to the competition of ferromagnetic and antiferromagnetic interactions within intrachain of the alternating double EO and double EE azido bridging mode together with a relevant single-ion anisotropy of octahedral cobalt(II) ions and a possible structure phase transition at low temperature.^{7,26,27,36,58} Obviously from the structural data, complex **1** which was crystallized in orthorhombic system with high centrosymmetric space group *Immm* presented the disordered amino group on the ampyz moiety and the disordered terminal EO azido bridge arising from related crystallographic mirror planes and inversion center. We suppose that these disordered positions and inversion centers between the Co^{II} sites somewhere are possibly demolished at very low temperature and develop to the exact atomic location in the crystal lattice with the lower space group. Therefore, the antisymmetric coupling for **1** possibly exists at low temperature together with the single-ion anisotropy of octahedral Co^{II} ion yielding a big canting angle for **1**, as similarly observed in other reported weak ferromagnets with large canting angles.^{5,37,38,46,47,59,60} Moreover the interchain and the interlayer weak antiferromagnetic coupling of **1**, which originate from *trans*-ampyz bridging shortly between the azido Co^{II} chain and the interlayer hydrogen bonding between NH_2 on ampyz and symmetric double EE azido bridges, would justify the observed maximum of susceptibility at $H_c < 600$ Oe. In a magnetic field below 600 Oe, the residual magnetic moments due to spin canting on the chains are weak antiferromagnetically coupled to each other (Figure 7, inset). In stronger fields above 600 Oe, the amplitude of the applied magnetic field can overcome the interchain and interlayer weak antiferromagnetic coupling leading to the observed metamagnetic-like behavior of **1**. However, because of the great spin–orbit coupling of Co^{II} ions, the magnetic interaction might be more complicated. Generally, the coexistence of spin canting and metamagnetism is found in the system consisting of a large anisotropy, which leads to a significant spin canting through increasing the possibility of antisymmetric exchange and may induce a metamagnetic transition in the presence of competing interactions within the structure.^{40,42,61–65}

It is worthwhile to compare the magnetic properties of **1** and **2** with that of the reported Co^{II} complexes containing similar

Table 4. Magnetic Properties for the Complexes Containing the Alternating Double EO and Double EE Azido Bridging Mode

complex ^a	D	crystal system, space gr.	magnetic behavior ^b	ref.
<i>trans</i> -Monodentate Coligands				
[Mn(3-Et-4-Mepy) ₂ (N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	66
[Mn(3-bzpy) ₂ (N ₃) ₂] _n	1D	monoclinic, <i>C</i> 2/ <i>c</i>	overall AF	9
[Mn(4-azpy) ₂ (N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	not reported	67
<i>cis</i> -Monodentate Coligand				
[Mn(3,5-lut) ₂ (N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	overall AF	9
<i>cis</i> -Bidentate Chelating Coligands				
[Ni(bpy)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	C and M	7
[Co(bpy)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	C and M	7
[Fe(bpy)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	C and M	7
[Mn(bpy)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	7,8
[Mn(bpm)(N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	overall AF	68
[Ni(dmen)(N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	overall AF	69
[Ni(aep)(N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	overall AF	69
[Mn(L ¹)(N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	overall AF	35
[Mn(L ²)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	35
[Mn(L ³)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	35
[Mn(L ⁴)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	35
[Mn(L ⁵)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	35
[Mn(L ⁶)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	overall AF	70
[Mn(2-pmp)(N ₃) ₂] _n	1D	monoclinic, <i>C</i> 2/ <i>c</i>	overall AF	71
[Mn(taiEt)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	C (<i>T</i> _c = 40 K)	36
[Mn(dpq)(N ₃) ₂] _n	1D	triclinic, <i>P</i> $\bar{1}$	C (<i>T</i> _c = 6 K)	58
[Mn(dpa)(N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>c</i>	C (<i>T</i> _c = 15 K)	57
[Co(dpa)(N ₃) ₂] _n	1D	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	C (<i>T</i> _c = 12.4 K)	26
<i>trans</i> -Bidentate Bridging Coligands				
[Mn(L ⁷)(N ₃) ₂] _n	2D	triclinic, <i>P</i> $\bar{1}$	overall AF	72
[Co(2,2'-bpe)(N ₃) ₂] _n	2D	triclinic, <i>P</i> $\bar{1}$	C (<i>T</i> _c = 12 K)	27
[Co(ampyz)(N ₃) ₂] _n (1)	2D	orthorhombic, <i>Immm</i>	C and M (<i>T</i> _c = 10 K)	this work
<i>cis</i> -Bidentate Bridging Coligand				
[Co(ampyz)(N ₃) ₂] _n (2)	3D	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	C (<i>T</i> _c = 16 K)	this work

^a Abbreviations: 3-Et-4-Mepy = 3-ethyl-4-methylpyridine, 3-bzpy = 3-benzoylpyridine, 4-azpy = 4-azidopyridine, 3,5-lut = 3,5-dimethylpyridine, bpy = 2,2'-bipyridine, bpm = bis(pyrazol-1-yl)methane, dmen = *N,N*-dimethylethylenediamine, aep = 2-aminoethylpyridine, L¹ = *N*-phenyl-2-carbaldimine, L² = *N*-(*p*-tolyl)-2-carbaldimine, L³ = *N*-(*m*-tolyl)-2-carbaldimine, L⁴ = *N*-(*p*-chlorophenyl)-2-carbaldimine, L⁵ = *N*-(*m*-chlorophenyl)-2-carbaldimine, L⁶ = *N*-(2-pyridylmethylene)octylamine, L⁷ = *N,N'*-Bis-(1-pyridin-3-yl-ethylidene) hydrazine, 2-pmp = 2-(pyrazol-1-ylmethyl)pyridine, taiEt = 1-ethyl-2-(*p*-tolylazo)-imidazole, dpq = dipyrro-(3,2-d:2',3'-f)-quinoxaline, dpa = 2,2'-dipyridylamine, and 2,2'-bpe = 1,2-bis(2-pyridyl)ethylene. ^b Abbreviations: C = canted antiferromagnetism, M = metamagnetism, and AF = antiferromagnetism.

alternating double EO and double EE azido bridging mode, as shown in Table 5. The comparison demonstrates that all compounds are hard magnets at 2 K (*H*_c ≈ 300–500 Oe) and only complex 1 which is in the highest-symmetry space group, shows the coexistence of big spin canting angle and metamagnetism whereas the others display very small spin canting angle. This unusual feature of 1 could be attributed to the above-mentioned significant antisymmetric exchange interaction between Co^{II} ions and the single-ion anisotropy of Co^{II} ion. In addition, the interlayer hydrogen bonding between NH₂ of ampyz and symmetric double EE azido bridges in 1 which are not found in other structures, might play the important role on the presence of the field-induced metamagnetic phase transition. In comparison with 1, complex 2 and the others which were crystallized in lower crystal systems reveal very small canting angles. This result indicates that the major magnetic

anisotropy of octahedral Co^{II} ion in 2 plays a key role on spin canting as well as a minor magnitude of antisymmetric coupling between Co^{II} ions which possibly arises from a distortion in the crystal framework, suppressing the inversion center at low temperature. The above-mentioned complex 2 shows the very close antiferromagnetic coupling *E*₂/*k* value to that reported for [Co(2,2'-bpe)(N₃)₂]_n but the Weiss constant and *E*₁/*k* value are much higher, which point to the very strong spin–orbital coupling of octahedral Co^{II} ions of 2. This extra inherent anisotropy of the Co^{II} ions for 2 might provide an additional contribution to a larger degree of spin canting, resulting in the observation of the higher *M*_r and the larger canting angle when comparing with [Co(2,2'-bpe)(N₃)₂]_n and [Co(dpa)(N₃)₂]_n. The *T*_N of 2 is slightly higher than other complexes owing to the closest Co···Co distance among the magnetic chains in 3D covalent framework of 2.

Table 5. Structural and Magnetic Data for Co^{II} Complexes Containing the Alternating Double EO and Double EE Azido Bridging Mode

	compound ^a			
	1	2	[Co(2,2'-bpe)(N ₃) ₂] _n	[Co(dpa)(N ₃) ₂] _n
dimension	2D	3D	2D	1D
co-ligand	<i>trans</i> -bridging	<i>cis</i> -bridging	<i>trans</i> -bridging	<i>cis</i> -chelating
crystal system	orthorhombic	monoclinic	triclinic	monoclinic
space group	<i>Immm</i>	<i>P2₁/n</i>	<i>P</i> $\bar{1}$	<i>P2₁/n</i>
Co–N–Co (deg)	101.7(3)	98.90(7)	102.25(14)	103.7
δ (deg) ^b	0	12.57(6)	33.8(1)	36.0
Co...Co (Å) ^c	7.1808(12)	7.1119(14)	8.322(2)	9.294
magnetic behavior	canted AF, metamagnetism	canted AF	canted AF	canted AF
θ (K)	−61.8(13) ^d	−119(5) ^d	−58(2) ^d	−40.0 ^e
T_N (K)	10	16	12	12.4
M_r (N β) ^f	0.29	0.004	0.002	0.002
H_c (Oe) ^g	350	450	300	500
α (deg) ^h	7.7	0.11	0.05	0.05
ref.	this work	this work	27	26

^a Abbreviations: 2,2'-bpe = 1,2-bis(2-pyridyl)ethylene and dpa = 2,2'-dipyridylamine. ^b The dihedral angle between the mean plane of Co(μ_2 -1,3 N₃)₂Co and the Co–N–N plane. ^c The shortest Co...Co distance among alternating double EO and double EE azido-Co^{II} chain. ^d The best fit to Curie–Weiss law above 150 K. ^e The best fit to Curie–Weiss law above 210 K. ^f Remanent magnetization at 2 K. ^g Coercive field at 2 K. ^h Canting angle based on the equation $\alpha = \sin^{-1} M_r/M_s$ ($M_s = 2.16$ N β).

CONCLUSIONS

By using the versatile ampyz spacer, two high dimensional cobalt(II) azido inorganic–organic hybrid frameworks, which contain similarly alternating double EO and double EE azido-bridged Co^{II} chains, were obtained from the different preparative methods. The high symmetric square-grid structure of **1** from the layer diffusion method, which consists of *trans*-ampyz bridging between octahedral Co^{II} centers in axial positions, presents the coexistence of a big spin canting angle and metamagnetism below 10 K. The canting angle is estimated to be 7.7°, and the critical field for metamagnetic phase transition is ≈ 600 Oe at 2 K. The interlayer hydrogen bonding between the amino group of the ampyz spacer and the symmetric double EE azido bridges plays an important role in the field-induced metamagnetic phase transition. The spin canting of **1** could be attributed to the significant antisymmetric exchange arising from the structure phase transition at low temperature and the great role of magnetic anisotropy of the Co^{II} ion. Whereas the 3D framework containing the *cis*-ampyz bridging among Co^{II} centers of **2** was synthesized from the hydrothermal technique, it was crystallized in a lower space group and exhibited only small spin-canted antiferromagnetism below 16 K. It suggests that the large magnetic anisotropy in **2** might contribute a spin canting together with small antisymmetric coupling between Co^{II} ions, arising from a distortion in the crystal net at low temperature, which is frequently found in the related complexes containing the same bridging mode of the azide. These results provide a motivation for future investigations and demonstrate the importance of the crystal engineering of inorganic–organic hybrid framework in the field of molecular-based magnetic materials.

ASSOCIATED CONTENT

S Supporting Information. X-ray crystallographic information files (CIF) for **1**–**2** (CCDC nos. 823144 and 823145),

IR and UV–vis spectra, XRPD patterns, and additional magnetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Toward the Design of Ferromagnetic Molecular Complexes: Magnetostructural Correlations in Ferromagnetic Triply Bridged Dinuclear Cu(II) Compounds Containing Carboxylato and Hydroxo Bridges

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In the present work we present a comprehensive study of the magneto-structural correlations of a series of ferromagnetic triply heterobridged Cu(II) dinuclear compounds containing $[\text{Cu}_2(\mu\text{-O}_2\text{CR})(\mu\text{-OH})(\mu\text{-X})(\text{L})_2]^{2+}$ ions (where X = OH₂, Cl[−], OMe[−] and L = bpy, phen, dpym) which have the particularity of being all ferromagnetic. The present theoretical study, based on hybrid density functional theory (DFT) calculations, leads to strong conclusions about the role of the pentacoordination geometry of the Cu(II) ions (square base pyramidal (SP) or trigonal bipyramidal (TBP) coordination) and the nature of the third bridging ligand in determining the final value of the magnetic coupling constants in this series of compounds. These investigations point toward the existence of a maximum value for the ferromagnetic interaction and may offer some useful information to synthetic chemists aiming at obtaining new compounds with enhanced ferromagnetism.

Introduction

The search for molecular magnets with specific properties is a continuously challenging field for synthetic chemists.^{1,2} The appropriate design of new compounds with improved features requires knowing magneto-structural correlations. Both experimental and theoretical viewpoints are extremely useful to successfully prepare the desired compounds with diverse structural and magnetic properties. Especially, compounds with ferromagnetism are of great interest for technological applications, and polynuclear Cu(II) compounds provide very useful models to disclose the relationship between molecular structure and magnetic properties. Among the different possible families of Cu(II) containing molecules, Cu(II) dinuclear complexes have been widely investigated since the early 1970s,³ their magnetic behavior arising mostly from the Cu open-shell 3d orbitals in an effective 3d⁹ electronic configuration. This particular electronic structure with the spin density being strongly localized in the open shell 3d orbitals permitted Kahn et al.¹ to develop the concept of

magnetic orbitals, a keystone in establishing and understanding useful magneto-structural correlations. A particular and special feature of Cu(II) dinuclear complexes is the ability of this ion to adopt diverse coordination geometries in different chemical environments and accepting a wide variety of bridging ligands. From the study of mono- and dibridged di-Cu(II) complexes, it has been established that the sign and magnitude of the magnetic coupling constant depends on the nature of the bridging ligands, the geometry of the dinuclear core, and the coordination environment of the metal atoms.¹ For heterodibridged systems, it has been reported that countercomplementary effects can arise between the ligands, where positive and negative contributions to the final value of the magnetic coupling constants (*J*), defining the observed ferro- or antiferromagnetic behavior, are competing.^{4–6}

Another, yet different, family of Cu(II) complexes exists where the two metals are triply bridged. These compounds are of special interest because of their existence in a wide diversity of topologies, intramolecular magnetic exchange

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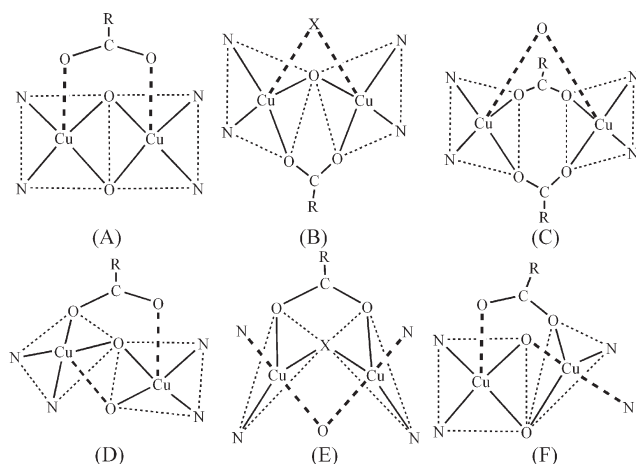


Figure 1. Representation of the structural features of the local environment of each of the Cu centers defining the A–F classes of triply bridged dinuclear complexes considered in this work. Notice that the dotted lines define the type of basis (square base pyramidal 4 + 1 coordination (SP) or trigonal bipyramidal 3 + 2 coordination (TBP)) and dashed lines indicate apical bond for SP and axial positions for TBP coordination.

pathways, and magneto-structural correlations.^{6–10} In this series of Cu(II) compounds, the metal atoms exhibit a 5-fold coordination with a broad range of distorted geometries between regular trigonal bipyramid and regular square-based pyramid. The global topologies of these compounds can be described in terms of the relative arrangement of the two five-coordinate environments (square base pyramidal (SP) or trigonal bipyramidal (TBP) coordination), giving rise to different classes (A–F) of compounds as shown in Figure 1. These particular structural features are useful to further understand the relationships between molecular structure and the final value of the intramolecular magnetic exchange interaction in the triply bridged dinuclear unit. In this sense, it is worth to mention that class C compounds have been broadly studied and it is known that the magnetic coupling is dominated by the two carboxylato groups which, in general, lead to antiferromagnetic coupling. Consequently, this class will not be studied in the present work.

In a previous study, magneto-structural correlations have been investigated for some of these compounds by means of the simple Extended Hückel (EH) method, and a linear correlation has been found for class B compounds allowing a first step toward a proper understanding.⁷ Nevertheless, the qualitative nature of the electronic structure description provided by the empirical EH method is of limited use for both interpretation and a quantitative description of magnetic systems. This is because the final value of the magnetic coupling is strongly dominated by subtle electron correlation effects, as shown by the landmark paper by de Loth et al.¹¹

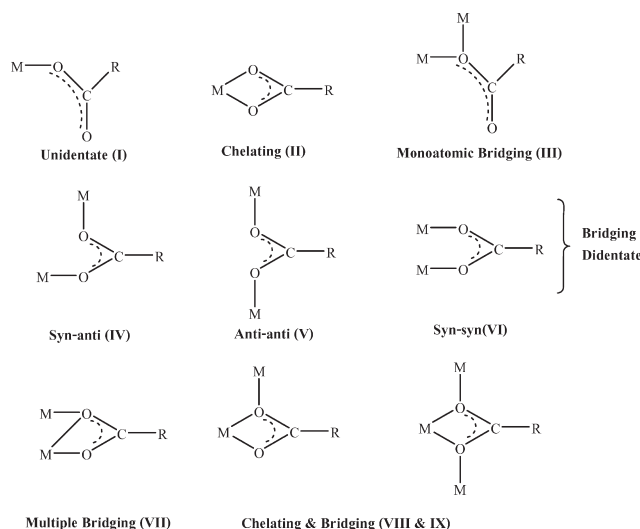


Figure 2. Topologies of the different bridging ligands contained in the molecules under study leading to the different nuclearity and variety of topologies as shown in Figure 1. Notice the presence of a π system involved in the different coordination modes.

and the subsequent analysis by Calzado et al.^{12,13} Ideally, one can make use of mapping procedures and compute the magnetic coupling constants accurately via appropriate configuration interaction calculations¹⁴ although, because of the extreme computational resources required, this is only possible for model systems with simplified ligands. Alternatively, one can make use of second order multiconfigurational approaches¹⁵ or take advantage of recent advances in density functional theory (DFT) based methods.^{16,17}

In the present work we present a comprehensive study of the magneto-structural correlations of this extended series of triply bridged Cu(II) dinuclear compounds using state of the art hybrid DFT based calculations, and the results are compared to available data on similar dinuclear complexes. It is important to stress the fact that, while most of the Cu(II) dinuclear complexes exhibit an antiferromagnetic coupling, all compounds investigated in the present work have the particularity of being ferromagnetic thus making them more attractive for potential new technologies employing molecular magnets. In this sense, the present theoretical study allows one to extract strong conclusions about the role of a third bridging ligand in determining the final value of the magnetic coupling constants for a specific global topology in this series of compounds and may offer some useful information to synthetic chemists aiming at obtaining new compounds with enhanced ferromagnetism.

Brief Description of the Bridging Ligands and Crystal Structures

The bridging carboxylate ligands are extremely flexible with versatile coordination modes since each oxygen atom may act as a unidentate, chelate, monatomic bridge and triatomic bridge with *syn-syn*, *syn-anti*, *anti-anti* configurations.

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Table 1. List of the Dinuclear Triply-Bridged Copper(II) Compounds and Experimental Magnetic Properties^a

compound	number	class	<i>J</i> (cm ⁻¹)	ref.
[Cu ₂ (μ-O ₂ CH)(μ-OH) ₂ (dpyam) ₂](ClO ₄)·H ₂ O	1	A	112.7	[7]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(dpyam) ₂](S ₂ O ₈)	2	B	not available	[7]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(bpy) ₂](NO ₃) ₂	3	B	not available	[7]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(phen) ₂](BF ₄) ₂ ·0.5H ₂ O	4	B	120.8	[7]
[Cu ₂ (μ-O ₂ CCH ₂ CH ₃)(μ-OH)(μ-OH ₂)(phen) ₂](NO ₃) ₂	5	B	not available	[7]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(bpy) ₂](ClO ₄) ₂	6	B	38.6	[6]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(phen) ₂](ClO ₄) ₂	7	B	120.0	[8]
[Cu ₂ (μ-O ₂ CCH ₂ CH ₃)(μ-OH)(μ-OH ₂)(bpy) ₂](ClO ₄) ₂	8	B	148.9	[8]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-Cl)(bpy) ₂](ClO ₄)·8.5H ₂ O	9	B	145.3	[7]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-Cl)(dpyam) ₂](ClO ₄)·0.5H ₂ O	10	E	79.1	[9]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-Cl)(dpyam) ₂](PF ₆)	11	E	79.7	[10]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-OMe)(dpyam) ₂](ClO ₄)	12	E	62.5	[9]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-OMe)(dpyam) ₂](PF ₆)	13	E	47.8	[10]
[Cu ₂ (μ-O ₂ CC ₂ H ₅)(μ-OCOC ₂ H ₅)(μ-OH)(dpyam) ₂](ClO ₄)	14	D	24.1	[10]

^a Note that positive *J* values correspond to a ferromagnetic ground state.

These features are able to generate complexes with different nuclearity and variety of topologies as shown in Figure 2 below and have been widely exploited in bioinorganic^{18,19} and molecular magnetic materials chemistry (see refs 7–10 and references therein). Concerning the chelating ligands, 1,10-phenanthroline(phen), 2,2'-bipyridine(bpy), and 2,2'-bipyridylamine(dpyam) have been used in this work as a terminal didentate chelating ligand. The phen, bpy, and dpyam ligands represent a sequence of increasingly flexible chelating nitrogen ligands. The flexibility or/and the rigidity of these chelate ligands affect the dinuclear unit giving rise the variety of topologies discussed above (Figure 1). Additionally, the crystal lattice of dinuclear complexes may be stabilized by a variety of intermolecular non-covalent interactions; the more flexible dpyam chelate ligand is usually available to present the intra/intermolecular H-bonding from back H atom, while, more rigid bpy and phen ligands prefer to generate intra/intermolecular π–π stacking and CH···π interactions between pyridine groups. Consequently, the differences in the crystal packing interactions may give rise to a wide range of topologies on the dinuclear unit although the molecular entity remains. Hence, magnetic coupling depends on the global topology of the dinuclear unit and on the local Cu(II) environment, not on the crystal packing although intermolecular interactions can induce significant structural distortions.

The global topologies of the dinuclear triply bridged copper(II) compounds considered in the present work reveal the 5-fold coordinated complexes containing a carboxylato bridge which can be classified in four different families, namely, classes A, B, E, and D for compounds **1**, **2–9**, **10–13**, and **14**, respectively: Class A compound reveals the coplanar bases with a square pyramidal geometry for both Cu(II) environments with two hydroxo bridges linked in the equatorial positions. On the other hand, class B compounds display non-coplanar bases with a square pyramidal geometry for both Cu(II) ions. Here, the triatomic carboxylato and hydroxo bridges are arranged in the basal positions. Class E compounds show non-coplanar bases with a trigonal bipyramidal geometry for both Cu(II) ions and one hydroxo bridge in an axial–axial configuration. Finally, the only class D compound displays non-coplanar bases with a square

pyramidal geometry for both Cu(II) ions but with the hydroxo bridge displaced to an equatorial–equatorial configuration and two carboxylato (monatomic and triatomic) bridges are displaced to an axial–equatorial configuration.

The list of dinuclear triply bridged Cu(II) compounds considered in the present work and the available magnetic data are reported in Table 1.

Description of Magnetic properties

For dinuclear Cu(II) systems exhibiting magnetic interactions between the two paramagnetic ions, the magnetization versus temperature curves describing the magnetic behavior of these compounds can be approached, at first order, by the Bleaney–Bowers expression²⁰ which takes into account both the phenomenological Landé *g*-factor and the magnetic coupling constant *J*. For the model Heisenberg spin Hamiltonian as in eq 1

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 \quad (1)$$

the *J* value coincides with the energy difference between the singlet and triplet spin states of the corresponding dinuclear complex arising from the allowed combinations of the local doublet states of each one of the Cu ions in the d⁹ electronic configuration. This energy gap can be related to the energies of the frontier orbitals: the larger their energy separation, the stronger the antiferromagnetic contribution to *J* is. In turn, the singly occupied molecular orbitals (SOMOs) can be approached as the symmetric and antisymmetric combinations of the magnetic orbitals of each center, which consists of the antibonding combination of the metallic atomic orbitals which holds the unpaired electron with the adequate molecular orbitals of their coordinated ligands.

The singlet–triplet energy gap can be estimated using appropriate wave function methods or DFT based methods.¹⁴ In the latter, one must realize that the commonly used Kohn–Sham implementation based on the use of a single Slater determinant for the reference system of non-interacting electrons does not allow to describe open-shell singlets.^{21–23} The broken symmetry procedure suggested

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earlier by Noodleman^{24–26} and by Yamaguchi^{27–29} for the SCF-X α and UHF methods, provides a way to approach these states provided spin symmetry is recovered by proper spin projection;³⁰ in this case, the singlet–triplet gap is just twice the energy difference between the high-spin (approximate triplet) and the broken symmetry solution. Alternatively, one can make use of the Restricted Open Shell Kohn–Sham (ROKS) or Restricted Ensemble Kohn–Sham (REKS) formalisms.^{21–23}

It is also important to note that the final value of the calculated magnetic coupling constant depends on the choice of the exchange–correlation potential (i.e., the DFT method chosen). It is well-known in solid state chemistry that pure LDA and GGA functionals provide poor descriptions of magnetic systems such as transition metal oxides and halides (NiO, cuprates, manganites, etc.) which belong to a large class of compounds denoted as strongly correlated materials.¹⁴ The typical inconsistency of the LDA or GGA descriptions of the electronic structure and magnetic properties of many of these materials consists in an incorrect description of the insulating character (the magnitude and the nature of the calculated gap is too small or zero and usually of d–d type), poor spin localization (low spin states are almost close shell in nature), and showing important differences between high spin and low spin charge/spin distribution leading to strongly overestimated ferro or antiferromagnetic coupling constants. A very poor correlation with available experimental magnetic data does not allow one to confer predictive utility to these kinds of approaches. In the case of molecules, a similar behavior is observed regarding the spin and charge localization (i.e., too strong charge/spin delocalization) that also leads to a strong overestimation of either ferro or antiferromagnetic interactions and a very different nature of magnetic solutions with useless predictive utility. However, widely used hybrid functionals have shown to provide a much better and consistent description of solids and molecules and, more important, the estimated values of different properties including magnetic coupling constants are of enough predictive accuracy to provide useful magneto-structural correlations (see ref 14 and references therein).

In general, more elaborated hybrid potentials such as the M06 family or the range-screened hybrid functionals provide significantly better results,^{16,17} although all strongly depend on the amount of non-local Fock exchange chosen.¹⁴ Therefore, we rely on simpler hybrid functionals which are known to provide excellent magneto-structural correlations³¹ even if the calculated J value may differ from experiment by an almost constant factor.^{14,30,32}

In the following we summarize the most salient magnetic features of each class of triply bridged Cu(II) dinuclear compounds considered in the present work.

Class A Compounds. In class A compound (**1**) both metal atoms exhibit a distorted square base pyramidal 4 + 1 coordination (SP), with the basal planes defined by the coordinating atoms of the terminal ligand and the hydroxo bridges at the squares, strongly bonding the Cu(II) ions located at their centers. For compound **1**, the apical positions are occupied by the oxygen atoms of the formate bridge in a *syn,syn* conformation, but the Cu–O apical bonds are considerably weaker than the basal ones as can be argued from the longer distances, 2.34 Å versus 1.95–2.01 Å, respectively. The tight basal bonds place the unpaired electron of the d⁹ of each metal center in a d_{x²–y²} orbital pointing directly to the basal donors so the main magnetic exchange pathways go through the hydroxo bridges. This is clear from the calculations described below since their oxygen atoms accommodate the highest spin densities (0.095 au) while the formate oxygen atoms are almost free of it (0.0002 au). The fact that the hydroxo bridges follow almost exactly the Hodgson and Hatfield's linear relationships^{6,33} between the singlet–triplet gap and the Cu–O–Cu angle (moderate ferromagnetism from +115 to +123 cm^{–1} expected versus the +112 cm^{–1} experimental value or the +125 cm^{–1} BHHLYP calculated value, see below) confirms the secondary role of the formate bridge in the magnetic exchange for this class A compound.

Class B Compounds. Compounds in class B (**2–6**) show experimental moderately ferromagnetic coupling constants in the 120–150 cm^{–1} range except for **6** which displays a smaller value (+38.6 cm^{–1}). Their dinuclear core is also formed by two 4 + 1 SP Cu(II) ions sharing three bridging ligands, but in this case there are one hydroxo and one carboxylato bridges at basal positions, and one water molecule (or a chloride anion for **9**) in the apex. As found in compound **1**, the apical bonds are clearly longer than the basal ones (2.34–2.46 Å for aquo and 2.63–2.66 Å for chloro ligands compared to the distances in the 1.92–2.03 Å range for basal atoms) and therefore similar magnetic orbitals evolve. This suggests again that the apical bridge should not contribute significantly to the magnetic exchange between the metal atoms (spin densities on the oxygen atoms of the water bridges were found to be almost zero in all calculations). Hence, in these dinuclear systems one can interpret the resulting magnetic behavior as being mainly due to exchange interactions through the hydroxo and carboxylato ligands. In such a case, a countercomplementary effect is expected between the hydroxo bridge, which generates ferromagnetic interaction due to the orbital orthogonality, and one triatomic bridge in *syn-syn* configuration which usually contributes a weak antiferromagnetic interaction.⁶

For class B complexes it is possible to trace a correlation between structure and experimental magnetic exchange interaction using available data for compounds **4**, **7**, **8**, and **9** (see Figure 3). We excluded compound **6** from the list because the published J value was obtained from a

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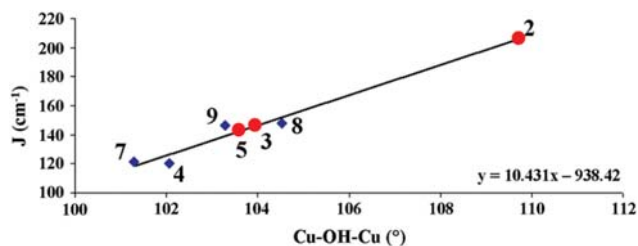


Figure 3. Plot of experimental J (cm^{-1}) versus Cu–OH–Cu angle (degrees) for class B compounds **4**, **7**, **8**, and **9**. The points corresponding to compounds **2**, **3**, and **5** (red circles) are as predicted from this linear correlation and, obviously, fit perfectly on the line.

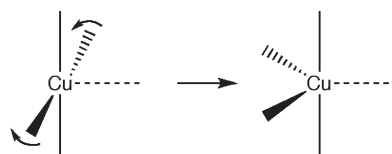
partial high temperature zone (50–200 K) fitting of the experimental data,⁶ which introduces a high uncertainty on the estimated coupling constant that lies far away from the trend line. Figure 3 shows a clear linear correlation between the experimental J value and the Cu–OH–Cu angle. This correlation indicates that the larger this structural parameter, the larger the J value (one could predict J values for compounds **2**, **3**, and **5** as +205.2, +146.1, and +142.0 cm^{-1} , see below). However, a larger number of the detailed structures and their magnetic properties are required for a clear correlation to be observed. In fact, this correlation has to be taken with caution as it will be clear from the calculated values and magnetostructural correlations discussed in the forthcoming sections using the more elaborated hybrid DFT approaches that include electron correlation effects.

Class C Compounds. This class is the most frequently studied and the magnetic coupling is dominated by the two carboxylato groups which, in general, lead to anti-ferromagnetic coupling and have been broadly studied. Consequently, this class will not be further commented.

Class E Compounds. Class E compounds **10–13** show a weaker ferromagnetic interaction (from +47 to +80 cm^{-1}). They can be described as two trigonal bipyramidal (TBP) coordinated Cu(II) centers where the axial positions are occupied by a nitrogen atom of the chelating terminal ligand and the oxygen atom of the hydroxo bridge, the latter involving the strongest bridging bonds (1.90–1.92 Å). Further, an oxygen atom of the carboxylato bridge occupies one equatorial position of each metal and shows moderately strong Cu–O bonds (2.15–2.20 Å, slightly longer than for B-class compounds), and the remaining nitrogen atom of the dpyam terminal ligands holds the second equatorial position.

For compounds **10** and **11**, the third bridging ligand is a chlorine anion that occupies the remaining equatorial positions at 2.45–2.48 Å from the metal centers, the longest coordination bond distances although considerably shorter than in B-class complex **9**: the participation of this chloro bridge on the magnetic exchange seems not so negligible. On the contrary, for compounds **12** and **13** these positions are occupied by a methoxo bridge, considerably more basic than the chlorine anion, and thus showing stronger bonds to the metal (2.13–2.17 Å), comparable to those of formate. From this analysis it is hard to argue whether all three bridges will not be magnetically active.

Scheme 1



Previous work based on simple Extended Hückel arguments assigned the “*superexchange*” mechanism for these compounds to orbital orthogonality between the Cu magnetic orbitals and oxygen p-orbital via Cu–OH–Cu unit allowing two unpaired electrons spins to be coupled high spin.⁷ This allows one to assume that the dominant ferromagnetic interaction increases with increasing bridging angle (compounds **10–12**) up to a certain maximum value and then decreases (compounds **10–13**). However, no clear correlation has been observed for class E compounds reported in the literature. Hence, it is clear that more detailed structures and magnetic properties are required to study the magneto-structural correlation in this class of compounds. DFT results in the present work provide a more general framework to understand the origin of ferromagnetism in these compounds and for a new magnetostructural correlation.

Note that the metal coordination environments for B and E class compounds can be related to each other through the Berry pseudo-rotation mechanism, that allows the transformation of a SP to a TBP through small movements of the ligands around a pivot atom (the apical one) as shown in Scheme 1.

This transformation can be monitored with the use of the τ parameter proposed by Addison et al.³⁴ which is 0.0 for a perfect SP and 1.0 for a TBP. This allows one to relate B and E class compounds by calculating the τ parameter for each metal center of each dinuclear compound and to quantitatively classify the B and E-class complexes according to the sum of the τ values of both Cu(II) ions. Thus a value close to 2.0 indicates that the two Cu(II) have a TBP environment, a value close to 0.0 indicate that the two metal atoms have a SP coordination whereas a value near 1.00 will indicate that the two coordination of the metal centers is just intermediate between SP and TBP. In Figure 4 the molecular structure of two representative complexes and the expected magnetic orbitals are depicted for clarity. In this figure compounds **5** and **11** are shown as representative of the two limiting SP-SP and TBP-TBP structures for which the expected $d_{x^2-y^2}$ or d_{z^2} magnetic orbitals arising from the local d^9 atomic configuration of the Cu(II) centers are suggested (see discussion below).

Classes D and F Compounds. Let us now briefly comment on the role of dpyam as blocking ligand instead of bpy or phen. This ligand favors the TBP geometry because of the formation of a 6-membered chelate ring that yields a higher bite angle (90–91° compared to 80–82° for the α -diimines), necessary to bind the metal through an axial and one equatorial interaction. The only exception to this rule is the Cu(II) coordination sphere in the class-D compound **14**. For this complex, both metal

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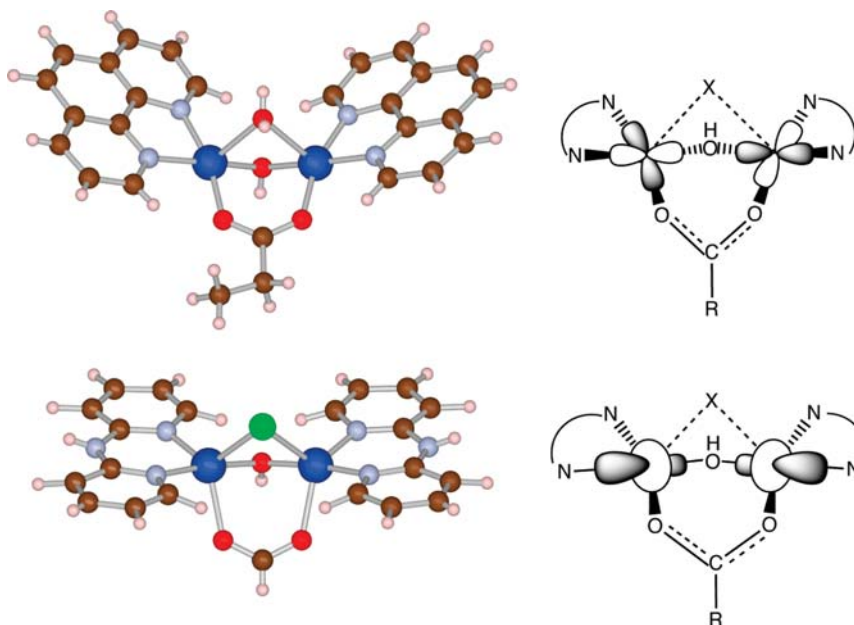


Figure 4. Molecular structure of compounds **5** (top) and **11** (bottom) as representative of the two limiting SP-SP and TBP-TBP structures. Besides the diagrammatic representation of the $d_{x^2-y^2}$ or d_{z^2} magnetic orbitals expected from the local environment of the Cu(II) centers are shown.

centers undergo noticeable distortions that are not fully accounted for by the Berry pseudo-rotation model. The Cu(1) atom can be considered in a mainly SP environment ($\tau = 0.22$) with the O(4) atom of the monodentate bridging propionate anion occupying the apical position at 2.32 Å. The high value of the dpyam bite angle (90.4°) is compensated by both a tetrahedral distortion of the basal plane (dihedral angle between the O(1)–Cu(1)–O(3) and N(1)–Cu(1)–N(2) planes of 25.7°) and a bending of the ligand (24.7° angle between the heterocyclic rings of the Cu(1)-chelating ligand). For Cu(2), the coordination environment is severely distorted from SP which is considered to be intermediate between SP and TBP ($\tau = 0.43$), although the O(5) atom of the monodentate bridging propionate lies at 2.80 Å from the metal atom, thus suggesting a very weak interaction that causes the O(4)–Cu(2)–N(5) equatorial angle to widen up to 146.2° . In addition, the equatorial bond between the Cu(2) atom and the O(2) has a long length (2.24 Å) comparable to an apical SP bond which corresponds to that typical of TBP. Because of these factors, compound **14** has the most asymmetrically coordinated magnetic centers.

It is possible to extrapolate the trends exhibited by either class B (the two Cu(II) in SP) or class E compounds (the two Cu(II) in TBP) to class F compounds which have one of the Cu(II) metal centers in SP and the other one in TBP coordination. In spite of its magnetic interest, the number of representative compounds belonging to this class is rather limited and according to the previous correlations with rather weak coupling.³⁵

Computational Details

Hybrid DFT calculations have been carried out to extract the magnetic coupling constants for all the complexes and to investigate magneto-structural correlations. The spin

polarized formalism based on a single determinant description has been considered to describe the open shell electronic states of lowest energy that correspond in all cases to the triplet ground state (described by means of a $S_z = 2$ solution, denoted as FM solution) and the first excited state that corresponds to an open shell singlet (described by means of a suitable $S_z = 0$ broken symmetry solution, denoted as BS solution). As described in section III, using the broken symmetry approach the relation between the energies of high spin and low spin solutions and J is given by $J = E(\text{BS}) - E(\text{FM})$ if the spin Hamiltonian corresponds to the expression in eq 1.

The two hybrid DFT based schemes used are the well-known and widely used B3LYP functional^{36,37} and a simplified Becke Half-and-Half functional³⁸ defined as

$$E_{xc}^{\text{BHHLYP}} = 0.5 \cdot E_x^{\text{HF}} + 0.5 \cdot E_x^{\text{LSDA}} + E_c^{\text{LYP}}$$

and denoted as BHHLYP. These DFT methods have been shown to predict reasonable estimates for the magnetic coupling constants of antiferromagnetic compounds¹⁴ although the information concerning ferromagnetic coupling is rather scarce.¹⁶ Recently developed hybrid functionals such as M06 or the range separated hybrids have shown to provide accurate estimations of magnetic coupling constants^{16,17} of dinuclear magnetic complexes and strongly correlated solids. In particular, the long-range separated hybrid functionals provide calculated J values in excellent agreement with experiment.¹⁷ These recent developments are becoming accessible in the new versions of commonly used general quantum codes but still are of limited accessibility. Therefore, in this work we have chosen two standard functionals, namely, B3LYP and BHHLYP, because of their general availability for practical applications and, also, because of the consistency of the results observed in a large amount of theoretical studies to provide meaningful magnetostructural correlations.

Standard all electron Gaussian Type Orbitals (GTO) basis sets have been used to represent the electronic density of the

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dinuclear Cu(II) complexes described in the previous section with a molecular structure extracted from the experimentally determined crystallographic structures reported in the references included in Table 1. For Cu(II) ions, a 6-3111+g basis set^{39,40} extended with an f-function ($\zeta = 0.528$) has been used (corresponding to a [14s9p5d1f/9s5p3d1f] contraction) whereas a 6-31g* basis set has been used for the remaining atoms (corresponding to a [4s/2s] contraction for H atoms, a [10s4p1d/3s2p1d] contraction for C, N, and O atoms⁴¹ and a [16s10p1d/4s3p1d] contraction for Cl atoms.⁴² Single-point energy evaluation runs were carried out for the crystallographic structures of the isolated dinuclear ions without further geometry optimization. This prevents mixing structural and electronic effects and introducing errors in the magnetic coupling constants arising from errors in the structure optimization. In two cases, compounds **12** and **13**, the H atom belonging to the OH bridging group was adjusted to a position close to that corresponding to the remaining systems since, on the one hand, the available crystallographic positions were not consistent with the typical bridging mode of this group and, on the other hand, the calculated data clearly indicate a deviation from the trend exhibited by the whole series of compounds. Hence, we used $d(\text{O}-\text{H}) = 0.90 \text{ \AA}$ with the O-H bond forming an angle of $\sim 40^\circ$ with the vector normal to the Cu-O(H)-Cu plane and closer to the carboxylate group whereas the Cu-O distances and all the remaining structure has been fixed to the crystallographic data. All calculations were carried out using the Gaussian03 suite of programs.⁴³

We end this section by noting that spin contamination is rather small, and in line with results found in previous studies. For all the systems and methods considered in this work, the expected values for the square of the total spin operator ($\langle S^2 \rangle$) are in the [2.004–2.006] range for the ferromagnetic (or high spin) solution and in the [0.989–1.005] range for the low spin (broken symmetry) solutions, that is, a maximum deviation of +0.006 from the $\langle S^2 \rangle = 2.000$ value for a triplet state and a maximum deviation of –0.011 from the $\langle S^2 \rangle = 1.000$ value for a perfect 50% singlet–triplet mixing state expected for a single Slater determinant broken symmetry description of a localized open-shell singlet. These values are, in our opinion, small enough to trust the J values obtained from this spin polarized single determinant approximation to the singlet–triplet energy gap.

Results and Discussion

At first sight, comparing the experimental and calculated magnetic coupling constants for compounds **2–14** is quite

Table 2. Calculated J and Addison τ Values (Aggregate and Components) for the Dinuclear Triply-Bridged Copper(II) Compounds Listed in Table 1^a

compound	$\tau (\tau_1 + \tau_2)$	J_{calc}		J_{exp}
		BHLYP	B3LYP	
1		125.5	220.3	112.7
2	0.86 (0.43 + 0.43)	53.2	120.9	
3	0.40 (0.21 + 0.19)	79.6	166.3	
4	0.37 (0.21 + 0.16)	80.4	166.6	120.8
5	0.27 (0.08 + 0.19)	85.6	181.4	
6	0.37 (0.21 + 0.16)	83.2	169.0	38.6
7	0.34 (0.20 + 0.14)	80.5	169.7	120.0
8	0.37 (0.21 + 0.16)	87.0	176.7	148.9
9	0.69 (0.41 + 0.28)	69.4	146.8	145.3
10	1.34 (0.67 + 0.67)	83.6	185.7	79.1
11	1.44 (0.72 + 0.72)	78.3	161.3	79.7
12	1.28 (0.64 + 0.64)	82.4	162.6	62.5
13	1.14 (0.57 + 0.57)	34.2	108.1	47.8
14	0.65 (0.22 + 0.43)	57.6	99.2	24.1

^aNote that positive J values correspond to a ferromagnetic ground state.

frustrating (Table 2) since, contrarily to broad experience for antiferromagnetic compounds,^{14,31} the overall agreement between calculation and experiment is rather poor although, except for compound **6** (see above discussion), the experimental singlet–triplet value is always between the two sets (BHLYP and B3LYP) of calculated values. At this point one may wonder whether the experimental measurements are accurate enough or the calculations are failing. Two comments are appropriate here. First, magnetic measurements for ferromagnetic compounds are more delicate than for antiferromagnetic complexes because they are strongly influenced by remaining paramagnetic impurities and because the interaction between the ferromagnetic molecules cannot be neglected as it is currently done in the models used to fit magnetic susceptibility to experiments. For instance, for the present compounds, the fitting procedures leads to antiferromagnetic zJ' mean field parameters in the –0.2 to –0.9 range and a 6% content of paramagnetic impurities.² Moreover, the published J value for compound **6** was obtained from a partial high temperature zone (50–200 K) fitting of the experimental data, which introduces even more uncertainty to the estimated coupling constant. Second, there is a large body of evidence that hybrid DFT calculations are able to properly describe the trends for antiferromagnetic and ferromagnetic compounds and, depending on the exchange-correlation potential used, even to accurately reproduce the experimental values.^{16,17,31} Hence, one may suggest to trust the calculated values, at least in what concerns the main trends, and inspect the information provided by the calculations in detail. To this end it is convenient to make use of the structural parameter τ introduced by Addison et al.³⁴ and discussed in the previous section. In Figure 5, the BHLYP calculated J values of class B and class E compounds are plotted with respect to the sum of the τ values for each metallic centers obtained by the PLATON code.⁴⁴ This plot reveals interesting magnetostructural correlations which are not apparent from the experimental values only. In addition and in spite of the different values predicted by BHLYP and B3LYP, the experimental values lie in the range of values

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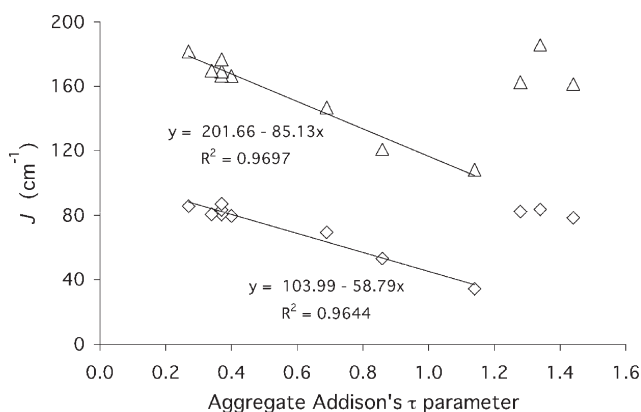


Figure 5. Plot of the B3LYP (triangles) and BHHLYP (diamonds) calculated J values (in cm^{-1}) versus the aggregate Addison's τ parameter for classes B (2–9 plus 13) and for E compounds (10–12).

predicted by both methods and both methods predict the same trends. However, one must warn that available structural data from measurements on the complexes of interest in the present work do not cover a broad enough range of aggregate τ values to firmly confirm the trends predicted above. In any case, results in Figure 5 clearly show that the proposed magnetostructural relationships discussed above are meaningful.

In fact, it appears that for class B compounds 2 to 9, the calculated J values, predicted by the BHHLYP (or by the B3LYP functional), correlate reasonably well with the sum of the experimental τ parameters corresponding to each Cu atom. However, this result is opposite to the observations by Kahn¹ and Journaux⁴⁵ for the antiferromagnetic J coupling constants for several oxalato dinuclear Cu(II) complexes with pentacoordinated environments. These authors found that the closer the coordination to SP, the larger the antiferromagnetic interactions (more negative J values) whereas Figure 5 reveals that for the class B compounds examined in the present work, the closer the coordination to SP, the larger the ferromagnetic interactions (more positive J values). This is because the oxalate system and the present class B compounds exhibit different topologies and different magnetic behavior. Interestingly enough, compound 13, which according to the structural data and also to the τ value has been classified as belonging to class E, follows the correlation above for class B. This is because the τ value is very close to the lower bound of τ values defining class E and, therefore, the calculated J value and the magnetostructural correlation above seem to provide a more solid argument than those from simple structural data. Accepting that compound 13 behaves as class B leaves us with only three compounds in class E with the subsequent difficulty to obtain a meaningful magnetostructural correlation. Nevertheless, the plot in Figure 5 shows that J also correlates with the aggregate τ parameter although with a much smaller slope.

Kahn¹ and Journaux⁴⁵ interpreted the enhancement of the antiferromagnetic coupling as arising from the increasing in the overlap of the metal magnetic orbitals, mainly the $d_{x^2-y^2}$ atomic orbital of the d^9 metal atom, with the bridging ligand with a concomitant intensification of the coupling pathway through the basal positioned bridges, whereas the distant

apical ligands are not involved in magnetic exchange. On the contrary, for TBP environments the magnetic orbital is d_{z^2} in nature, in such a way that the exchange pathways through the bridging ligands would be less intense but magnetic interaction is now spread across all five ligand atoms and involves all three bridges. For the triply bridged complexes studied in the present work, the arguments above are illustrated in Figure 4 along with two representative structures studied in the present work. However, one must recall that magnetic interactions are strongly dominated by electron correlation effects and, hence, simple orbital interpretations may be misleading, especially for ferromagnetic interactions. A proper interpretation would require a deep analysis of configuration interaction wave functions such as those reported by Cabrero et al.^{12,13} for model systems.

Next, we analyze the magnetostructural correlation shown in Figure 5 in depth. For B-class compounds, the magnetic orbitals are located on the basal plane pointing directly toward the oxygen atoms of the hydroxo and carboxylato bridges (Figure 4, top), which have short bond distances and hence are effective in coupling the exchange interactions between the two paramagnetic ions. From orbital arguments, the resulting moderately large ferromagnetic interaction can be explained invoking the countercomplementary effect,⁶ except for the above commented compound 6. Note that the apical aqua ligand (third bridge) do not contribute to the magnetic exchange, as their spin density is negligible in both triplet and BS solutions for all calculations. However, it is worth mentioning that the B3LYP calculations for complex 9 on the triplet state lights up some spin density on the chlorine bridge (0.7% versus 0 in the BS singlet). Interestingly enough, all calculations show an increase of spin density in the oxygen atom of the hydroxo bridge in the triplet state which is even larger than for the Cl bridge suggesting an active role of this bridging ligand in the magnetic interactions.

Next, let us focus on the E-class complexes where the metal contribution to magnetic orbitals is d_{z^2} (Figure 4, bottom) with the axial lobe pointing toward the shortest Cu-bridge distances (1.90–1.92 Å) which correspond to the hydroxo bridge. This strongly suggests that the hydroxo bridge is the responsible one for the most intense exchange pathway, which is confirmed by the high spin density values for the oxygen atom of the hydroxo group (~9% and ~17% in the BHHLYP and in B3LYP triplet calculations, respectively). Both equatorial bonds are weaker but, contrarily to what is found for class B, they are of comparable strength, indicating an active participation in the magnetic coupling. In fact, the spin density on the oxygen atoms of the carboxylato ligands is similar to that found in class B, but now the third bridge (chlorine atom for compounds 10 and 11) lights up in the triplet state with a non negligible spin density of 3% from BHHLYP and 7% upon B3LYP. This is clear from the spin density plots⁴⁶ for the ferromagnetic ground state of compound 11 (the compound with largest aggregate τ) and also for compound 5 (the compound with smallest aggregate τ) shown in Figure 5. Note, that the magnetic orbitals arising from these calculated spin density plots is in agreement with the qualitative arguments depicted in Figure 6 and evidence the large spin polarization of the hydroxo groups. This explains that the calculated value for compounds 10 and 11

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(46) Spin density plots have been generated using the VESTA package version 2.0.3 by Momma, K.; Izumi, F. *J. Appl. Crystallogr.* **2008**, 41, 653.

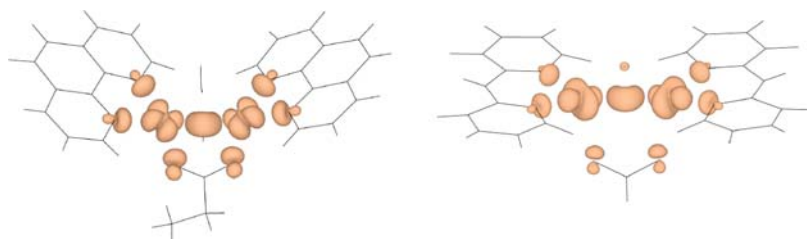


Figure 6. Spin density plots for the ferromagnetic ground state of compounds **5** (left) and **11** (right). Notice that these correspond to the two compounds with smallest and largest aggregate τ value, respectively.

corresponds to ferromagnetic couplings larger than expected from the magnetostructural correlation found for class B compounds (including **13**) based on the aggregate τ parameter (see Figure 5). This evidences the important role played by Cl (or methoxo in **12**) as the third bridge. This behavior may be due to the higher σ - and π -donor character of chloro ligands compared to water. These interactions are similar to those occurring for the hydroxo bridge, but because of its weaker field and higher covalency, chloro bridging ligands are able to allow further magnetic interactions between the Cu atoms with a reduced Cu–Cl–Cu angle (over 75 degrees) which, according to Hatfield's trends,³³ seems to favor ferromagnetic exchange. Nevertheless, experimental coupling constants for compounds **10** and **11**, together with the dubious value for compound **6**, are below $+100 \text{ cm}^{-1}$ indicating that the magnetic activity of the chloro bridge does not compensate the overall bond weakening because of the TBP geometry of the metals.

Compounds **12** and **13** belong to class E and have the peculiarity that the third bridge is a methoxo ligand. They have the same chemical formula for the dinuclear cation and only differ in the counterion which is percholate for **12** and hexafluorophosphate for **13**. This chemical difference leads to two structurally similar dinuclear ions, with differences induced mostly by the crystal packing. The most important variations are 0.1 Å in the Cu–Cu distance, 5° in the Cu–O(H)–Cu and Cu–O(CH₃)–Cu angles, and differences in the aggregate τ parameters for the Cu(II) ions, 0.64 and 0.57 for **12** and **13**, respectively. Noticeably, the magnetic coupling constant for **12** is 30% larger than for **13**. For these two compounds all attempts to carry out DFT calculations using the original crystal structure failed to converge. This has been attributed to an inaccurate assignment of the position of the hydrogen atom of the hydroxo bridge in these crystallographically symmetric compounds, that resulted in a rather strange trigonal-planar geometry for the oxygen atom. To achieve a more chemically sound nearly tetrahedral configuration, we then moved the hydrogen atom of the OH bridging ligand toward the carboxylato bridge. This small variation in the atomic position of this H atom lead to calculations that easily converge and to reasonable magnetic coupling values, which are the ones included in Table 2. It is important to point out that **12** and **13** exhibit the characteristic feature of the triplet state spin density “lighting on” over the oxygen atom of the hydroxo bridge (similar values to that reported for **10** and **11**), but here also over the oxygen atom of the methoxo bridge with similar contribution (from 0 to 6 or 17% in BHHLYP and B3LYP methods). This result suggests that the methoxo bridge contributes to the ferromagnetic exchange in a strength comparable to that of the hydroxo bridge. Nevertheless, the dominating factor for the magnetic

coupling in both compounds seems to be the coordination geometry of the copper atoms: the τ values for the Cu(II) ions in **13** is 0.57 (1.14 aggregate), very close to that of Class B compounds, in such a way that their calculated J value is in accordance with that expected for the class B magnetostructural correlation above commented. On the contrary, calculated and experimental J values for complex **12** align better to the ones found for the remaining E class compounds as the τ values for **10**, **11**, and **12** are not so different compared to compound **13** although here the number of compounds is too small to extract a meaningful correlation.

Complex **14** belongs to class D compounds where, like in class B, the metal atoms lie in a mainly SP coordination although the environment of the Cu(2) with $\tau = 0.43$ corresponding to a nearly intermediate geometry is considerably more distorted than the one corresponding to Cu(1) where $\tau = 0.22$. In this case, the pyramids do not share the same bridging ligand at the apical positions (Figure 1). For this complex, the basal planes accommodating the $d_{x^2-y^2}$ metallic contribution to the magnetic orbitals are almost perpendicular, and the hydroxo bridge is the only one sharing both basal planes and is tightly bonded to both Cu(II) ions. The O(3) and O(2) atoms from the $\mu^2(\eta^1, \eta^1)$ -bridging carboxylate occupy one Cu(1) basal and one Cu(2) apical positions, respectively, and the O(4) atom of the $\mu^2(\eta^2)$ -carboxylate lies at the apical position of Cu(1) and one basal position of Cu(2). In this complex, only the O(1) atom of the hydroxo ligand changes significantly its spin density from singlet to triplet states (from almost zero to 9% or 16% for BHHLYP and B3LYP, respectively). Presumably this is the only bridge that plays a noticeable role in the magnetic exchange and, consequently, a small ferromagnetic interaction is expected because of the topological orthogonality of the magnetic orbitals.¹

Next, we discuss possible magnetic exchange pathways for class D compound **14**. A first possibility involves a single Cu–OH–Cu (101.8°) unit which links Cu(II) centers in an basal–basal configuration. This structure can occur because of the nearly intermediate geometry ($\tau = 0.43$) of one of the Cu(II) centers. Consequently, another possible pathway is the triatomic carboxylato bridge, and the small J value ($+24.1 \text{ cm}^{-1}$) may result from a countercomplementary effect between the monatomic bridge, with a small bridging angle which usually contributes the ferromagnetic interaction due to the orthogonality between the Cu magnetic orbitals and the oxygen p-orbital, and the triatomic carboxylato bridge which usually contributes to an antiferromagnetic interaction.

Conclusions

In this work we used hybrid DFT calculations to investigate the magnetic coupling and magnetostructural correlation of a

series of Cu(II) dinuclear complexes which have the common particularity, over other well-known families of Cu(II) dinuclear complexes, of incorporating a third bridging ligand, resulting in three different bridging ligands. The addition of this ligand is not innocent since it turns out to largely favor ferromagnetic interactions, as opposed to the broad class of Cu(II) dinuclear complexes with one or two bridging ligands which usually result in an antiferromagnetic compound.

Comparison of calculated and experimental values of the isotropic magnetic coupling constant J is not as straightforward as it may seem because, on the one hand, the calculated results depend strongly on the amount of Fock exchange used in the exchange correlation functional and, on the other hand, the accuracy of the measured values is not as good as for antiferromagnetic compounds. The good news is that calculated values (BHHLYP and B3LYP) lead to a range of values where almost all experimental data fit. However, analysis of the experimental data and comparison to structural data does not reveal any meaningful correlation. Assuming that the calculated values are good enough to provide a meaningful trend allows one to unravel a very interesting magnetostructural correlation for class B compounds, namely, that the magnitude of the calculated magnetic coupling constant correlates almost quantitatively with the sum of the Addison's τ parameter of each Cu(II) cation. The existence of this correlation opens the way for the guided synthesis of new complexes with higher ferromagnetic character that may in turn lead to important technological applications.

Concerning the relationship between J and the Cu–OH–Cu angle discussed above, one must advert that it fits the experimental data on the set of compounds **4**, **7**, **8**, and **9** only and not for the rest of compounds investigated in the

present work. Nevertheless, we must realize that for this set, the aggregate τ range is very narrow (between 0.34–0.37). Therefore, the almost constant value of this coordination parameter implies that variations of J can be attributable to the Cu–OH–Cu angle. For fixed τ , this empirical correlation does not show up from the calculated values although a dispersion of the J values in a restricted J interval ($\sim 10 \text{ cm}^{-1}$) is observed. More experimental data on compounds having diverse combinations of aggregate τ and Cu–OH–Cu angles are needed to properly investigate this double dependency.

To conclude, using ligands favoring the square based pyramidal coordination on each Cu(II) atom in a triple bridge is the key to obtain complexes with enhanced ferromagnetic character. Available data for class E compounds also indicate that this enhancement can also be achieved by using a third ligand favoring the interaction through the $d_{x^2-y^2}$ orbitals. In addition, the theoretical correlation indicates that there is an upper limit of $+200 \text{ cm}^{-1}$ (when aggregate τ is 0) for the ferromagnetic coupling in this kind of hetero-triply bridged compounds, and this fact must be accounted by the experimentalists.

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Synthesis and crystal structure of two new dinuclear oxalato-bridged copper(II) complexes containing bis(2-pyridyl)amine as a ligand

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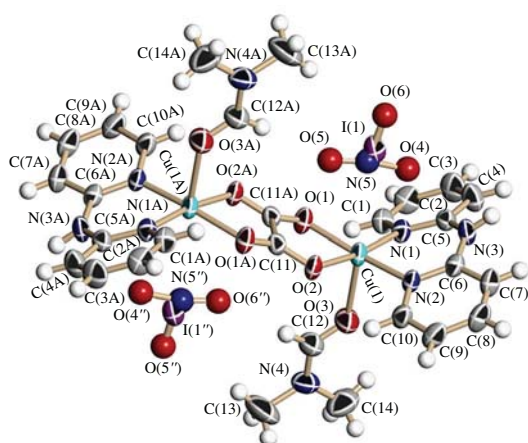
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Two new dinuclear oxalate-bridged copper(II) complexes $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{DMF})_2](\text{I})_{1.6}(\text{NO}_3)_{0.4}$ and $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{DMF})_2](\text{ClO}_4)_2$ (dpyam = di-2-pyridylamine) were prepared directly from their components by the molar ratio method and their crystal structures were determined by X-ray crystallography.

Over the last two decades increasing interest has been devoted to study of exchange interactions between metal ions through extended bridging groups in dinuclear and polynuclear metal complexes.¹ Dinuclear copper(II) complexes with the oxalate dianion acting as a bis-didentate bridging ligand are suitable model compounds for magneto-structural correlations.^{2–14} General trends of magnetic behaviours of these compounds are well established, the oxalate bridge being very efficient in transmission of the antiferromagnetic interactions between the two copper(II) atoms.⁴ The crystal structures, spectroscopic properties and magneto-structural correlation of the most relevant complexes were described previously.⁵ The exchange interaction between copper ions *via* the oxalate bridge is strongly dependent on the geometry around the copper ions, which is sensitive to the nature of counterions, solvent molecules and terminal ligands. In order to extend the investigation by modifying to other counterions and solvents, this paper reports the synthesis and the results of the structure determination of dinuclear oxalate-bridged copper(II) complexes, $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)$ -

$(\text{DMF})_2](\text{I})_{1.6}(\text{NO}_3)_{0.4}$ **1** and $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{DMF})_2](\text{ClO}_4)_2$ **2**.[†]

The structure of **1** consists of the centrosymmetric dinuclear cation $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{DMF})_2]^{2+}$ and non-coordinating I^- and NO_3^- anions in site occupancies of 0.8 and 0.2, respectively (Figure 1).[‡] Each Cu^{II} centre is pentacoordinated to two nitrogen atoms of a dpyam ligand and two oxygen atoms of the oxalate bridge [Cu–N/O distances vary from 1.970(3) to 2.021(2) Å] in the basal plane, with the axial site occupied by an oxygen atom of DMF [$d(\text{Cu}^{\text{II}}\text{--O})$ 2.270(3) Å] giving approximately $\text{CuN}_2\text{O}_2\text{O}'$ chromophore. The Cu...I (3.415 Å) and Cu...ONO₂ (2.990 Å) distances are quite long, which have been considered as a very weak interaction.¹⁵ Several parameters are used to define the coordination environment around the pentacoordinated metal center, and one of the most commonly used parameters is the factor τ ($\tau = 0$ for an ideal square pyramid, and $\tau = 1$ for an ideal trigonal bipyramid), the value of which is zero, suggesting an almost ideal square pyramidal geometry of Cu^{II} . The four basal atoms are not coplanar, showing a slight tetrahedral distortion with a dihedral angle of 9.8(1)° formed



between the CuN_2 and CuO_2 planes. The copper atoms are slightly (by 0.004 Å) displaced from the basal planes toward the apical positions and are slightly linked through a bis-didentate oxalate molecule with a $\text{Cu}\cdots\text{Cu}$ separation of 5.219(1) Å; the dihedral angle formed between the basal plane and the oxalate plane of $16.4(1)^\circ$ agrees with the planar central $\text{Cu}\text{--ox}\text{--Cu}$ core.⁷ The non-coordinated iodide and nitrate anions occur in the same positions in the lattice structure, which have 80 and 20% occupancies for I^- and NO_3^- , respectively. The weak hydrogen bonding occurs between the amine N atom and the I^- ($\text{N}\cdots\text{I}$ distances 3.656 Å) and the N_{amine} and $\text{O}_{\text{nitrate}}$ ($\text{N}\cdots\text{O}$ distances 2.974 Å) of neighbouring units.

The structure of complex **2** (Figure 2)[‡] is isotypic only in terms of Cu^{II} based complex with **1**. The geometry around the copper atom can be considered as an almost square pyramidal environment ($\tau = 0$). The corresponding $\text{Cu}\text{--O}$ and $\text{Cu}\text{--N}$ distances in the basal plane are in the range from 1.972(2) to 2.011(2) Å, while the axial $\text{Cu}\text{--O}_{\text{DMF}}$ bond distance [2.204(2) Å] is significantly longer than those in the basal plane. The four donor atoms on the equatorial plane are not perfectly planar, showing a small tetrahedral distortion, with a dihedral angle of $15.5(1)^\circ$ formed between the CuO_2 and CuN_2 planes. Both copper atoms are linked through an oxalate bridge, with a $\text{Cu}\cdots\text{Cu}$ distance of 5.221(6) Å and the dihedral angle formed between the basal plane and the oxalate plane is $17.4(1)^\circ$. The copper atom is lifted 0.008 Å out of that plane toward the apical position. The perchlorate anion is close to the coordination sphere of $\text{Cu}(\text{I})$ but the quite long $\text{Cu}\cdots\text{OClO}_3$ distance of 3.041 Å seems to indicate a very weak interaction. The hydrogen bonding occurs between the amine N atom and an O atom of neighbouring perchlorate with a $\text{N}\cdots\text{O}$ contact of 2.998(1) Å.

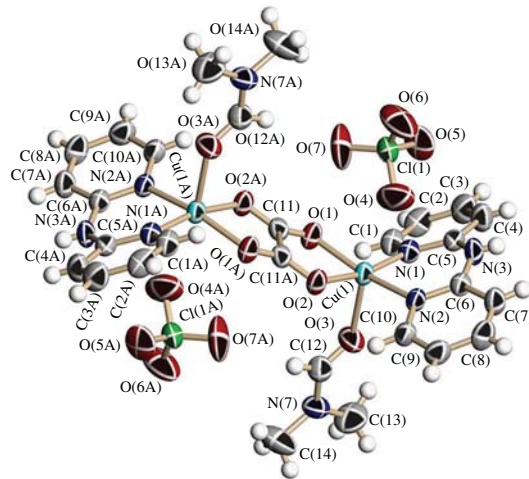


Figure 2 Plot of the structure of $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{DMF})_2](\text{ClO}_4)_2$. Atoms with an 'A' are generated by a mirror plane. Selected bond lengths (Å): $\text{Cu}(\text{I})\text{--N}(\text{I})$ 1.972(2), $\text{Cu}(\text{I})\text{--N}(\text{2})$ 1.983(2), $\text{Cu}(\text{I})\text{--O}(\text{1})$ 2.011(1), $\text{Cu}(\text{I})\text{--O}(\text{2})$ 1.994(2), $\text{Cu}(\text{I})\text{--O}(\text{3})$ 2.204(2), $\text{Cu}(\text{I})\text{--O}(\text{4})$ 3.041(1), $\text{Cu}(\text{I})\text{--Cu}(\text{1A})$ 5.221(6); selected bond angles ($^\circ$): $\text{N}(\text{1})\text{--Cu}(\text{1})\text{--N}(\text{2})$ $91.22(9)$, $\text{N}(\text{1})\text{--Cu}(\text{1})\text{--O}(\text{2})$ $168.16(9)$, $\text{O}(\text{2})\text{--Cu}(\text{1})\text{--O}(\text{1})$ $82.76(8)$, $\text{N}(\text{1})\text{--Cu}(\text{1})\text{--O}(\text{3})$ $91.76(9)$, $\text{N}(\text{2})\text{--Cu}(\text{1})\text{--O}(\text{2})$ $92.59(9)$, $\text{N}(\text{2})\text{--Cu}(\text{1})\text{--O}(\text{3})$ $94.56(9)$, $\text{N}(\text{1})\text{--Cu}(\text{1})\text{--O}(\text{1})$ $91.25(9)$, $\text{O}(\text{2})\text{--Cu}(\text{1})\text{--O}(\text{3})$ $99.10(9)$, $\text{N}(\text{2})\text{--Cu}(\text{1})\text{--O}(\text{1})$ $167.84(9)$, $\text{O}(\text{1})\text{--Cu}(\text{1})\text{--O}(\text{3})$, $97.26(9)$.

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[‡] Crystallographic data for **1**: at 273(2) K crystals of $\text{C}_{28}\text{H}_{32}\text{N}_8\text{Cu}_2\text{O}_{7.2}\text{I}_{1.6}$ are triclinic, space group $P\bar{1}$, $a = 8.4614(4)$, $b = 8.9112(4)$ and $c = 12.3824(6)$ Å, $\alpha = 71.913(1)^\circ$, $\beta = 76.329(1)^\circ$, $\gamma = 80.225(1)^\circ$, $V = 857.68(7)$ Å³, $Z = 1$, $M = 973.50$, $d_{\text{calc}} = 1.889$ g cm⁻³, $\mu(\text{MoK}\alpha) = 3.095$ cm⁻¹, $F(000) = 476$.

Crystallographic data for **2**: at 293(2) K crystals of $\text{C}_{28}\text{H}_{32}\text{N}_8\text{Cu}_2\text{O}_{14}\text{Cl}_2$ are triclinic, space group $P\bar{1}$, $a = 8.4780(5)$, $b = 9.1158(6)$ and $c = 12.7487(8)$ Å, $\alpha = 70.055(10)^\circ$, $\beta = 74.391(10)^\circ$, $\gamma = 77.445(1)^\circ$, $V = 883.39(10)$ Å³, $Z = 1$, $M = 902.60$, $d_{\text{calc}} = 1.679$ g cm⁻³, $\mu(\text{MoK}\alpha) = 1.434$ cm⁻¹, $F(000) = 460$.

Intensities of 4658 and 10621 reflections for **1** and **2**, respectively, were collected at 273 K for **1** and at 293 K for **2**, on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinements were performed using the program SAINT [Siemens. SAINT, Version 4]. An empirical absorption correction with the SADABS program¹⁶ was applied, which resulted in transmission coefficients ranging from 0.527 to 1.000 for complex **1** and from 0.776 to 1.000 for complex **2**.

The structures were solved by direct methods and refined by a full matrix least-squares method on F_{obs}^2 with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package. For **1** and **2**, respectively, the refinement converged to $wR_2 = 0.0878$ and 0.0976 , $\text{GOF} = 1.037$ and 1.041 for all independent reflections [$R_1 = 0.0340$ and 0.0480 was calculated against F for 3083 and 4245 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXS-97 and SHELXL-97. For complex **1**, the I^- anion has an occupancy factor of 0.80. Simultaneously, there is a nitrogen atom from NO_3^- ion practically coincident with the I^- with an occupancy factor of 0.20. Introducing the fractional NO_3^- ion into the model caused the R value to drop from 0.062 to 0.034. All hydrogen atoms in **2** were located in a difference Fourier map and refined isotropically, while all hydrogen atoms in **1** were fixed and allowed to ride on attached atoms. The ClO_4^- anion in **2** is disordered, with two conformers having occupancy factors of 0.5.

CCDC 689326 and 689327 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

New Trinuclear Carbonato-Bridged Copper(II) Complexes: Synthesis, Crystal Structure, and Spectroscopic Properties¹

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Abstract—New trinuclear carbonato-bridged copper(II) complexes, $[\text{Cu}_3(\text{Bipy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**I**) and $[\text{Cu}_3(\text{Phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**II**) (Bipy = 2,2'-bipyridine and Phen = 1,10-phenanthroline), have been synthesized and characterized by X-ray crystallography. In the trinuclear units, a carbonate anion triply bridges three Cu atoms in a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ mode. The environment around each copper(II) center is five-coordinate ranging between intermediate to distorted square-pyramidal geometry. In the crystal packing, the molecule of **I** is involved in a variety of intra/intermolecular non-covalent interactions such as intra/intermolecular stacking and $\text{CH}\cdots\pi$ interactions between the pyridine groups of the chelated ligand, leading to a one-dimensional arrangement of **I**. In complex **II**, the molecule is involved in both intra- and intermolecular Phen–Phen π -stacking, forming a three-dimensional network. The spectroscopic (IR, diffuse reflectance, and EPR spectra) properties and the preliminary results of magnetic measurements of both complexes are investigated and compared to other closely related trinuclear copper(II) complexes.

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INTRODUCTION

The coordination chemistry of the carbonate anion has received considerable attention for many years, especially in polynuclear carbonato-bridged copper(II) complexes. More recently inspiration for this field was drawn from bioinorganic chemistry [1, 2] and from the relationship between the coordination modes of the carbonate ligand and the magnetic properties [3–11]. The carbonate anion is an extremely versatile bridging ligand, each oxygen atom of this anion may act as a monodentate, bridging Bifunctional, or trifunctional ligand able to generate complexes with different nuclearity including dinuclear [10, 11], trinuclear [7–9], tetranuclear [3], and hexanuclear species [5] and even one- or two-dimensional systems [4, 6]. In function of the coordination mode of the carbonate ligand, the magnetic behavior of complexes varies greatly: from strongly coupled to moderate or weak antiferromagnetic complexes and even ferromagnetic ones. Several polynuclear carbonato-bridged copper(II) complexes resulted from the fixation of CO_2 from air [1, 12] and from direct preparation from the carbonate salt. In spite of the general interest, only a limited number of previous reports are available of a systematic study of procedures for the synthesis of dif-

ferent nuclearities [5]. With our aim of the synthetic methods and magnetochemistry of the μ -carbonato coordination complexes with the di-2-pyridylamine (**Dpyam**), 2,2'-bipyridine (**Bipy**), and 1,10-phenanthroline (**Phen**) as a chelating N-donor ligands, different copper salts were used as starting reagents to study the ability of this system in fixing atmospheric CO_2 or Na_2CO_3 . Both synthetic methods were carried out as a continuation of our earlier research and the result of direct preparation allows us to generate two new trinuclear copper(II) complexes, $[\text{Cu}_3(\text{Bipy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**I**) and $[\text{Cu}_3(\text{Phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**II**). We report herein the synthesis, crystal structure, and spectroscopic properties (IR, reflectance, EPR) and the preliminary results of the magnetic measurements of both complexes.

EXPERIMENTAL

Reagent and physical measurements. All reagents are commercial grade materials and were used without further purification. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrophotometer as KBr discs in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a UV-VIS-NIR scanning spectrophotometer and a UV-

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3101PC (SHIMADZU) spectrophotometer in the 3000–52000 cm⁻¹ spectral range. X-band powder EPR spectra were obtained on a Bruker-EMXplus electron spin resonance spectrometer (field calibrated with DPPH; $g = 2.0036$). Magnetic susceptibility measurements (5–350 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Synthesis of I. Complex **I** was prepared by adding a warm solution (10 ml) of Bipy (0.312 g, 2.0 mmol) in DMF to a warm aqueous solution (10 ml) of Cu(CF₃SO₃)₂ (0.362 g, 1.0 mmol), and then a warm aqueous solution (5 ml) of Na₂CO₃ (0.052 g, 0.5 mmol) was added. On slow evaporation in air, blue crystals of **I** were formed after two weeks. The yield of the complex was 55%.

For C₆₅H₄₈N₁₂F₁₂O₁₆S₄Cu₃ (**I**)

anal. calcd., %: C, 43.14; H, 2.67; N, 9.29.

Found, %: C, 43.20; H, 2.62; N, 9.31.

Synthesis of II. A warm aqueous solution (10 ml) of Cu(CF₃SO₃)₂ (0.362 g, 1.0 mmol) was added by a warm solution (7 ml) of Phen (0.396 g, 2.0 mmol) in 5 : 2 ratio of methanol to DMF followed by a warm aqueous solution (5 ml) of Na₂CO₃ (0.035 g, 0.3 mmol). After two weeks, green crystals of **II** were formed. The crystals were filtered off and dried in air. The yield of the complex was 60%.

For C₇₇H₄₈N₁₂F₁₂O₁₆S₄Cu₃ (**II**)

anal. calcd., %: C, 47.78; H, 2.44; N, 8.68.

Found, %: C, 47.56; H, 2.49; N, 8.65.

X-ray diffraction analysis. Data for complex **I** were collected at 273 K on a 4 K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å) using the SMART program [13]. Raw data frame integration was performed with SAINT [14], and the correction for Lorentz and Polarization effects was also applied. An empirical absorption correction by using the SADABS program [15] was applied, which resulted in transmission coefficients ranging from 1.000 to 0.606 Å for **I**. The structure was solved by direct methods and refined by the full-matrix least-squares method on (F_{obs})² with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package [16]. All hydrogen atoms in **I** were geometrically fixed and allowed to ride on the attached C atoms. All oxygen and fluorine atoms of trifluoromethanesulfonate groups in **I** are disordered with site occupancies of 0.50 including one carbon atom of the triflate mole-

cule. The water oxygen atom of **I** is refined with site occupancies of 0.5.

Reflection data for complex **II** were collected at 293 K on a 1 K Bruker SMART CCD area-detector diffractometer (graphite-monochromated MoK_α radiation, $\lambda = 0.71073$ Å). Data reduction and cell refinements were performed using the SAINT program [17]. An empirical absorption correction by using the SADABS [15] program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.841 for **II**. All non-H atoms were refined anisotropically. All hydrogen atoms in **II** were geometrically fixed and allowed to ride on attached atoms. The carbonate group in **II** are found to be disordered with site occupancies of 0.5. Two water oxygen atoms of **II** are refined with site occupancies of 0.25. All oxygen and fluorine atoms of three trifluoromethanesulfonate groups in **II** are found to be disordered with site occupancies of 0.50. The fourth triflate group is also disordered, and attempts have been made in range possibilities to locate disordered atoms but were unsuccessful. Finally, we decided to refine them as an ordered molecule with quite high but reliable temperature factors. The bond distances of two triflate molecules were restrained with the DFIX 1.57(1), 1.32(1), and 1.86(1) commands for some S–O, C–F, and C(77)–S(4) bond lengths, respectively, with an isotropic refinement of F(8)A. The crystal and refinement details for complexes **I** and **II** are listed in Table 1. Selected bond lengths and bond angles are listed in Table 2. The coordinates of the atoms and the thermal parameters were deposited with the Cambridge Crystallographic Data Centre (nos. 669505 and 669506 for structures **I** and **II**, respectively; deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The structure of complex **I** consists of trinuclear [Cu₃(Bipy)₆(μ₃-CO₃)]⁴⁺ units, which is shown in Fig. 1. The asymmetric unit also contains four non-coordinating trifluoromethanesulfonate anions and half a molecule of lattice water. The three copper(II) atoms are connected to each other through the oxygen atoms from the bridging carbonate group with the μ₃-η¹:η¹:η¹-CO₃ coordination mode, giving a triangular array of copper(II) atoms. Each copper(II) ion has a five-coordinate environment, four nitrogen atoms from the Bipy ligands, and one oxygen atom from the carbonate bridging ligand. The five-coordinate environment of Cu(1) is a distorted square pyramid with a τ value of 0.39, the structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles, τ describes the relative amount of trigonality, $\tau = 0$ for a square pyramid, and $\tau = 1$ for a trigonal bipyramid [18]. The coordination geometry of Cu(2) ($\tau = 0.04$) is a nearly regular square pyramidal environment with a basal plane formed by three nitrogen atoms of the two Bipy groups and the oxygen atom of the bridging car-

Table 1. Crystallographic data and details of the experiment and refinement of complexes **I** and **II**

Parameter	Value	
	I	II
<i>M</i>	1800.01	1944.13
<i>T</i> , K	273(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	2	4
<i>a</i> , Å	13.9419(1)	16.0783(9)
<i>b</i> , Å	14.0207(2)	20.2017(11)
<i>c</i> , Å	22.4682(1)	24.7053(14)
α , deg	80.5600	90
β , deg	73.6390(10)	103.3980(10)
γ , deg	61.8990(10)	90
<i>V</i> , Å ³	3714.81(6)	7806.1(8)
ρ_{calcd} , g cm ^{−3}	1.609	1.654
μ , mm ^{−1}	1.067	1.023
<i>F</i> (000)	1818	3542
Crystal size, mm	0.35 × 0.33 × 0.13	0.20 × 0.09 × 0.05
θ range for data collection, deg	1.65 < θ < 27.23	1.32 < θ < 28.02
Limiting indices	−17 ≤ <i>h</i> ≤ 17	−21 ≤ <i>h</i> ≤ 21
	−17 ≤ <i>k</i> ≤ 18	−26 ≤ <i>k</i> ≤ 26
	−22 ≤ <i>l</i> ≤ 28	−34 ≤ <i>l</i> ≤ 34
Number of measured reflections	23338	104767
Number of independent reflections	16 173 (<i>R</i> _{int} = 0.0255)	18 836 (<i>R</i> _{int} = 0.1338)
Number of refined parameters	1234	1305
GOOF	1.016	1.027
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0556, <i>wR</i> ₂ = 0.1407	<i>R</i> ₁ = 0.0914, <i>wR</i> ₂ = 0.1705
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1054, <i>wR</i> ₂ = 0.1701	<i>R</i> ₁ = 0.1876, <i>wR</i> ₂ = 0.2124
Residual electronic density (max/min), e Å ^{−3}	0.758/−0.657	1.060/−0.651

Table 2. Selected bond lengths and bond angles of complexes **I** and **II***

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
I			
Cu(1)–N(1)	2.015(3)	Cu(2)–N(8)	2.171(3)
Cu(1)–N(2)	2.196(4)	Cu(2)–O(2)	1.997(3)
Cu(1)–N(3)	1.997(3)	Cu(3)–N(9)	1.988(3)
Cu(1)–N(4)	2.018(3)	Cu(3)–N(10)	2.129(3)
Cu(1)–O(1)	1.952(3)	Cu(3)–N(11)	2.066(3)
Cu(2)–N(5)	2.002(4)	Cu(3)–N(12)	1.970(3)
Cu(2)–N(6)	2.019(4)	Cu(3)–O(3)	2.006(3)
Cu(2)–N(7)	2.023(3)		
II			
Cu(1)–N(1)	1.994(5)	Cu(2)–N(8)	2.122(5)
Cu(1)–N(2)	2.122(5)	Cu(2)–O(2)	2.046(10)
Cu(1)–N(3)	1.998(5)	Cu(2)–O(1)A	1.999(9)
Cu(1)–N(4)	2.088(5)	Cu(3)–N(9)	2.108(5)
Cu(1)–O(1)	2.060(11)	Cu(3)–N(10)	2.012(5)
Cu(1)–O(3)A	1.952(9)	Cu(3)–N(11)	2.099(5)
Cu(2)–N(5)	2.098(5)	Cu(3)–N(12)	1.998(5)
Cu(2)–N(6)	1.992(5)	Cu(3)–O(3)	2.010(10)
Cu(2)–N(7)	1.999(4)	Cu(3)–O(2)A	1.977(9)
Angle	ω, deg	Angle	ω, deg
I			
N(1)Cu(1)N(3)	173.5(1)	O(2)Cu(2)N(6)	171.6(1)
O(1)Cu(1)N(4)	150.0(1)	N(9)Cu(3)N(12)	176.7(1)
N(5)Cu(2)N(7)	174.0(1)	O(3)Cu(3)N(11)	142.9(1)
II			
N(1)Cu(1)N(3)	178.5(2)	N(8)Cu(2)O(2)	144.9(3)
N(4)Cu(1)O(3)A	144.8(3)	N(10)Cu(3)N(12)	178.8(2)
N(6)Cu(2)N(7)	178.2(2)	N(9)Cu(3)O(3)	146.5(3)

* Symbol A is disorder form.

bonato group. The environment geometry around Cu(3) ($\tau = 0.56$) is intermediate five-coordinate but slightly distorted toward a trigonal bipyramid via a Berry–Twist process [19]. The three longer bonds in the trigonal planar plane are two nitrogen atoms of the Bipy ligand (Cu–N(10) 2.129(3) and Cu–N(11) 2.066(3) Å) and one oxygen of carbonato ligand

(Cu–O(3) 2.006(3) Å). The two shorter bonds in the axial positions involve two nitrogen atoms of the different two Bipy ligands (Cu–N(9) 1.988(3) and Cu–N(12) 1.970(3) Å). This is typical for the trigonal-bipyramidal geometry [20]. The distances between the copper(II) atoms are Cu(1)–Cu(2) 5.192, Cu(1)–Cu(3) 4.680, and Cu(2)–Cu(3) 4.566 Å,

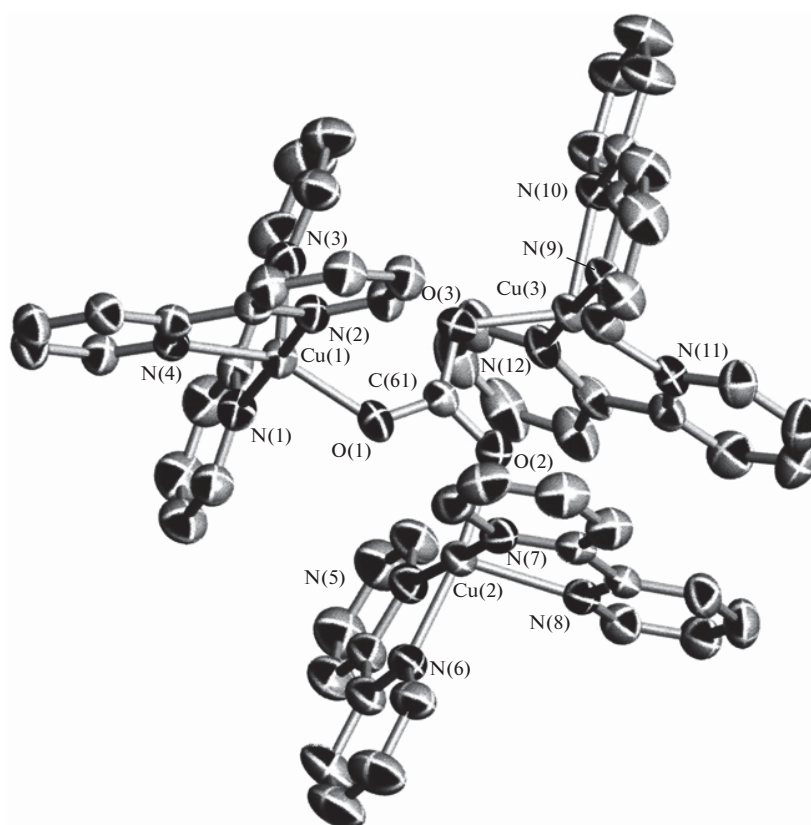


Fig. 1. Molecular structure and the atomic numbering scheme for complex **I** (thermal ellipsoids are shown at the 30% level). Hydrogen atoms, triflate anions, and water molecules are omitted for clarity (the same is in Figs. 3, 4).

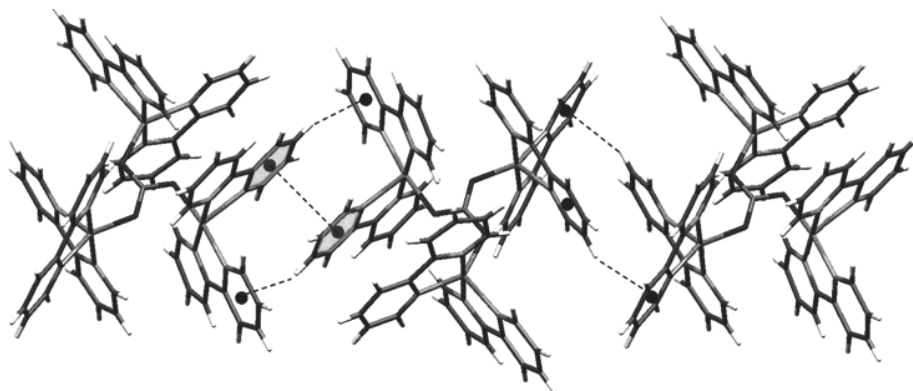


Fig. 2. Packing diagram of **I** showing the one-dimensional chain formed by Bipy-Bipy π -stacking and $\text{CH}\cdots\pi$ interactions along the crystallographic z axis.

respectively. The influence of intra- and intermolecular Bipy-Bipy π -stacking (contact distance 3.777 Å) and the $\text{CH}\cdots\pi$ interactions [21] (contact distance ranging in 2.802–2.898 Å) has been considered to play a role in this molecular structure, forming the one-dimensional chains along a z axis as shown in Fig. 2.

The structure of complex **II** (Fig. 3) is similar to that of complex **I**. In complex **II**, the carbonate bridging ligand is disordered with occupancies of oxygen atoms of 0.5. The geometries of all three copper(II) centers are described as being intermediate five-coordinate with τ values of 0.58, 0.56, and 0.54 for Cu(1),

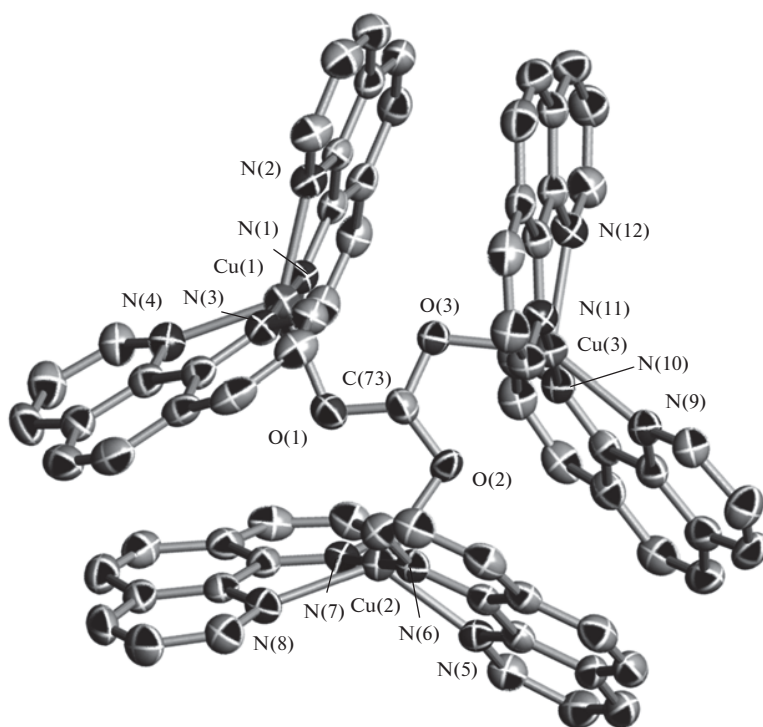


Fig. 3. Molecular structure and the atomic numbering scheme for complex **II** (thermal ellipsoids are shown at the 50% level).

Cu(2), and Cu(3), respectively. The intra- and intermolecular interactions are stabilized by Phen–Phen π -stacking between the Phen planes from neighboring trimer molecules. These interactions exhibit rather short centroid–centroid distances ranging from 3.539 to 3.675 Å (<3.8 Å) [22], forming a three-dimensional network as shown in Fig. 4.

The infrared spectra of complexes **I** and **II** in addition to the Bipy and Phen vibrations show the broad and intense bands of the stretching of CF_3SO_3^- at 1276 $\nu_{\text{as}}(\text{S–O})$, 1158 $\nu_{\text{as}}(\text{C–F})$ and 1031 $\nu_{\text{s}}(\text{S–O}) \text{ cm}^{-1}$ for **I** and 1277 $\nu_{\text{as}}(\text{S–O})$, 1153 $\nu_{\text{as}}(\text{C–F})$ and 1029 $\nu_{\text{s}}(\text{S–O}) \text{ cm}^{-1}$ for **II** [23]. The IR spectra of both compounds also show bands characteristic of the carbonate bridge with a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ mode appeared as the out-of-plane vibration [7] at 836 cm^{-1} for **I** and 755 cm^{-1} for **II**, as these spectral ranges are completely transparent in the mononuclear compounds $[\text{Cu}(\text{Bipy})_3](\text{CF}_3\text{SO}_3)_2$ [7] and $[\text{Cu}(\text{Phen})_3](\text{CF}_3\text{SO}_3)_2(\text{H}_2\text{O})$ [24]. The asymmetric stretching vibration normally occurred in a range of 1470–1380 cm^{-1} for the tridentate carbonate ligand is overlapped by the vibrations of the Bipy and Phen with nearly D_{3h} symmetry [25].

The electronic reflectance spectra of the trinuclear compounds show two well-resolved bands with nearly equal intensity at approximately 14 200 and 10 200 cm^{-1}

for **I**, 13 100 and 9900 cm^{-1} for **II**. These features correspond to a predominantly distorted square pyramidal geometry in **I** and an intermediate five-coordinated geometry in **II**, which is typically lower in energy for the latter case. This yields a tentative one-electron orbital sequence of $d_{x^2-y^2} \gg d_{xy} \approx d_{xz} \approx d_{yz}$ [26] and two $d\text{--}d$ transitions, $d_{xy}, d_{yz}, d_{zx} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ are assigned for both distorted square pyramidal and intermediately five-coordinate chromophores.

The EPR spectra of complexes **I** and **II** were recorded as a polycrystalline powder a room temperature (RT) and at 77 K from 0–600 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$).

Complexes **I** and **II** show almost similar EPR spectra at RT and at 77 K with a very broad signal ($g = 2.13$ for **I** and $g = 2.34$ for **II**), whose values can be attributed to the mononuclear impurity. Other triplet signals seem to be obscured by the broad signal at around $g = 2.13$, which is usually observed with a range of distorted geometries within the complex. In both cases, also a half-field signal is observed at around $g = 4.33$ (164 mT), which supports the existence of a weak coupling between the copper(II) ions.

In addition, the magnetic measurements have been performed from 5 to 350 K and the preliminary results of both complexes were reported. The magnetic behavior of both complexes agrees with a weak ferro-

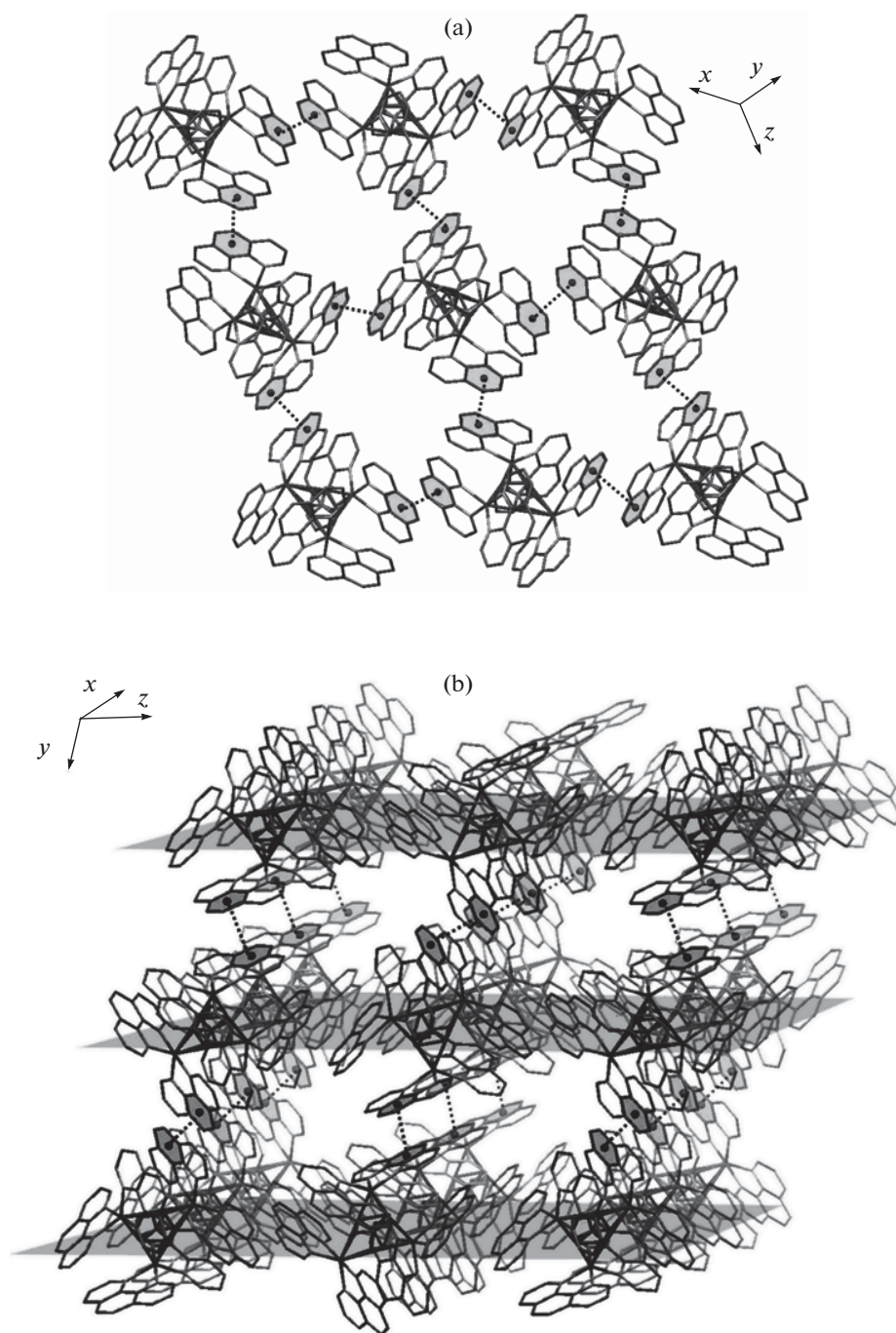


Fig. 4. Packing diagram of **II**: two-dimensional layer formed by Phen–Phen π -stacking in xz plane (a), and side view of Phen–Phen π -stacking between 2D layers in the xz plane along the crystallographic y axis, forming the three-dimensional network (b).

magnetic exchange interaction. Complexes **I** and **II** have the trinuclear carbonato-bridged triangular Cu(II) units with the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ coordination mode, which is usually performed the magnetic interaction ranging between weak antiferromagnetic to weak ferromagnetic interaction [7–9].

In this paper, two new trinuclear carbonato-bridged copper(II) complexes have been successfully synthesized by the direct preparation method. Their molecular structures and spectroscopic properties are fully characterized. The structures of both complexes are similar with the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ coordination mode of

the carbonato bridge. The preliminary result of the magnetic property reveals a weak ferromagnetic interaction.

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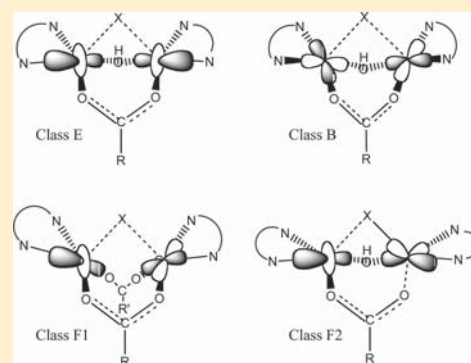
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New Series of Triply Bridged Dinuclear Cu(II) Compounds: Synthesis, Crystal Structure, Magnetic Properties, and Theoretical Study

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Supporting Information

ABSTRACT: Five new triply bridged dinuclear Cu(II) compounds have been synthesized, and their magnetic properties have been measured and characterized. The magnetic coupling constants (J) of these compounds plus a previously structurally characterized compound of the same type have been derived by appropriate fitting of the experimentally measured molar susceptibility variation with the temperature. Two of the compounds are ferromagnetically coupled, and three are antiferromagnetically coupled with J values in the $[-150, +40]$ cm⁻¹ range. The validity of the structural aggregate Addison's parameter as a qualitative magneto-structural correlation is confirmed. The origin of the magnetic interactions and the magnitude of the magnetic coupling have been analyzed by means of density functional theory-based calculations using a variety of state of the art exchange-correlation potentials. It is shown that the long-range separated LC- ω PBE provides the overall best agreement with experiment for this family as well as for a set of previously reported hetero triply bridged dinuclear Cu(II) compounds, especially for ferromagnetic systems.



INTRODUCTION

The study of magnetochemistry in di- and polynuclear Cu(II) coordination compounds is of interest due to the diverse structural and magnetic properties of these systems and, especially, because of the possibility to design structures exhibiting strong ferromagnetism. The design, synthesis, and magnetic characterization of these types of systems is still challenging. In addition, this family of systems is usually presented as representative of the simplest possible models for magnetic complexes since the Cu(II) ions in a d^9 electronic configuration exhibit only one unpaired electron per magnetic center. This feature allows one to search for a deeper understanding of ferro- and antiferromagnetic interactions and to derive useful magneto-structural correlations from either experimental or theoretical points of view which provide a guide toward magnetic complexes with enhanced ferromagnetism.^{1,2}

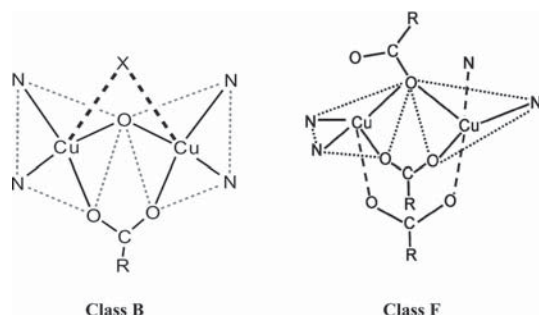
This work follows from previous research focusing on the dinuclear triply bridged copper(II) compounds which have shown to exhibit a great diversity of topologies, intramolecular magnetic exchange phenomena, and magneto-structural correlations.^{3–8} In these compounds, the five coordination of the Cu(II) ion displays an extensive range of distorted geometries ranging from regular trigonal bipyramid to regular square-based pyramid. Their global

topologies can be described in terms of the relative arrangement of the two five-coordinate environments, giving rise to different classes of compounds termed A to F in previous work.³ The knowledge of these topologies is useful to unravel the relationships between structural features and the value of the intramolecular magnetic exchange interaction in the triply bridged dinuclear unit. In the previously mentioned study, the magneto-structural correlations were investigated with the help of semiempirical Extended Hückel calculations and linear correlations were found for class B compounds.³ However, a more quantitative approach is needed to fully understand the magnetic interactions in these compounds and to accurately predict their magnetic coupling constant J . More recently, a deep investigation on the magneto-structural correlations in this series of compounds, which show ferromagnetic behavior, was carried out⁹ using density functional theory (DFT)-based calculations. Results have shown that for class B compounds the calculated magnetic coupling constant values almost quantitatively correlate with the sum of Addison's τ parameter of each Cu(II) ion. This class provides a clear example of enhanced ferromagnetic

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Scheme 1



behavior using ligands favoring the square-based pyramidal coordination on each Cu(II) atom which involves magnetic interaction mainly through the Cu(II) $d_{x^2-y^2}$ orbitals. On the other hand, calculated J values for class E compounds reveal that a third ligand plays a key role in enhancing ferromagnetism in this class which involves mainly the interaction through the Cu(II) d_{z^2} orbitals.

To extend our knowledge on the magnetic behavior and the magneto-structural correlations of these triply bridged dinuclear compounds with different topologies (Scheme 1), we successfully synthesized two new hetero triply bridged dinuclear Cu(II) compounds in class B $\{[Cu_2(phen)_2(\mu-OH)(\mu-OH_2)(\mu-O_2CC(CH_3)_3)](ClO_4)_2\}$ (1) and $[Cu_2(bpy)_2(\mu-OH)(\mu-O_2CCH_2CH_3)(\mu-O_2SOCF_3)](CF_3SO_3)(DMF)_{0.5}$ (2); we also consider one structurally reported³ class B compound $[Cu_2(phen)_2(\mu-OH)(\mu-OH_2)(\mu-O_2CCH_2CH_3)](NO_3)_2$ (3). From the existing literature, it appears that the number of class F compounds for which both structural and magnetic data is available is found to be very limited. Hence, three new homo triply bridged dinuclear Cu(II) compounds in class F, $[Cu_2(bpy)_2(\mu-OCOPh)(\mu-O_2CPh)_2]X$ with $X = ClO_4^-$ (4), BF_4^- (5), and PF_6^- (6) have been synthesized and characterized. Details of the synthesis, characterization, and crystal structure of the new compounds are reported. Also, values of the magnetic coupling constants extracted from magnetic susceptibility measurements are compared to theoretical calculations using a wide range of state of the art DFT methods including the newest range-separated hybrid functionals. Incorporating the present systems to previously published ferromagnetic triply bridged di-Cu(II) compounds allows us to propose a more complete open-shell database which may be very useful to systematically investigate the performance of newly developed exchange-correlation functionals in predicting magnetic coupling constants in these and more complicated magnetic systems as well as to generalize an important previously reported magnetostructural correlation for triply bridged di-Cu(II) complexes.⁹

MATERIALS AND MEASUREMENTS

1,10-Phenanthroline, 2,2'-bipyridine, sodium trimethylacetate monohydrate, sodium propionate, and sodium benzoate were purchased as commercial chemicals from Aldrich. All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined using a Perkin-Elmer PE-2400 CHNS/O Analyzer.

IR spectra were recorded on Spectrum One FT-IR spectrophotometer as KBr disk in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer, over the range 8000–18000 cm^{-1} .

Magnetic susceptibility measurements for compounds 1–6 were carried out on polycrystalline samples at the Servei de Magnetoquímica of the Serveis Científic-Tècnics of the Universitat de Barcelona. They were carried out with a Quantum Design SQUID MPMS-XL magnetometer working in the temperature range 2–300 K at magnetic fields of 500 G (2–30 K) and 10 kG (2–300 K). For compounds 1 and 3, due the small amounts of available samples (30 and 60 mg, respectively), the measurements were repeated twice. Diamagnetic corrections for the measured susceptibilities were estimated from the Pascal tables. The EPR spectra of microcrystalline samples of 1–6 were recorded at X-band frequency ($\nu \sim 9.4362$ GHz) with a Bruker ES-200 spectrometer in the temperature range 300–4 K.

Synthesis. $\{[Cu_2(phen)_2(\mu-OH)(\mu-OH_2)(\mu-O_2CC(CH_3)_3)](ClO_4)_2\} \cdot 2-(CH_3CH_2OH)$ (1). A warm ethanol solution (25 mL) of phen (0.198 g, 1.0 mmol) was added to a warm aqueous solution (15 mL) of $Cu-(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol). Then, $(CH_3)_3CCO_2Na$ solid (0.124 g, 1.0 mmol) was added to the mixture, yielding a clear dark blue solution. After 1 week, bluish-violet rectangle-shaped crystals of compound 1 were obtained. The crystals were filtered off, washed with mother liquor, and air-dried. Yield: ca. 30%. Anal. Calc. for $Cu_4C_{60}H_{60}N_8O_{25}Cl_4$: C, 42.66; H, 3.59; N, 6.64. Found: C, 42.12; H, 3.51; N, 6.66%.

$[Cu_2(bpy)_2(\mu-OH)(\mu-O_2CCH_2CH_3)(\mu-O_2SOCF_3)](CF_3SO_3)(DMF)_{0.5}$ (2). A warm aqueous solution (5 mL) of $Cu(CF_3SO_3)_2$ (0.361 g, 1.0 mmol) was added to a mixed methanol and DMF (20:3) solution of bpy (0.156 g, 1.0 mmol). Then, $CH_3CH_2CO_2Na$ solid (0.096 g, 1.0 mmol) was added to the mixture, yielding a clear blue solution. After 1 week, bluish-violet hexagonal shaped crystals of compound 2 were obtained. The crystals were filtered off, washed with mother liquor, and air-dried. Yield: ca. 60%. Anal. Calc. for $Cu_2C_{26.5}H_{25.5}N_{4.5}O_{9.5}S_2F_6$: C, 36.82; H, 2.98; N, 7.29. Found: C, 36.25; H, 2.86; N, 7.20%.

$[Cu_2(phen)_2(\mu-OH)(\mu-OH_2)(\mu-O_2CCH_2CH_3)](NO_3)_2$ (3). Compound 3 was synthesized by the method described previously in ref 3. Yield: ca. 30%. Anal. Calc. for $Cu_2C_{27}H_{24}N_6O_{10}$: C, 45.07; H, 3.36; N, 11.68. Found: C, 45.01; H, 3.25; N, 11.83%.

$[Cu_2(bpy)_2(\mu-OCOPh)(\mu-O_2CPh)_2](ClO_4)$ (4) and $[Cu_2(bpy)_2(\mu-OCOPh)(\mu-O_2CPh)_2](BF_4)$ (5). The warm aqueous solution (10 mL) of $Cu-(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol) was added to a warm methanol solution (20 mL) of bpy (0.156 g, 1.0 mmol). Then, solid $C_6H_5CO_2Na$ (0.144 g, 1.0 mmol) was added to the mixture, yielding a clear greenish-blue solution. After 1 week, greenish-blue hexagonal shaped crystals of compound 4 were obtained. The crystals were filtered off, washed with mother liquor, and air-dried. Yield: ca. 65%. Anal. Calc. for $Cu_2C_{41}H_{31}N_4O_{10}Cl$: C, 54.57; H, 3.47; N, 6.21. Found: C, 54.28; H, 3.38; N, 6.78%. Compound 5 was prepared in similar manner using $Cu(BF_4)_2 \cdot nH_2O$. Yield: ca. 70%. Anal. Calc. for $Cu_2C_{41}H_{31}N_4O_6BF_4$: C, 55.35; H, 3.52; N, 6.30. Found: C, 55.24; H, 3.32; N, 6.38%.

$[Cu_2(bpy)_2(\mu-OCOPh)(\mu-O_2CPh)_2](PF_6)$ (6). The warm aqueous solution (10 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mmol) was added to a warm methanol solution (20 mL) of bpy (0.156 g, 1.0 mmol). Then, solid $C_6H_5CO_2Na$ (0.144 g, 1.0 mmol) was added to the mixture. After that, solid of KPF_6 or $(NH_4)PF_6$ (2.0 mmol) was added, yielding a clear greenish-blue solution. After 1 week, greenish-blue hexagonal shaped crystals of compound 6 were obtained. The crystals were filtered off, washed with mother liquor, and air-dried. Yield: ca. 60%. Anal. Calc. for $Cu_2C_{41}H_{31}N_4O_6PF_6$: C, 51.95; H, 3.30; N, 5.91. Found: C, 51.75; H, 3.13; N, 6.08%.

Crystallography. X-ray single-crystal data for all compounds were collected at 293 K. Reflection data were collected on a 1K Bruker SMART APEX CCD area-detector diffractometer using rotating mode, graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at a detector distance of 4.5 cm and swing angle of -30° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0° , 88° , 180°), and each exposure of 40 s covered 0.3° in ω . Raw data frame integration was performed with SAINT,¹⁰ which also applied correction for Lorentz and

Table 1. Crystallographic and Refinement Data for Compounds 1, 2, and 4–6^a

Compound	1	2	4	5	6
Empirical formula	Cu ₄ N ₈ C ₆₀ H ₆₀ O ₂₅ Cl ₄	Cu ₂ N _{4.5} C _{26.5} H _{25.5} O _{9.5} S ₂ F ₆	Cu ₂ N ₄ C ₄₁ H ₃₁ O ₁₀ Cl ₁	Cu ₂ N ₄ C ₄₁ H ₃₁ O ₆ B ₁ F ₄	Cu ₂ N ₄ C ₄₁ H ₃₁ P ₁ F ₆
Formula weight	1689.28	864.30	902.31	889.67	947.83
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	C2/c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	8.8313(2)	28.9098(11)	11.48420(10)	11.526(2)	11.5546(2)
b (Å)	18.8577(6)	14.4295(6)	21.6488(3)	21.490(4)	22.31590(10)
c (Å)	20.5115(6)	17.6698(7)	15.9640(4)	15.927(3)	15.9854(2)
α (°)	90.1850(10)	90.00	90.00	90.00	90.00
β (°)	94.0770(10)	115.3140(10)	109.6090(10)	109.23(3)	109.9900(10)
γ (°)	96.4580(10)	90.00	90.00	90.00	90.00
V (Å ³)	3385.46(17)	6663.2(5)	3738.77(11)	3725.0(13)	3873.52(8)
Z	2	4	4	4	4
D _{calc} (g cm ⁻³)	1.632	1.694	1.603	1.586	1.625
μ (mm ⁻¹)	1.483	1.493	1.277	1.217	1.223
F(000)	1690	3420	1840	1808	1920
Crystal size (mm)	0.08 × 0.13 × 0.20	0.05 × 0.23 × 0.40	0.38 × 0.38 × 0.55	0.28 × 0.33 × 0.43	0.10 × 0.13 × 0.35
Number of reflection collected	15972	24886	28002	9471	27590
Number of unique reflections (<i>R</i> _{int})	10870 (0.0290)	9673 (0.0351)	10619 (0.0193)	5095 (0.0161)	10756 (0.0423)
Data/restraints/parameter	10870/1/936	9673/10/463	10619/0/684	5095/2/683	10756/0/701
Goodness-of-fit	1.013	1.062	1.050	1.027	0.888
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0612 <i>wR</i> ₂ = 0.1558	<i>R</i> ₁ = 0.0810 <i>wR</i> ₂ = 0.2670	<i>R</i> ₁ = 0.0313 <i>wR</i> ₂ = 0.0859	<i>R</i> ₁ = 0.0307 <i>wR</i> ₂ = 0.0795	<i>R</i> ₁ = 0.0388 <i>wR</i> ₂ = 0.0791
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1144 <i>wR</i> ₂ = 0.1815	<i>R</i> ₁ = 0.1392 <i>wR</i> ₂ = 0.3083	<i>R</i> ₁ = 0.0469 <i>wR</i> ₂ = 0.0905	<i>R</i> ₁ = 0.0406 <i>wR</i> ₂ = 0.0862	<i>R</i> ₁ = 0.0993 <i>wR</i> ₂ = 0.0934
Largest difference in peak and hole (e ³)	1.062 and -0.679	2.638 and -0.892	0.319 and -0.743	0.300 and -0.517	0.316 and -0.523

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

Polarization effects. An empirical absorption correction using the SADABS¹¹ program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.678, 1.000 to 0.761, 1.000 to 0.747, 1.000 to 0.809, and 1.000 to 0.749 for 1, 2, and 4–6. The structures were solved by direct methods and refined by full-matrix least-squares method on (*F*_{obs})² using the SHELXTL-PC Version 6.12 software package.¹²

For compound 1, all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier carbon atoms except those of hydroxo bridges, H(1A) and H(5A), and water bridging molecules, H(2A), H(6A), and H(7A), while a hydrogen atom of one water bridging molecule and an ethanol molecule could not be located. All nonhydrogen atoms were refined anisotropically. The Cl(4)–O(22) bond distance of perchlorate group was restrained with the DFIX 1.45(1) command. An ethanol molecule was disordered with site occupancies of 0.5. In compound 2, all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier carbon atoms except hydrogen atoms of the hydroxo bridge and DMF molecule. All nonhydrogen atoms were refined anisotropically, except some atoms of noncoordinated triflate anion. For bridging triflate, the oxygen atoms of SO₃ group were disordered with site occupancies of 0.5. The triflate counteranion was disordered, and attempts have been made to locate disordered atoms in a range of reasonable possibilities but were unsuccessful. Finally, we decide to refine as the ordered molecule and it was restrained to the bond distance with the DFIX 1.42(1), 1.86(1), and 1.32(1) commands for the S–O, C–S, and C–F, respectively, leading to quite high but reliable temperature factors. The free DMF molecule was also disordered and restrained of the bond distance with the DFIX 1.23(1), 1.35(1), and 1.47(1) commands for the C(31)–O(17), N(6)–C(31), and N(6)–C(32), respectively. For

compound 4, all hydrogen atoms were located by difference synthesis and refined isotropically, while all nonhydrogen atoms were refined anisotropically. The perchlorate anion was disordered with site occupancies of oxygen atoms of 0.52 and 0.48. In compound 5, all hydrogen atoms were located by difference synthesis and refined isotropically, while all nonhydrogen atoms were refined anisotropically. The tetrafluoroborate molecule was disordered with site occupancies of 0.5, and it was restrained with the DFIX 1.34(1) Å, for the B(1)–F(1) and B(1)–F(1A) bond lengths. Finally, for compound 6, all hydrogen atoms were located by difference synthesis and refined isotropically except a hydrogen atom, H(7), on pyridine ring of bpy and those of benzoate bridging ligands, H(25), H(37), H(38), and H(40). All nonhydrogen atoms were refined anisotropically. The tetrafluoroborate molecule is disordered with site occupancies of 0.5.

Computational Details. The different series of hybrid DFT calculations have been carried out using rather large standard basis sets of Gaussian Type Orbitals (GTO). Thus, a 6-311+G extended with an *f*-function (exponent(*f*) = 0.528) has been used for Cu and 6-31G(d) for the remaining atoms. All calculations have been carried out in the unrestricted (spin-polarized) formalism. Clearly, in this type of formalism, the spin symmetry is not guaranteed.^{13–15} Nevertheless, approximate triplet (T) states have been obtained from the unrestricted Kohn–Sham formalism using a single Slater determinant with two unpaired electrons (i. e., *S*_z = 1) whereas to estimate the energy of the open shell singlet state we have relied on the broken-symmetry (BS) approach imposing *S*_z = 0. In this way, the singlet–triplet gap energy has been obtained on the basis of the expectation value of the Heisenberg Hamiltonian as in eq 1

$$\hat{H} = -J \hat{S}_1 \cdot \hat{S}_2 \quad (1)$$

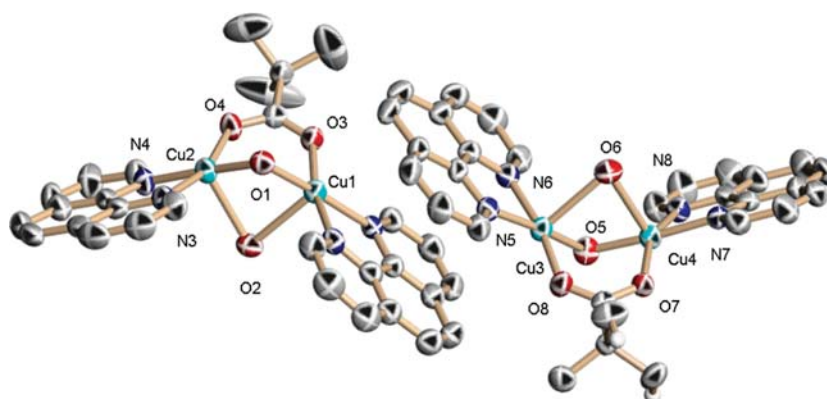


Figure 1. Two independent dinuclear Cu(II) cationic units and atomic numbering scheme for compound **1** (Thermal ellipsoids are shown at 30% level). Hydrogen atoms, perchlorate anions, and ethanol molecules are omitted for clarity.

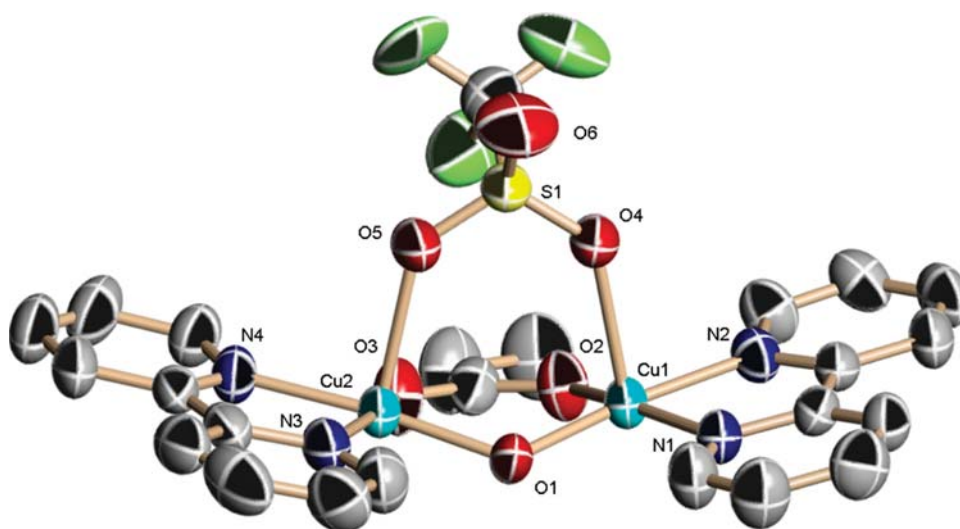


Figure 2. Molecular structure and atomic numbering scheme for compound **2** (Thermal ellipsoids are shown at 50% level). Hydrogen atoms, triflate counteranions, and DMF molecule are omitted for clarity.

that leads to the approximate relation:

$$J = 2[E(\text{BS}) - E(\text{T})] \quad (2)$$

where $E(\text{BS})$ is the energy of the broken-symmetry state and $E(\text{T})$ is the energy of the spin unrestricted approximation to the triplet state.¹⁶ Here, it is important to stress that eq 2 takes into account the so-called spin projection, which aims to recover the spin symmetry lost in the BS approach and which is inherent to the use of a single Kohn–Sham determinant.^{17–19} Alternative methods for calculating J couplings without the use of spin symmetry²⁰ lead to results that are not always accurate²¹ when high quality range separated functionals like those employed in this paper are used. All calculations were carried out using the Gaussian09 suite of programs.²²

RESULTS AND DISCUSSION

The crystal structures and their refinement details for compounds **1**, **2**, and **4–6** are listed in Table 1. Selected bond lengths and angles are given in Tables 1–5 of the Supporting Information file which also contains a description of the crystal structures. Here, we just provide a very short description and hence mention that $\{[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CC}(\text{CH}_3)_3)](\text{ClO}_4)_2\}_2(\text{CH}_3\text{CH}_2\text{OH})$, hereafter referred to as compound **1**, has an asymmetric unit

consisting of two independent triply bridged dinuclear Cu(II) units, four perchlorate counteranions, and one ethanol molecule (Figure 1). $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-O}_2\text{SO}_2\text{CF}_3)]\text{-}(\text{CF}_3\text{SO}_3)(\text{DMF})_{0.5}$, referred to as **2**, consists of a dinuclear $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-O}_2\text{SO}_2\text{CF}_3)]^+$ cation, with trifluoromethanesulfonate counteranion and a half of DMF (Figure 2). $[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)]\text{-}(\text{NO}_3)_2$, referred to as **3**, was described previously.³ Dinuclear cations of compounds **1**, **2**, and **3** consist of two Cu(II) atoms each having a chelating bidentate terminal ligand and sharing three bridging ligands (one hydroxo, one carboxylato, and one water molecule for **1** and **3** and one triflate ligand for **2**) in such a way that a CuN_2O_3 chromophore defines a distorted square pyramidal pentacoordinated environment around the magnetic center with X atom in Scheme 1 at the apex of the SP. These three complexes are then classified as class B. On the other hand, $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OCOPh})(\mu\text{-O}_2\text{CPh})_2]\text{X}$ with $\text{X} = \text{ClO}_4^-$ (**4**), BF_4^- (**5**), and PF_6^- (**6**) crystallize in the monoclinic space group $P2_1/c$ with similar unit cell parameters, as shown in Table 1. The structure of these compounds is similar to those described above except that the three bridging ligands are two bidentate and one monodentate carboxylates, leading to a distorted trigonal bi-

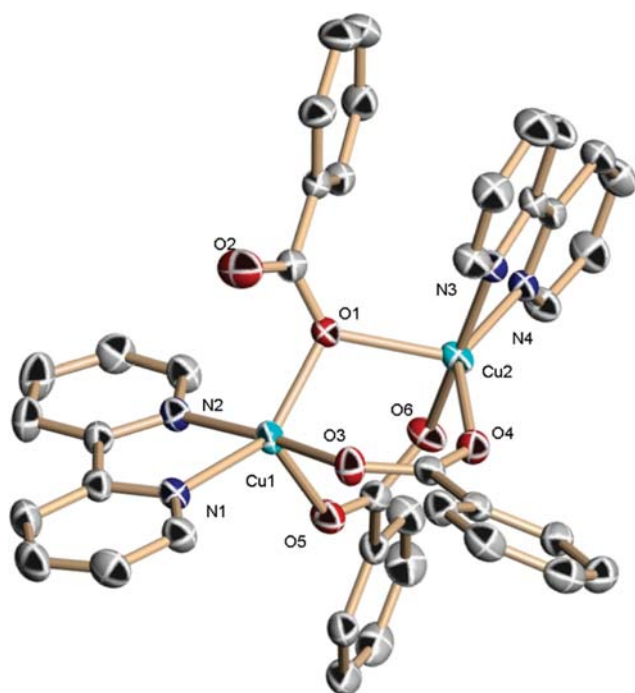


Figure 3. Molecular structure and atomic numbering scheme for compounds 4–6 (Thermal ellipsoids are shown at 30% level). Hydrogen atoms, perchlorate, tetrafluoroborate, and hexafluorophosphate anions for compounds 4, 5 and 6 are omitted for clarity.

pyramidal geometry around the magnetic Cu(II) centers (Figure 3). According to the definition established in previous work,⁹ compounds 4, 5, and 6 belong to class F (see Supporting Information). Note that the previously reported class F compound, [Cu₂(dpyam)₂(μ-OCOCH₃)(μ-O₂CCH₃)(μ-OH)](PF₆)(H₂O) (XV),⁸ consists of two carboxylato and one hydroxo bridges. Due to the influence of these structural features in the magnetic behavior of the compounds, we will distinguish from now on between F1 (antiferromagnetic, one μ-(O,O)-carboxylato and two μ-(O,O′)-carboxylato bridges) and F2 (ferromagnetic, one hydroxo, and one μ-(O,O) and one μ-(O,O′) bridging carboxylates) classes, respectively.

Spectroscopic Features and Magnetic Characterization. *Infrared Spectra.* The infrared spectra display a broad band at 3504 cm⁻¹ for 1 and 3567 cm⁻¹ for 2, which can be assigned to the bridging OH vibration of the hydroxo ligands and/or lattice water. The spectra also exhibit the intense bands at 1550 and 1424 cm⁻¹ for 1 and 1542 and 1448 cm⁻¹ for 2, corresponding to the ν_{as}(COO⁻) and ν_s(COO⁻) vibrations of bridging trimethylacetate and propionate for 1 and 2, respectively. Broad and intense bands of the stretching of ν_{as}(ClO₄⁻) at 1096 cm⁻¹ for 1 and CF₃SO₃⁻ at 1260 ν_{as}(S–O), 1162 ν_{as}(C–F), 1032 ν_s(S–O), and 637 δ(S–O) cm⁻¹ for 2 were observed. The IR spectra of compounds 4–6 present the broad and intense bands of the stretching for ionic ClO₄⁻ anion (1091 cm⁻¹ for 4), ionic BF₄⁻ anion (1056 cm⁻¹ for 5), and ionic PF₆⁻ anion (841 cm⁻¹ for 6).²³ The spectra of these compounds also show two broad and intense bands at 1567 and 1384 cm⁻¹ for 4, 1568 and 1385 cm⁻¹ for 5, and 1567 and 1383 cm⁻¹ for 6, corresponding to the ν_{as}(COO⁻) and ν_s(COO⁻) vibrations of benzoate bridging ligand.

uv–Visible Spectra. The diffuse reflectance spectra of compounds 1 and 2 display a broad band (16 000 cm⁻¹ for 1 and

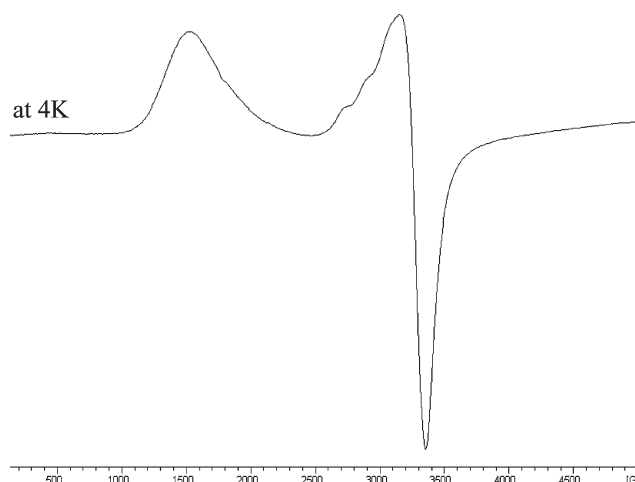


Figure 4. EPR spectrum of compound 1 at 4 K.

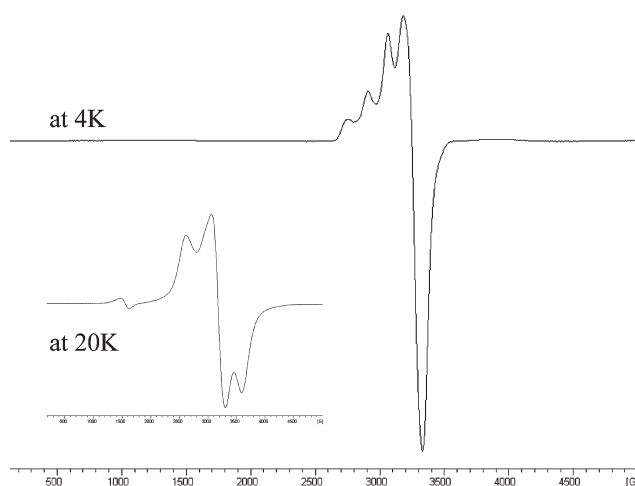


Figure 5. EPR spectrum of compound 4 at 4 K and at 20 K (see inset).

16 370 cm⁻¹ for 2) and a lower energy shoulder (13 140 cm⁻¹ for 1 and 13 830 cm⁻¹ for 2). These features are typical and correspond to the d_{xy}, d_{yz}, d_{xz} → d_{x²-y²}, and d_{z²} → d_{x²-y²} transitions for the square pyramidal geometry of the triply bridged dinuclear copper(II) compounds.³ However, the corresponding spectra for compounds 4–6 show a single broad band centered at ca. 11 930 for 4, 11 900 for 5, and 11 960 cm⁻¹ for 6, corresponding to an intermediate five-coordinate geometry.²⁴

Electron Paramagnetic Resonance Spectra. The EPR spectra of the compounds 1–6 (X-band, ν ~ 9.4362 GHz) have been recorded at different temperatures between 4 and 300 K for polycrystalline solid samples. The general shape of the spectra at 4 K corresponds to the two types shown in Figure 4 for ferromagnetic systems (compounds 1 to 3) and in Figure 5 for antiferromagnetic systems (4 to 6).

In the case of ferromagnetic systems, the principal transition band near g ~ 2.1, corresponding to Δm_s = 1, shows some asymmetry but maintains the center of the band as T goes from 300 to 4 K, slightly increasing the intensity of the signals. The half field transition near g ~ 4.4, corresponding to Δm_s = 2, shows important intensity with respect to the Δm_s = 1 transition and

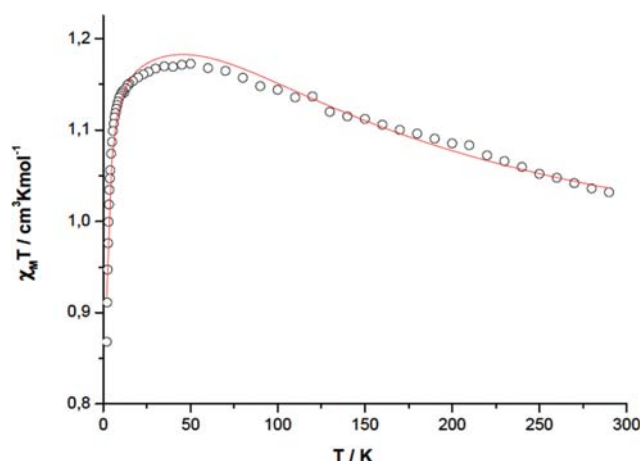


Figure 6. Plot of magnetic susceptibility–temperature product ($\chi_M T$) versus (T) temperature for compound 1.

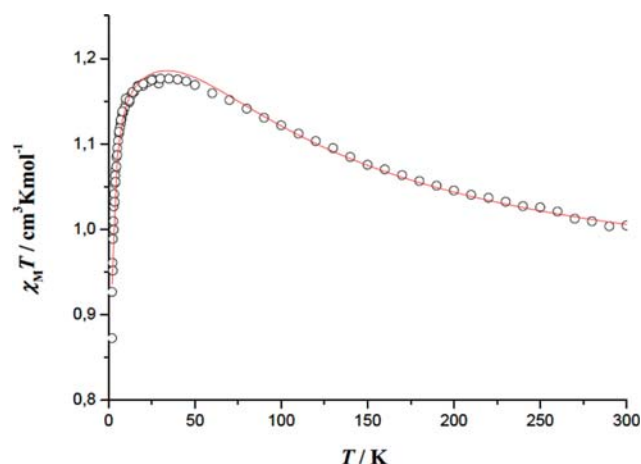


Figure 7. Plot of magnetic susceptibility–temperature product ($\chi_M T$) versus (T) temperature for compound 2.

demonstrates that the signal is originated by an electronic triplet state. The fine structure is apparent at 4 K but to resolve it, even tentatively, goes well beyond the scope of the present work.

The spectra of the antiferromagnetic systems (compounds 4 to 6) are quite different, and the shape is strongly dependent on the temperature: at 300 K, a broad symmetric doublet signal appears near $g \sim 2.1$ for $\Delta m_s = 1$ and the signal near $g \sim 4.4$ corresponding to $\Delta m_s = 2$ is almost unobservable. As temperature decreases, the main transition evolves to show an apparent fine structure and the half field transition for $\Delta m_s = 2$ becomes more intense and is very clear for temperatures around 20 K. Finally, when T approaches 4 K, the half field signal disappears and the principal signal at $g \sim 2.1$ becomes quite asymmetrical and shows a complex fine structure. The half field transition for $\Delta m_s = 2$ is observed, and its intensity increases as T decreases, reaches a maximum at intermediate temperatures, and disappears at low temperature. This behavior is consistent with a singlet–triplet electronic system with antiferromagnetic ground state and small J value.

Magnetic Properties. Molar magnetic susceptibility (χ_M) measurements were carried out using microcrystalline samples of compounds 1–6. The $\chi_M T$ vs T plots for 1–3 (Figures 6, 7, and 8, respectively) show a room temperature $\chi_M T$ product value of 1.03, 1.00, and 0.97 $\text{cm}^3 \text{K mol}^{-1}$ for 1, 2, and 3, respectively, slightly higher to that expected for two uncoupled Cu(II) ions. Lowering the temperature causes the $\chi_M T$ product to continuously increase until reaching plateau values of 1.17 $\text{cm}^3 \text{K mol}^{-1}$ at 50 K for 1, 1.18 at 35 K for 2, and 1.15 at 30 K for 3. On further cooling, $\chi_M T$ shows an abrupt descent for the three compounds, which clearly suggests that this quantity tends to zero when temperature tends to 0 K. This behavior can be explained by the existence of ferromagnetically coupled Cu(II) pairs responsible of the high temperature regime, where the low-lying triplet state was increasingly populated in detriment of the singlet state. Below liquid nitrogen temperature, small antiferromagnetic intermolecular interactions manifest and tend to couple the triplet states in such a way that the $S = 1$ spin vectors cancel each other, and a null global magnetization is approached.

One may note that the magnetic measurements for the ferromagnetic compounds 1 and 3 in Figures 6 and 8 exhibit some noise in the low temperature regime. Nevertheless, this feature is fully reproducible and hence cannot be attributed to defects in the sample, which has been further checked in variable

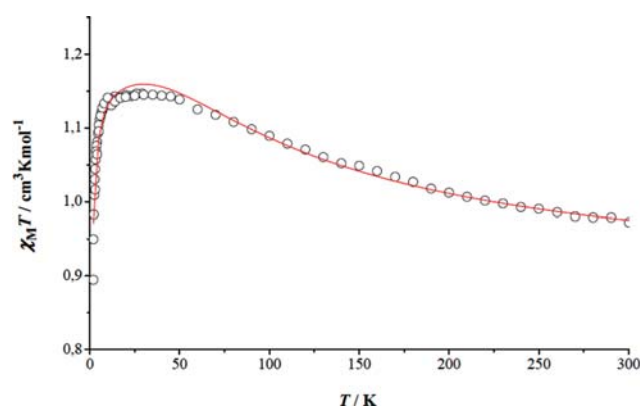


Figure 8. Plot of magnetic susceptibility–temperature product ($\chi_M T$) versus (T) temperature for compound 3.

field magnetization experiments. Since the noise appears only in the low temperature part of the curve, its influence on the final value of the ferromagnetic coupling constants is rather limited. Unfortunately, it is very difficult to trace the origin of the noise, and a possible explanation is the presence of some magnetic impurities below the detection limit of our equipment.

Compounds 4–6 show a shape of the $\chi_M T$ vs T curves which is typical of antiferromagnetically coupled Cu(II) pairs. At room temperature, the $\chi_M T$ values are 0.81, 0.83, and 0.86 $\text{cm}^3 \text{K mol}^{-1}$, respectively, close to the value expected for two uncoupled Cu(II) ions. On cooling down, $\chi_M T$ decreases slowly to show a strong descent in the 80–20 K region until reaching values near to zero below 10 K. This behavior is illustrated in Figure 9 for compound 4, as the curves for products 5 and 6 are very similar.

To account for the magnetic behavior of the dinuclear Cu(II) complexes 4–6 and to evaluate the corresponding coupling constant J , defined as the singlet–triplet splitting, we fitted the experimental susceptibility data using the Bleaney–Bowers equation.²⁵ For the ferromagnetic compounds 1–3, we corrected the above expression with a mean-field Weiss θ parameter to account for the small antiferromagnetic intermolecular interactions detected in the low temperature region for these

ferromagnetic dinuclear complexes:

$$\chi_M(T - \theta) = \frac{N\beta^2 g^2}{k_B} \frac{2e^{J/k_B T}}{1 + 3e^{J/k_B T}} \quad (3)$$

For compound **1**, as there is no unambiguous way to separate the exchange contributions of each dinuclear cation, the assumption of equal coupling constants was imposed in the procedure. Best-fit parameters were obtained by minimization of the error function $R = \sum \{[(\chi_M T)_{\text{calc}} - (\chi_M T)_{\text{exp}}]^2 / (\chi_M T)_{\text{exp}}^2\}$, and results are shown in Table 2. It is worth noting that magnetic data and fitting results for ferromagnetic compounds **1** and **3** are not quite accurate, mainly due to both the small amount of pure samples available (30 and 60 mg, respectively) for the applied magnetic field and available equipment. Likewise, one must also consider the intrinsic low accuracy and overparametrization problems involving the fitting of ferromagnetically coupled Cu(II)–Cu(II) systems with rather large molecular weights. Note that in the antiferromagnetic compounds $\chi_M T$ ranges from 0 to 0.8 whereas in the case of the ferromagnetic ones it ranges from 0.9 to 1.2 only. The much shorter range $\chi_M T$ leads to a more difficult fitting to the magnetic model, especially because here one has one additional parameter in the fitting, the intermolecular Curie–Weiss temperature. Nevertheless, the g values obtained from the fitting are consistent with those determined by EPR and also reported in Table 2. This provides further support of the accuracy of the J values thus obtained which are discussed below.

The experimental J values for class B compounds **1**, **2**, and **3** are +151.2, +104.5, and +98.4 cm^{−1}, respectively. An explanation for such a trend can be made in terms of countercomplementary effect between the hydroxo bridge which generates ferromagnetic interaction due to the orbital orthogonality and one triatomic bridge in *syn,syn* equatorial–equatorial configuration which usually contributes to a weak antiferromagnetic interaction. The experimental results of magnetic properties (J values) and structural data are summarized in Table 3 for class B compounds **1**–**3**.

The magnetic properties of present class F compounds show a weak antiferromagnetic interaction with the J values of −39.4, −39.7, and −31.4 cm^{−1} for **4**, **5**, and **6**, respectively. An explanation can also be made invoking the countercomplementary effect between the monoatomic bridge and the triatomic bridge in *syn*–*syn* configuration. As there are two triatomic bridges, the dominant (weak) antiferromagnetic interaction is observed for all three compounds. On the other hand, the known class F compound **XV** shows the weak ferromagnetic interaction ($J = +10.13$ cm^{−1})⁸ as expected from the presence of two monoatomic bridges with bridging angles of 102.7(2) and 86.8(2)° and one triatomic bridge. Furthermore, in **XV**, these angles result in the increase of the magnetic orbital orthogonality as compared to the bridging angles of 109.7(1)°, 109.5(1)°, and 108.3(1)° for **4**–**6**, respectively. Magnetic data of all class F compounds is summarized in Table 4.

Theoretical Study of Magnetic Coupling. In order to investigate the magneto-structural correlations for triply bridged dinuclear Cu(II)–Cu(II) molecular systems and to compare the performance of several exchange–correlation density functional potentials in predicting their magnetic coupling constants, we have estimated the singlet–triplet gap through a series of DFT calculations. These are all of hybrid type since it is now well established that pure functional based on the local density approach (LDA) or any of the different generalized gradient

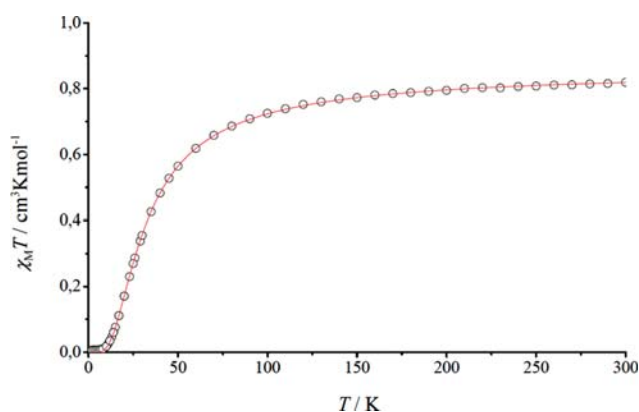


Figure 9. Plot of magnetic susceptibility–temperature product ($\chi_M T$) versus (T) temperature for compound **4**.

Table 2. Experimental Normal and Half-Field (at 20 K) EPR Signals and Best-Fit Susceptibility Data to eq 3 (g_{iso} , J_{exp} , and θ) for Compounds **1**–**6**

Compound	g	$g_{1/2}$	g_{iso}	J_{exp} (cm ^{−1})	θ (K)	R ($\times 10^{-4}$)
1	2.014	4.370	2.19 ± 0.01	$+151.2 \pm 6.0$	-0.62 ± 0.02	1.6
2	2.065	4.427	2.20 ± 0.01	$+104.5 \pm 3.5$	-0.59 ± 0.02	1.2
3	2.093	4.396	2.17 ± 0.01	$+98.4 \pm 3.2$	-0.43 ± 0.02	1.8
4	2.126	4.325	2.14 ± 0.01	-39.4 ± 0.2		0.2
5	2.118	4.375	2.17 ± 0.01	-39.7 ± 0.1		0.1
6	2.119	4.311	2.17 ± 0.01	-31.4 ± 0.5		0.6

approaches (GGAs) largely overestimate the magnitude of the magnetic coupling constants.^{26,27} This is not the case with hybrid functional although agreement with experiment required a careful analysis of the fraction of nonlocal Fock exchange included in the exchange potential. Therefore, a series of calculations has been carried out for compounds **1**–**6** using the well-known and widely used stand-alone hybrid functionals BHandHLYP and B3LYP derived from the GGA potentials,^{28,29} M06 and M06-2X from the meta GGA functionals family,^{30–32} and HSE³³ and LC- ω PBE³⁴ from the range-separated family recently introduced by Scuseria and co-workers.

Here, let us just recall that the popular B3LYP hybrid-DFT functional incorporates 20% of Fock exchange and a 80% of Becke gradient corrected form of the exchange potential, together with a gradient corrected correlation potential. This method exhibits a good performance in the quantitative description of main group thermochemistry³⁵ but presents some problems when studying the magnetic coupling of open shell systems such as transition metal polynuclear complexes, where magnetism is strongly dominated by electron exchange and both dynamical and nondynamical correlation effects.^{27,28} Like B3LYP, the BHandHLYP is a hybrid-DFT method derived from the GGA but, in this case, the mixture of HF and LDA is 50%:50% and performs better for calculating the magnetic coupling in some systems. The M06 family of meta GGA functionals includes the density, its gradient, and an additional term better approximating the kinetic density potential. The most representative functionals of this family are the M06 and M06-2X, which include 27% and 54% of HF exchange, respectively, although the latter has been optimized for main group chemistry calculations. The performance of the M06 family in

Table 3. Structural and Magnetic Data for Class B Triply-Bridged Dinuclear Copper(II) Compounds^a

Compound ^b	Geom ^c	τ	ϕ	γ	Class	Cu–X			J_{exp}	ref ^d
						Axial	Equatorial	Cu–OH–Cu		
$[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CC}(\text{CH}_3)_3)](\text{ClO}_4)_{1/2}(\text{CH}_3\text{CH}_2\text{OH})$ (1)	SP, SP	0.10, 0.22 0.08, 0.26	117.7, 120.4	9.9, 16.2 8.8, 21.2	B	2.419, 2.379 2.425, 2.369	1.911–2.015 1.893–2.012	103.8, 105.3	151.2	pw
$[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-O}_2\text{SOCF}_3)](\text{CF}_3\text{SO}_3)(\text{DMF})_{0.5}$ (2)	SP, SP	0.14, 0.15	154.8	11.2, 11.8	B	2.351, 2.354	1.906–2.019	122.3	104.5	pw
$[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)](\text{NO}_3)_2$ (3)	SP, SP	0.19, 0.21	122.3	14.6, 12.2	B	2.344, 2.368	1.925–2.029	103.6	98.4	3, pw
$[\text{Cu}_2(\text{dpym})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{S}_2\text{O}_8)$ (II)	SP, SP	0.43	164.4	40.4	B	2.414	1.911–2.023	109.6	n.d.	3
$[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{NO}_3)_2$ (III)	SP, SP	0.21, 0.19	120.5	14.5, 11.6	B	2.347, 2.460	1.938–2.017	104.0	n.d.	3
$[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{BF}_4)_{1/2} \cdot 0.5\text{H}_2\text{O}$ (IV)	SP, SP	0.21, 0.16	114.6	17.0, 8.6	B	2.374, 2.390	1.925–2.008	102.1	120.8	3
$[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{ClO}_4)_2$ (VI)	SP, SP	0.14, 0.25	118.1		B	2.379, 2.405	2.006–2.010	103.8	38.6	3
$[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{ClO}_4)_2$ (VII)	SP, SP	0.02, 0.14	113.8	16.4, 8.2	B	2.360, 2.375	1.933–2.020	101.3	120.0	3
$[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)](\text{ClO}_4)_2$ (VIII)	SP, SP	0.20, 0.16	120.1	15.0, 10.9	B	2.382, 2.415	1.920–2.005	104.5	148.9	3
$[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-Cl})]\text{Cl} \cdot 8.5\text{H}_2\text{O}$ (IX)	SP, SP	0.41, 0.28	123.0	27.4, 18.9	B	2.632, 2.657	1.936–2.029	103.3	145.3	3

^a Geom stands for the coordination of Cu(1) and Cu(2); τ is the aggregate Addison for Cu(1)/Cu(2) and Cu(3)/Cu(4) pairs, and ϕ is the angle between basal planes and γ the tetrahedral twist angle, both in degrees. Cu...Cu and Cu–X distances are in Å and Cu–OH–Cu angles in degrees. J_{exp} is the experimentally derived magnetic coupling constant in cm^{-1} . Abbreviations: bpy = 2,2'-bipyridine; dpym = di-2-pyridylamine; phen = 1,10-phenanthroline; n.d. = not determined; pw = present work. ^c SP = distorted square pyramid.

describing magnetic coupling in Cu(II) dinuclear complexes has been examined by Valero et al. and found to provide a systematic improvement over B3LYP.¹⁷

Nevertheless, most hybrid functionals fail to correctly describe the asymptotic decay of the exchange potential in insulator molecular systems, which is found extremely slow ($-c/r$ versus the expected $1/r$ trend, c being the fraction of nonlocal exchange). This effect delocalizes in excess the spin density of the paramagnetic centers across the ligands and results on increased coupling constants. In order to solve these problems, Vydrov and Scuseria implemented a long-range corrected hybrid functional (denoted as LC- ω PBE), which restores the proper asymptotic limit using the HF exchange to describe the long-range electron–electron interactions, whereas a GGA functional is used to describe the short-distance interactions in a gradual way:

$$E_{\text{xc}}^{\text{LC}-\omega\text{PBE}}(\omega) = E_{\text{x}}^{\text{LR}-\text{HF}}(\omega) + E_{\text{x}}^{\text{SR}-\text{PBE}}(\omega) + E_{\text{c}}^{\text{PBE}} \quad (4)$$

The standard value of $\omega = 0.40a_0^{-1}$ provides an excellent performance, and it is the one used in this work. Likewise, Heyd, Scuseria, and Ernzerhof presented a short-range corrected HSE hybrid³⁴ for the correct description of semiconducting or metallic periodic bulk systems: it avoids the problems found when treating the HF exchange in periodic calculations for semiconductor or metallic systems by switching it on at short electron–electron distances, whereas at long electron–electron distances the PBE functional is exclusively used:

$$E_{\text{xc}}^{\text{HSE}}(\omega) = aE_{\text{x}}^{\text{LR}-\text{HF}}(\omega) + (1-a)E_{\text{x}}^{\text{SR}-\text{PBE}}(\omega) + E_{\text{c}}^{\text{PBE}}(\omega) \quad (5)$$

In this case, the value of $\omega = 0.11a_0^{-1}$ has been shown to be the most appropriate, so the HSE06 (the recommended version of the full Heyd–Scuseria–Ernzerhof functional) stand alone functional has been chosen for the calculations performed in this work. The performance of range separated functional in describing magnetic coupling has been recently explored¹⁸ using the same open shell database employed by Valero et al.¹⁷ whereas Phillips and Peralta studied systematically the effect of the range separation ω parameter on the calculated J values.¹⁹

To obtain a more complete open-shell database of systems involving two unpaired electrons and to further investigate the performance of these recently developed functionals, we have also carried out calculations for the similar series of triply bridged dinuclear Cu(II) compounds studied previously⁹ using now the meta and range-separated functionals above-mentioned. To avoid any possible misleading arising from the numbering of the different compounds, those corresponding to compounds studied in previous work are referred to in roman numbers (i.e., compound 4 in ref 9 is compound IV here).

In all cases, the molecular structure of the dinuclear complexes has been extracted from the experimentally determined crystallographic structures, except in the cases of compounds 1, XII, and XIII, where the position of the hydrogen atom belonging to the OH bridging group was not consistent with the typical bond length and bridging mode of this group and hence adjusted to $d(\text{O}–\text{H}) = 0.90 \text{ \AA}$ and to a O–H bond forming an angle of aprox. 40° with the vector normal to the Cu–O(H)–Cu plane. All the remaining atom positions were taken from the crystallographic data.

Following the procedure described above and the basis set and computational details given in the corresponding section below, we have computed the singlet–triplet gap for compounds 1–6.

Table 4. Structural and Magnetic Data for Class F Triply-Bridged Dinuclear Copper(II) Compounds^a

Compound ^b	Geom ^c	τ	γ	Class	Cu...Cu	Cu—O—Cu	J_{exp}	ref ^b
[Cu ₂ (bpy) ₂ (μ -OCOPh)(μ -O ₂ CPh) ₂](ClO ₄) (4)	SP, interm.	0.38, 0.52	30.1	F1	3.386	109.7	−39.4	pw
[Cu ₂ (bpy) ₂ (μ -OCOPh)(μ -O ₂ CPh) ₂](BF ₄) (5)	SP, interm.	0.39, 0.52	30.6	F1	3.386	109.5	−39.7	pw
[Cu ₂ (bpy) ₂ (μ -OCOPh)(μ -O ₂ CPh) ₂](PF ₆) (6)	SP, interm.	0.35, 0.50	28.0	F1	3.384	108.3	−31.4	pw
[Cu ₂ (dpyam) ₂ (μ -OCOCH ₃)(μ -O ₂ CCH ₃)(μ -OH)](PF ₆)(H ₂ O) (XV)	SP, interm.	0.32, 0.51	25.3	F2	2.988	102.7, 86.8	10.13	8

^a All abbreviations, symbols, and units are as in Table 3. ^b Abbreviations: bpy = 2,2'-bipyridine; dpyam = di-2-pyridylamine; pw = present work.

^c SP = distorted square pyramidal. interm. = intermediate five coordinated geometry.

In order to obtain a more complete database, we have also considered the structurally characterized compounds **I**, **IV**, and **VI–XIV** studied in previous work.⁹ Calculations have been carried out using the B3LYP and BHandHLYP hybrid functionals, the M06 and M06–2X hybrid meta-GGA functionals, and the HSE and LC- ω PBE range separated functionals. The results, compared to experimental structural and magnetic values, are listed in Table 5. Before describing the calculated values, it is worth to recall that the antiferromagnetic triply bridged compounds **4–6** have one of the Cu(II) ions in a square-pyramidal (SP) environment and the other in a mainly trigonal-bipyramidal (TBP) pentacoordination, and hence, together with the ferromagnetic compound **XV**, they can be classified into the class F compounds (see Scheme 1 and ref 8). In the present compounds (see Scheme 2c), the main interaction between the magnetic orbitals occurs through the two O,O'-carboxylato bridges, while the monodentate bridging benzoate lies in the apical position of the SP, thus not participating in the superexchange interactions. For this reason, there are no countercomplementary effects through this ligand and only the antiferromagnetic pathways through both bidentate carboxylates remain active. We classify this type of triply bridged antiferromagnetic di-Cu(II) compounds as subclass F1. On the other hand, the ferromagnetic complexes **1–3** consist of two Cu(II) ions in a pentacoordinated square-pyramidal (SP) environment in which two basal positions are occupied by two bidentate terminal amines, and the other two are bonded to a μ -hydroxo and a bidentate μ -O,O'-carboxylato bridging ion, respectively. The apical positions share the third bridging ligand, which is a monodentate water molecule for compounds **1** and **3**, but a μ -O,O'-trifluoromethanesulphonate ion for **2**. According to previous work,³ they can be classified into triply bridged di-Cu(II) class B compounds (Scheme 2b). This molecular structure fixes the magnetic orbitals (and the spin density of the triplet state) over the $d_{x^2-y^2}$ Cu atomic orbitals and the oxygen donors of the basal bridging ligands that thorough the countercomplementary effect between the carboxylato and the hydroxo basal bridges resulting in a moderately large ferromagnetic interaction.⁴ As can be seen in Scheme 2b, the bridging ligands in apical position do not contribute to the magnetic superexchange, although in **2**, its triatomic nature is responsible for the opening of both the interbasal and Cu—O(H)—Cu angles up to 154.8 and 122.3 degrees respectively, due to its steric effect.

In previous work, a trend between the calculated B3LYP and BHHLYP magnetic coupling constants and the aggregate Addison's parameter was identified. Including the calculated values for the three new class B compounds (filled marks) into the plot of the B3LYP and BHHLYP calculated J values vs the aggregate Addison's parameter (Figure 10), one can readily see that that **3** lies close to the regression lines, whereas calculated values for **1** are rather higher and for **2** significantly lower. Nevertheless, if new regression lines are plotted which

Table 5. Calculated Values of the Coupling Constant J (in cm^{−1}) for Compounds **1–6, **I**, **IV**, and **VI–XV** Using Hybrid and Screened Functionals, Compared to Experimental Magnetic Values^a**

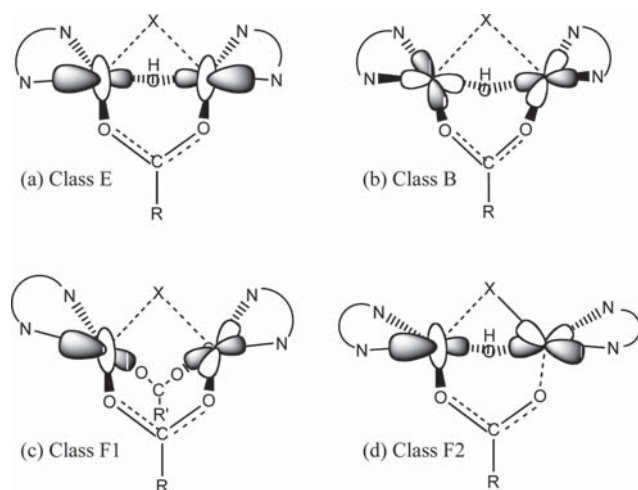
Compound	τ_{aggr}	J_{calc}						J_{exp}
		M06–2X	BHHLYP	LC- ω PBE	HSE	B3LYP	M06	
1	0.33	80.2	98.8	166.0	180.1	208.0	285.1	151.2
2	0.29	44.3	56.4	87.5	100.5	114.1	178.6	104.5
3	0.40	70.0	85.7	145.0	156.8	181.4	253.9	98.4
I		97.9	125.5	183.7	194.0	220.3	306.8	112.7
IV	0.37	64.9	80.4	134.6	145.6	166.6	232.1	120.8
VI	0.37	67.5	83.2	135.0	147.3	169.0	235.5	38.6
VII	0.34	65.1	80.5	135.7	147.8	169.7	238.8	120.0
VIII	0.37	70.4	87.0	140.1	153.8	176.7	248.2	148.9
IX	0.69	56.4	69.4	117.9	126.9	146.8	205.3	145.3
X	1.34	66.6	83.6	144.1	158.5	185.7	267.5	79.1
XI	1.44	43.6	78.3	130.2	140.4	161.3	237.2	79.7
XII	1.28	49.8	66.2	109.1	131.3	162.6	267.9	62.5
XIII	1.14	13.9	34.2	58.0	78.2	108.1	239.7	47.8
XIV	0.65	40.1	57.6	81.1	89.2	99.2	165.8	24.1
XV	0.84	−5.2	−15.9	−42.9	−45.3	−78.3	−34.8	10.1
4	0.90	−13.0	−12.2	−37.2	−56.1	−73.9	−74.5	−39.4
5	0.91	−13.0	−12.4	−36.3	−54.2	−70.9	−71.8	−39.7
6	0.84	−11.7	−11.0	−31.0	−47.4	−62.1	−62.5	−31.4

^a Best theoretical estimates are marked in bold. Roman numbers **I–XIV** correlate to the numbering scheme used in ref 9 whereas **XV** is used for compound **X** in ref 8.

include the new compounds into the fitting, one can observe that they are almost identical with that previously published, except for the rather lower quality of the actual regression coefficients. For these new compounds, neither of these two functionals predict the correct order of intensities in the experimental coupling constants (see Table 5), although the three J_{exp} values lie inside the theoretical intervals defined by the BHHLYP and B3LYP methods, a trend already observed in previous work.⁹

Let us now extend our investigation to the six above-mentioned density functional theory-based methods which in a way correspond to a systematic improvement toward the universal, yet unknown, exact exchange-correlation potential. We will also consider all the triply bridged di-Cu(II) compounds and will center our attention in the results displayed in Table 5, where values in bold indicate the best approximation to the experimental values. From results in Table 5, one can see that calculated values scale through the methods as M06–2X < BHandHLYP < LC- ω PBE < HSE < B3LYP < M06, roughly following the decrease of Hartree–Fock exchange, in line with the work of Martin and Illas, who postulated that for hybrid functionals the magnitude of J strongly depends on the exchange potential contribution and it is not largely affected by the choice of the correlation

Scheme 2



potential.^{27,28} It is also interesting to recognize that the calculated values which are closer to experimental ones (marked in bold) are mainly reached by the GGA hybrid BHandHLYP (50% of Fock exchange, 5 hits over 18) and, especially (8 hits over 18), by the range separated LC- ω PBE methods. For the new three antiferromagnetic compounds 4–6, it is undoubtedly clear that LC- ω PBE provides an excellent estimate of the experimental value, in accordance with the results of recent investigations about range-separated hybrid functionals.¹⁸

With the aim to further verify that the conclusions above are not fortuitous, we expand the compounds database to include a significantly wide range of magnetic interaction in triply bridged di-Cu(II) compounds and employ all the DFT methods. The complete set of results is graphically displayed in Figure 11, where calculated versus experimental single–triplet gap values are plotted for each method and compared to the perfect-fitting line in black color. The best slope of the J_{calc} vs J_{exp} regression line still corresponds to the LC- ω PBE functional (1.02), that brings the optimum global behavior on the overall ferro- and antiferromagnetic regions, with a reasonable mean accuracy (+20 cm^{−1} overestimation) and a moderate linear dispersion ($R^2 = 0.74$). It is worth noting that the second best results are achieved by the HSE screened functional, that was initially designed to deal with metals but which also aims to correct the wrong asymptotic behavior of the PBE functional. For the nonscreened hybrids, the BHandHLYP and B3LYP functionals show the best global behavior, indicating that the presence of a considerable fraction of Fock exchange is a crucial point to correctly describing the energy separation between these spin states.

To round off this work, we finally center our attention on the systems for which our rule-of-thumb does not work. For compounds 2 and IX, belonging to class B (Scheme 2b), the experimental J values are higher than those predicted by the LC- ω PBE hybrid, although these are still below those corresponding to the B3LYP limit. On the contrary, compounds VI and XIV lie even below the M06-2X limit. The case of the only representative of the F2 class (Scheme 2d) of ferromagnetic compounds, XV, is still worst: all functionals even fail for predicting the correct sign of J . All three complexes VI, XIV,

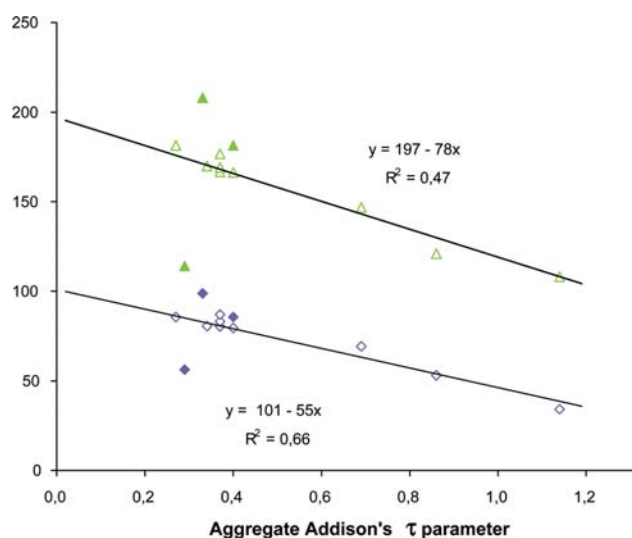


Figure 10. Plot of the B3LYP (triangles) and BHandHLYP (diamonds) calculated J values in cm^{−1} versus the aggregate Addison's parameter for class B compounds. New compounds are marked by filled symbols.

and XV are characterized by having small ferromagnetic coupling constants (+38, +24, and +10 cm^{−1}, respectively). For the three above-mentioned compounds, all DFT methods explored in this work fail to quantitatively approach the experimental coupling constant, and all exhibit a noticeable excess error: the best approximation (M06-2X) gives an overall 20 cm^{−1} overestimation. For the class F2 compound, all methods predict antiferromagnetic coupling, M06-2X being the one that gives the best approximation (15 cm^{−1} underestimation).

For the only example of ferromagnetic class F2 complex, we can see in the orbital representation drawn in Scheme 2d that the topology of their magnetic orbitals is very different from that of the antiferromagnetic class F1 compounds 4–6. In XV, the most intense interaction is between the two lobes of the d_{z^2} (TBP) and $d_{x^2-y^2}$ (SP) lobes through the hydroxo bridge, whereas the bidentate lies in the apical position of the SP coordination of Cu(1), thus debilitating their contribution to the countercomplementary effects and weakening the global ferromagnetic coupling by breaking the delicate balance between opposite interactions.

The fact that small ferromagnetic couplings in systems with countercomplementary bridges are hard to reproduce with the use of monodeterminantal methods was already noticed in previous papers and was attributed to the fact that DFT functions cannot fully account for dynamical electron correlation effects.³⁶ There, it was suggested that multiconfigurational post Hartree–Fock calculations could be needed to achieve a better fit for these systems, although the need of huge computational resources limited them to the use of complete active space second-order perturbation theory (CASPT2 method) on simplified model systems.³⁷ Nevertheless, it is the case that an error on the J sign, as we have observed in the present paper, was not detected. In fact, the delicate balance of the interelectronic interactions in such a feebly ferromagnetically coupled compound is still not described with enough accuracy, but the tailoring of new and

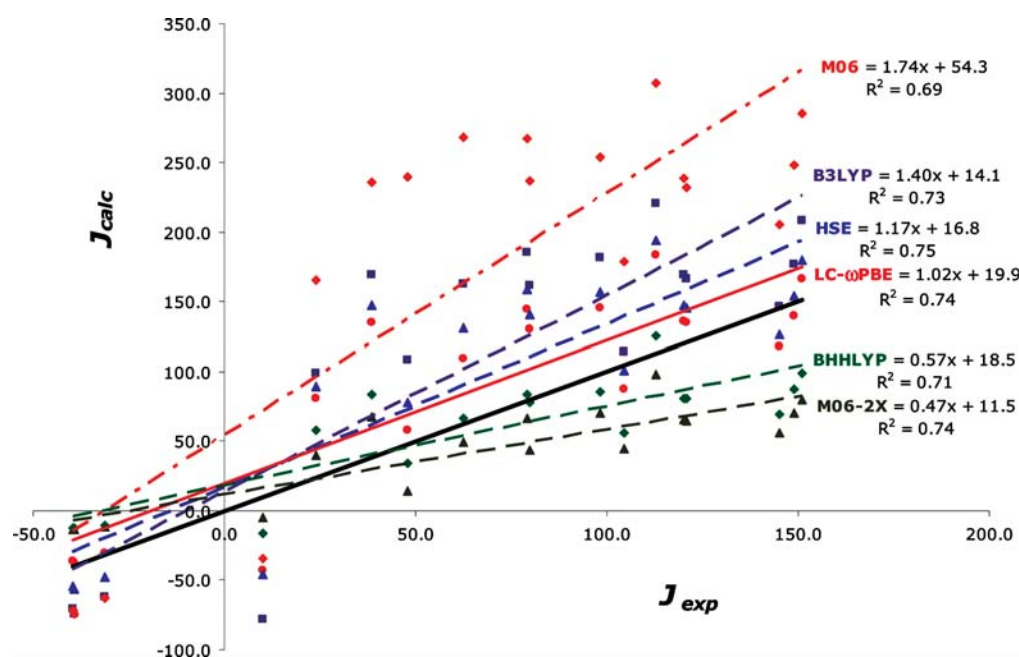


Figure 11. Calculated (J_{calc}) vs experimental (J_{exp}) values (in cm^{-1}) of the singlet–triplet gap for the Cu dinuclear complexes in Table 5. The black line corresponds to the perfect fit.

promising hybrid methods seems to tell us that we are in the correct way.

CONCLUSIONS

Hetero triply bridged dinuclear Cu(II) compounds form a very interesting class of systems with a broad range of values for the magnetic coupling constant. Here, we extend our knowledge of these materials by studying experimentally and theoretically the magnetic properties of two newly synthesized, $\{[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CC}(\text{CH}_3)_3)](\text{ClO}_4)_2\}_2(\text{CH}_3\text{CH}_2\text{OH})$ (**1**) and $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-O}_2\text{SO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)(\text{DMF})_{0.5}$ (**2**), one previously reported $[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)](\text{NO}_3)_2$ (**3**) class B compound, and three new homo triply bridged dinuclear Cu(II), $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OCOPh})(\mu\text{-O}_2\text{CPh})_2]\text{X}$ with $\text{X} = \text{ClO}_4^-$ (**4**), BF_4^- (**5**), and PF_6^- (**6**), class F compounds. Compounds **1–3** are found to be ferromagnetically coupled whereas compounds **4–6** are anti-ferromagnetically coupled. Values for the magnetic coupling constants have been derived by appropriate fitting of the experimental susceptibility data using the Bleaney–Bowers equation.²⁶

The origin of the magnetic interactions and the magnitude of the magnetic coupling have been analyzed by means of state of the art density functional theory-based calculations. Moreover, it is shown that, for class B and E compounds, the aggregate Addison's parameter provides a possible magneto-structural correlation, confirming the conclusion from previous work on similar compounds.⁹

From the whole set of DFT calculations carried out in the present work including the newly characterized compounds **1–6** and including data from previous work on other Cu(II) dinuclear complexes,⁹ one can conclude that the ideas behind range-separated functionals are on the right track to derive electronic structure methods that have to deal with subtle energy differences between well-defined states in molecular systems. In particular, the

fact that the slope of the experimental versus calculated J values is close to 1 for the LC- ω PBE provides a strong indication of the predictive character of this new density functional theory method.

ASSOCIATED CONTENT

S Supporting Information. A more detailed description of the crystal structure of compounds **1** to **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>. CCDC numbers 787996, 787997, 787998, 787999, and 788000 contain the supplementary crystallographic data for compounds **1**, **2**, and **4–6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk.

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Multiple-layer heterometallic $\text{Mn}^{\text{II}}\text{--Ag}^{\text{I}}$ coordination polymers constructed from $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ and $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units

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Abstract Two multiple-layer heterometallic $\text{Mn}^{\text{II}}\text{--Ag}^{\text{I}}$ coordination polymers, $\{\text{Mn}^{\text{II}}(\text{ampyz})(\text{H}_2\text{O})[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]\cdot\text{ampyz}\}_n$ (**1**) and $\{[\text{Mn}^{\text{II}}(\text{benzim})_2[\text{Ag}^{\text{I}}(\text{CN})_2]_2][(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]\cdot\text{H}_2\text{O}\}_n$ (**2**) where ampyz = 2-aminopyrazine and benzim = benzimidazole, have been prepared and structurally characterized. Compound **1** reveals a multiple-layer two-dimensional network with strong hexanuclear argentophilic interactions leading to an infinite three-dimensional framework. Compound **2** has an unprecedented double-layer two-dimensional squared grid-type network with (4,4) topology through $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ and $\pi\text{--}\pi$ interactions between two adjacent squared layers. These double-layer networks of **2** are linked to others by $\pi\text{--}\pi$ interactions, leading to a three-dimensional framework.

Introduction

The search for new coordination polymers is a challenge for coordination chemists, especially in areas of current interest such as supramolecular chemistry, crystal engineering and molecular magnetism. Such compounds have interesting functional properties such as molecular adsorption,

luminescence and catalysis [1–9]. The rational design and synthesis of new coordination polymers have been carried out by using judicious choices of transition metals and ligands to control the supramolecular topology and dimensionality. In addition, intermolecular interactions such as hydrogen bonding, $\pi\text{--}\pi$ stacking and van der Waals interactions can also greatly influence the resulting crystal structure and its dimensionality [10, 11]. In recent years, much effort has been devoted to developing new manganese(II) coordination polymers by the incorporation of dicyanoargentate(I) building blocks with mono-, di- or tetradentate co-ligands, which can show various types of dimensionality, structural architectures and magnetic properties [12–16]. The dicyanoargentate(I), $[\text{Ag}_2^{\text{I}}(\text{CN})_2]^-$ bridging ligand has frequently been employed to construct unique multidimensional (1D, 2D and 3D) coordination network architectures and to extend the stabilized coordination framework via silver...silver attractions (argentophilic interactions) [17, 18]. Interestingly, the self-assembly of this bridging ligand may lead to the formation of the $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ unit which has been shown to exhibit a remarkable diversity of coordination networks [19–21].

With the aim to extend these systems, our research group has attempted to design and synthesize new Mn(II) coordination polymers using dicyanoargentate(I) bridging ligands to increase the dimensionality and enhance the stability of whole frameworks via silver...silver interactions, while co-ligands such as 2-aminopyrazine (ampyz) and benzimidazole (benzim) are included to facilitate the intermolecular interactions, namely H-bonding and $\pi\text{--}\pi$ stacking, respectively, stabilizing the overall coordination framework. In this work, two new multiple-layer two-dimensional heterometallic $\text{Mn}^{\text{II}}\text{--Ag}^{\text{I}}$ coordination polymers were successfully synthesized and structurally characterized. Herein, we report the synthesis, spectroscopic

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characterization and crystal structures of $\{[\text{Mn}^{\text{II}}(\text{ampyz})\cdot(\text{H}_2\text{O})[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]]\cdot\text{ampyz}\}_n$ (**1**) and $\{[\text{Mn}^{\text{II}}(\text{benzim})_2[\text{Ag}^{\text{I}}(\text{CN})_2]_2][(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]\cdot\text{H}_2\text{O}\}_n$ (**2**).

Experimental

IR spectra were recorded as KBr disks on a Perkin-Elmer Spectrum One FTIR spectrophotometer in the 4,000–450 cm^{-1} range. Elemental analyses (C, H, N) were determined using a Perkin-Elmer PE-2400 CHNS/O Analyzer. All reagents were commercial grade materials and were used without further purification.

Synthesis of $\{[\text{Mn}^{\text{II}}(\text{ampyz})(\text{H}_2\text{O})\cdot[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]]\cdot\text{ampyz}\}_n$ (**1**)

An aqueous solution (10 mL) of $\text{Mn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.0905 g, 0.25 mmol) was added to a methanolic solution (5 mL) of ampyz (0.0476 g, 0.5 mmol). Then, an aqueous solution (10 mL) of $\text{K}[\text{Ag}^{\text{I}}(\text{CN})_2]$ (0.0498 g, 0.25 mmol) was added. After a week, yellow crystals of compound **1** were obtained. Yield ca. 50%. Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_{11}\text{OAg}_3\text{Mn}$: C (21.8%), H (1.7%) and N (21.5%). Found: C (21.6%), H (1.5%) and N (21.4%). IR (KBr, cm^{-1}): 3,494(s, $\nu(\text{O}-\text{H})$), 3,380(s, $\nu(\text{N}-\text{H})$), 2,159(s, $\nu(\text{C}\equiv\text{N})$), 1,629(m, $\nu(\text{C}=\text{C})$), 1,436(m, $\nu(\text{C}=\text{C})$), 1,211(m, $\nu(\text{C}-\text{N})$), 825(w, $\delta(\text{N}-\text{H})$).

Synthesis of $\{[\text{Mn}^{\text{II}}(\text{benzim})_2\cdot[\text{Ag}^{\text{I}}(\text{CN})_2]_2][(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]\cdot\text{H}_2\text{O}\}_n$ (**2**)

An aqueous solution (10 mL) of $\text{Mn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.0362 g, 0.1 mmol) was added to a methanolic solution (10 mL) of benzimidazole (0.0236 g, 0.2 mmol). Then, an aqueous solution (10 mL) of $\text{K}[\text{Ag}^{\text{I}}(\text{CN})_2]$ (0.0398 g, 0.2 mmol) was added. After a week, colorless plate-like crystals of compound **2** were obtained. Yield ca. 30%. Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{N}_{11}\text{OAg}_3\text{Mn}$: C (35.4%), H (2.3%) and N (17.5%). Found: C (35.5%), H (2.3%) and N (17.0%). IR (KBr, cm^{-1}): 3,328(s, $\nu(\text{N}-\text{H})$), 2,151(s, $\nu(\text{C}\equiv\text{N})$), 1,614(m, $\nu(\text{C}=\text{N})$), 742(s, $\delta(\text{C}-\text{H})$).

Caution! Although no problems were encountered in this work, perchlorate salts are potentially explosive and should be handled in small quantities.

X-ray crystallography

X-ray single-crystal data for both compounds were collected at 293 K. Reflection data were collected on a 1 K Bruker SMART APEX CCD area-detector diffractometer

using rotating mode, graphite-monochromated Mo K α radiation, ($\lambda = 0.71073 \text{ \AA}$) at a detector distance of 4.5 cm and swing angle of -30° . Raw data frame integration was performed with SAINT [22], which also applied correction for Lorentz and Polarization effects. An empirical absorption correction was applied using the SADABS [23] program, which resulted in transmission coefficients ranging from 1.000 to 0.697 and 1.000 to 0.707 for **1** and **2**, respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods on $(F_{\text{obs}})^2$ using the SHELXTL-PC Version 6.12 software package [24]. For compound **1**, all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier carbon atoms except those of the amine group on coordinated ampyz, H(5), H(6) and water molecule, H(7) and H(8), while hydrogen atoms of the ampyz lattice molecule could not be located. All non-hydrogen atoms were refined anisotropically. An ampyz lattice molecule lies on the inversion center, and the amine group of this molecule was disordered with site occupancies of 0.5. In compound **2**, all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier nitrogen and carbon atoms except those of the water lattice molecule. All non-hydrogen atoms were refined anisotropically. For the water lattice molecule, the oxygen atoms were disordered with site occupancies of 0.5.

Results and discussion

Description of crystal structures

$\{[\text{Mn}^{\text{II}}(\text{ampyz})(\text{H}_2\text{O})[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]]\cdot\text{ampyz}\}_n$ (**1**)

The asymmetric unit of compound **1** consists of two independent Mn^{II} centers located on an inversion center with the position occupancy of 0.5, two crystallographically independent units, $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ and $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ and a lattice ampyz molecule (Fig. 1a). The crystallographic data and selected bond distances and angles of compound **1** are shown in Tables 1 and 2, respectively.

The coordination sites of the two Mn^{II} centers, Mn(1) and Mn(2) are similar with four N atoms coordinated in an equatorial position, two N atoms of $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units (Mn–N, 2.230(2) and 2.232(2) $\text{\AA}$) and two N atoms of $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ units (Mn–N, 2.204(2) and 2.241(2) $\text{\AA}$). The axial positions are occupied by two N atoms of ampyz ligands (Mn–N = 2.324(1) $\text{\AA}$) for Mn(1) and two O atoms of water ligands (Mn–O = 2.163(1) $\text{\AA}$) for Mn(2) to give MnN_6 and MnN_4O_2 distorted octahedral chromophores for Mn(1) and Mn(2), respectively.

Fig. 1 **a** Asymmetric unit and atomic numbering scheme (thermal ellipsoids are shown at 50% level) and **b** two-dimensional network for compound **1** (symmetry code $i = 1 - x, 1 - y, -z$), hydrogen atoms and a lattice ampyz molecule are omitted for clarity

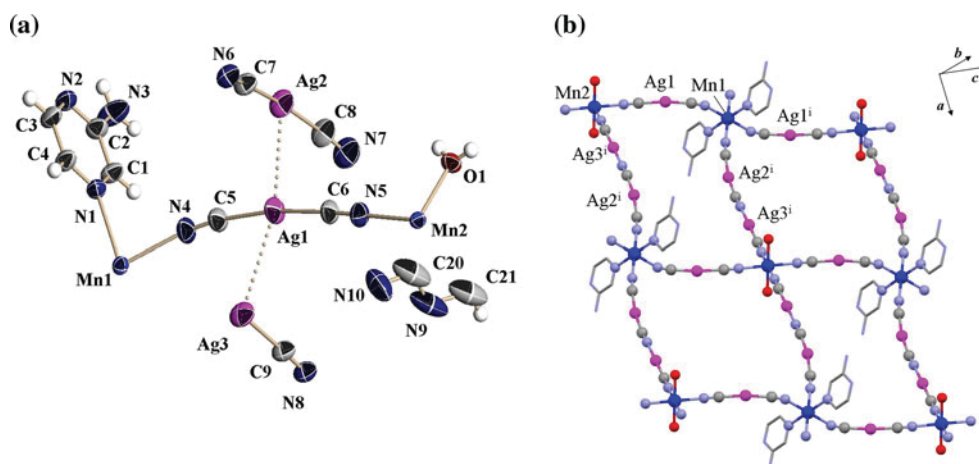


Table 1 Crystallographic and refinement data for compounds **1** and **2**

Compound	1	2
Empirical formula	$C_{22}H_{16}Ag_6Mn_2N_{19}O_2$	$C_{26}H_{18}Ag_3MnN_{11}O$
Formula weight	1335.64	879.06
T/K	293(2)	293(2)
Crystal system	Triclinic	Orthorhombic
Space group	$P-1$	$Pbca$
a (Å)	7.5739(3)	13.6499(7)
b (Å)	8.5028(4)	16.6200(8)
c (Å)	15.4945(7)	26.3379(13)
α (°)	99.5680(10)	90.00
β (°)	103.0090(10)	90.00
γ (°)	90.6710(10)	90.00
V (Å ³)	957.45(7)	5975.1(5)
Z	1	8
D_{calc} (g cm ⁻³)	2.303	1.954
μ (mm ⁻¹)	3.684	2.391
$F(000)$	629	3400
Crystal size (mm)	0.36 × 0.22 × 0.15	0.31 × 0.20 × 0.13
Number of reflection collected	13,070	58,327
Number of unique reflections (R_{int})	4,604(0.0250)	5,889(0.0340)
Data/restraints/parameter	4604/0/242	5889/0/389
Goodness-of-fit	1.062	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0224$ $wR_2 = 0.0543$	$R_1 = 0.0198$ $wR_2 = 0.0495$
R indices (all data)	$R_1 = 0.0247$ $wR_2 = 0.0555$	$R_1 = 0.0237$ $wR_2 = 0.0514$
Largest difference in peak and hole (e ³)	0.638 and -0.997	0.394 and -0.388

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

Along the crystallographic b axis, the Mn(1) and Mn(2) atoms are connected by $[Ag^I(CN)_2]^-$ units in an alternation of Mn(1) and Mn(2) sites to give an infinite 1D chain-like

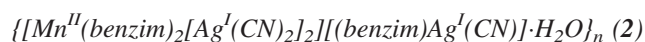
Table 2 Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for $\{[Mn^{II}(ampyz)(H_2O)[Ag_2^I(CN)_3][Ag^I(CN)_2]] \cdot ampyz\}_n$ (**1**)

Bond lengths			
Mn(1)–N(1)	2.324(1)	Mn(2)–O(1)	2.163(1)
Mn(1)–N(1) ^c	2.324(1)	Mn(2)–O(1) ^e	2.163(1)
Mn(1)–N(4)	2.230(2)	Mn(2)–N(5)	2.232(2)
Mn(1)–N(4) ^c	2.230(2)	Mn(2)–N(5) ^e	2.232(2)
Mn(1)–N(6) ^a	2.204(2)	Mn(2)–N(8)	2.241(2)
Mn(1)–N(6) ^d	2.204(2)	Mn(2)–N(8) ^e	2.241(2)
Ag(1)···Ag(2)	3.0320(3)	Ag(1)···Ag(3)	3.0530(3)
Ag(2)···Ag(2) ^f	3.3420(5)		
Bond angles			
N(1)–Mn(1)–N(4)	89.20(8)	O(1)–Mn(2)–N(5) ^e	91.06(8)
N(1)–Mn(1)–N(4) ^c	90.80(8)	O(1)–Mn(2)–N(8) ^b	91.52(8)
N(1)–Mn(1)–N(6) ^a	89.51(7)	O(1)–Mn(2)–N(8) ^g	88.48(8)
N(1)–Mn(1)–N(6) ^d	90.49(7)	O(1)–Mn(2)–O(1) ^e	180.00(3)
N(1)–Mn(1)–N(1) ^c	180.00(13)	N(5)–Mn(2)–N(5) ^e	180.000(1)
N(4)–Mn(1)–N(1) ^c	90.80(8)	N(5)–Mn(2)–N(8) ^b	89.63(8)
N(4)–Mn(1)–N(6) ^a	88.64(9)	N(5)–Mn(2)–N(8) ^g	90.37(8)
N(4)–Mn(1)–N(6) ^d	91.36(9)	N(5)–Mn(2)–O(1) ^e	91.06(8)
N(4)–Mn(1)–N(4) ^c	180.00(15)	N(8) ^c –Mn(2)–O(1) ^e	88.48(8)
N(1) ^e –Mn(1)–N(4) ^c	89.20(8)	N(8)–Mn(2)–N(5) ^e	90.37(8)
N(1) ^e –Mn(1)–N(6) ^d	89.51(7)	N(8)–Mn(2)–N(8) ^e	180.00(9)
N(4) ^e –Mn(1)–N(6) ^d	88.64(9)	O(1) ^g –Mn(2)–N(5) ^e	88.94(8)
N(6) ^b –Mn(1)–N(1) ^c	90.49(7)	O(1) ^g –Mn(2)–N(8) ^g	91.52(8)
O(1)–Mn(2)–N(5)	88.94(8)	N(5) ^g –Mn(2)–N(8) ^g	89.63(8)
		Ag(2)–Ag(1)–Ag(3)	165.148(10)

Symmetry code: $a = x, -1 + y, z$; $b = x, 1 + y, z$; $c = -x, -y, -z$; $d = -x, 1 - y, -z$; $e = 1 - x, 2 - y, 1 - z$; $f = 1 - x, 1 - y, 1 - z$ and $g = 1 - x, 1 - y, 1 - z$

structure with the Mn(1)⋯Mn(2) distance of 10.5260(4) Å. These chains are further linked by $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ units along the crystallographic a axis in the same manner of alternating Mn(1) and Mn(2) sites, leading to a 2D network (Fig. 1b) with the Mn(1)⋯Mn(2) distance of 15.6819(4) Å. Furthermore, the extended 2D networks include rather strong $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ (argentophilic) interactions between the $[\text{Ag}(\text{I})(\text{CN})_2]^-$ and $[(\text{NC})\text{Ag}(\text{I})(\text{CN})\text{Ag}(\text{I})(\text{CN})_2]^-$ groups of adjacent 2D layers along the crystallographic a axis. These interactions could be defined as the hexanuclear moieties (Fig. 2a), $[\text{Ag}(3)\cdots\text{Ag}(1)\cdots\text{Ag}(2)\cdots\text{Ag}(2)^i\cdots\text{Ag}(1)^i\cdots\text{Ag}(3)^i]$, symmetry code $i = 1-x, 1-y, -z$ with $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ distances of 3.0530(3), 3.0320(3) and 3.3420(5) Å for $\text{Ag}(1)\cdots\text{Ag}(3)$, $\text{Ag}(1)\cdots\text{Ag}(2)$ and $\text{Ag}(2)\cdots\text{Ag}(2)^i$, respectively. These $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ distances are significantly lower than 3.60 Å, the sum of the van der Waals radii of two Ag^{I} centers [17, 18]. Both the $[\text{Ag}^{\text{I}}(\text{CN})_2]$ and the $[\text{Ag}_2^{\text{I}}(\text{CN})_3]$ moieties are not perfectly linear (C(6)–Ag(1)–C(5) of 171.6(1)°, C(7)–Ag(2)–C(8) of 169.1(1)° and C(9)–Ag(3)–N(7) of 177.8(1)°, which could be due to the presence of argentophilic interactions. These interactions generate an infinite 3D structure of multilayer 2D networks, as illustrated in Fig. 2b and S1. The infinite 3D network of compound **1** is also stabilized by hydrogen bonding between coordinated water molecules and lattice ampyz molecule along the a axis (Figure S2).

Although containing the same $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ and $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units, the novel coordination network of the heterometallic $\text{Mn}^{\text{II}}\text{--Ag}^{\text{I}}$ compound **1** is distinct from those of related coordination polymers, such as $\{\text{Fe}^{\text{II}}(3,5\text{-Me}_2\text{py})_2\text{--}[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]\}_n$ (**I**) [5], $\{\text{Cd}^{\text{II}}(\text{pyz})_2[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]\}_n$ (**II**) [20] and $\{\text{Fe}^{\text{II}}(\text{pmd})_2[\text{Ag}_2^{\text{I}}(\text{CN})_3][\text{Ag}^{\text{I}}(\text{CN})_2]\}_n$ (**III**) [21] (3,5-Me₂py = 3,5-dimethylpyridine, pyz = pyrazine, and pm� = pyrimidine). These related compounds show interpenetrated 3D structures in which the distorted octahedral M^{II} sites are also coordinated by $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ and $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units in equatorial positions, but the axial positions are occupied by monodentate 3,5-Me₂py and bidentate bridging pyz and pm� ligands for **I**, **II** and **III**, respectively, whereas compound **1** shows a 3D structure of multiple-layer 2D networks involving strong hexanuclear argentophilic interactions with the axial positions coordinated by monodentate ampyz and aqua ligands.



The asymmetric unit of compound **2** consists of a Mn^{II} atom, two independent $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units, a $[(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]$ unit and a lattice water molecule (Fig. 3a). The crystallographic data and selected bond distances and angles for compound **2** are shown in Tables 1 and 3.

Fig. 2 **a** Hexanuclear Ag^{I} unit (symmetry code $i = 1-x, 1-y, -z$), **b** side view of multiple-layer 3D network via hexanuclear $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions Hydrogen atoms, coordinated ampyz, water and lattice ampyz molecules are omitted for clarity

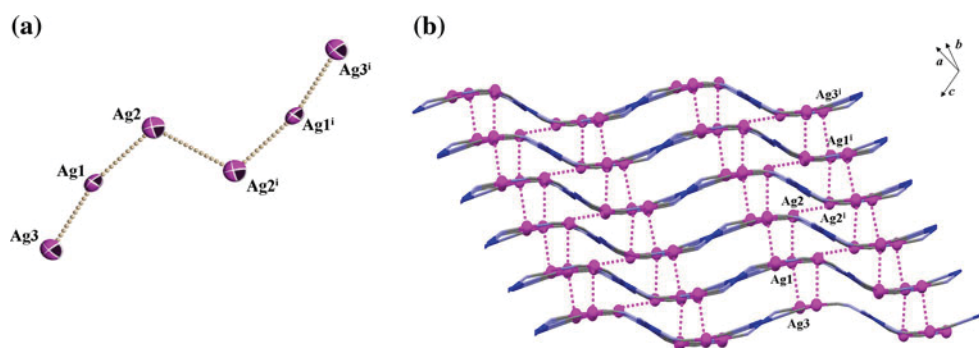


Fig. 3 **a** Asymmetric unit and atomic numbering scheme (thermal ellipsoids are shown at 50% level) and **b** two-dimensional squared layers with (4,4) topology for compound **2**. Hydrogen atoms and water lattice molecule are omitted for clarity

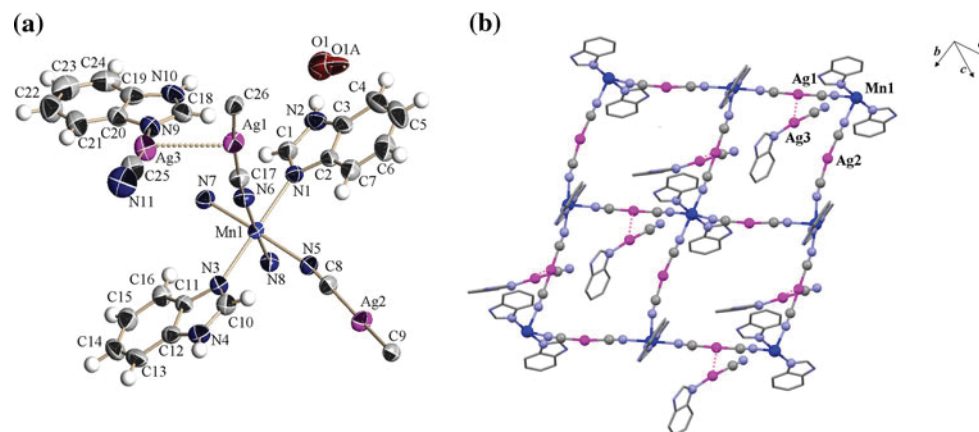
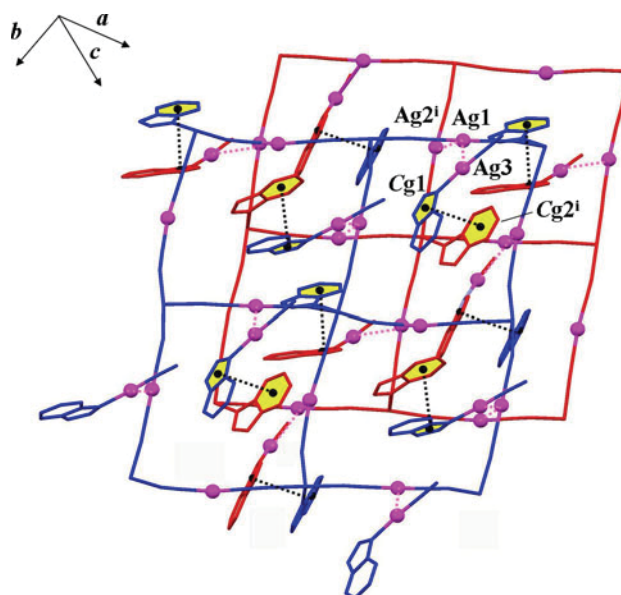


Table 3 Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for $\{[\text{Mn}^{\text{II}}(\text{benzim})_2[\text{Ag}^{\text{I}}(\text{CN})_2]_2][(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]\cdot\text{H}_2\text{O}\}_n$ (**2**)

<i>Bond lengths</i>			
Mn(1)–N(1)	2.273(1)	Mn(2)–N(6)	2.256(1)
Mn(1)–N(3)	2.240(1)	Mn(2)–N(7)	2.241(1)
Mn(1)–N(5)	2.276(1)	Mn(2)–N(8)	2.312(1)
Ag(1)⋯Ag(2)	3.2551(3)	Ag(1)⋯Ag(3)	3.1225(3)
<i>Bond angles</i>			
N(3)–Mn(1)–N(7)	94.62(6)	N(6)–Mn(1)–N(5)	90.47(7)
N(3)–Mn(1)–N(6)	89.80(6)	N(1)–Mn(1)–N(5)	92.63(6)
N(7)–Mn(1)–N(6)	95.30(7)	N(3)–Mn(1)–N(8)	92.38(6)
N(3)–Mn(1)–N(1)	176.26(6)	N(7)–Mn(1)–N(8)	84.71(7)
N(7)–Mn(1)–N(1)	87.46(6)	N(6)–Mn(1)–N(8)	177.81(6)
N(6)–Mn(1)–N(1)	86.91(6)	N(1)–Mn(1)–N(8)	90.90(6)
N(3)–Mn(1)–N(5)	85.62(6)	N(5)–Mn(1)–N(8)	89.51(7)
N(7)–Mn(1)–N(5)	174.22(7)	Ag(2)–Ag(1)–Ag(3)	131.873(8)

The Mn^{II} center has a MnN_6 chromophore in a distorted octahedral geometry in which the equatorial positions are occupied by the N atoms of two $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units (Mn–N, 2.241(1) and 2.276(1) Å) and two benzim ligands (Mn–N = 2.240(1)–2.273(1) Å), while the axial positions are occupied by the N atoms of another two $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units (Mn–N, 2.256(1) and 2.312(1) Å).

The Mn(II) atoms are connected by $[\text{Ag}(1)(\text{CN})_2]^-$ units along the crystallographic *a* axis, to give an infinite 1D chain-like structure with the Mn(1)⋯Mn(2) distance of 10.7365 (5) Å. These Mn(II) atoms are further coordinated by $[\text{Ag}(2)(\text{CN})_2]^-$ units along the crystallographic *b* axis with the Mn(1)⋯Mn(2) distance of 10.7704(5) Å, to give (4,4) topology of the 2D layer (Fig. 3b). Surprisingly, the structure of compound **2** also contains unexpected $[(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]$ units that are attached to the 2D layer network via $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions with Ag(1)⋯Ag(3) distance of 3.1225(3) Å. Interestingly, adjacent layers are linked together by two types of interlayer interactions, namely argentophilic and π - π interactions, leading to an unprecedented double-layer 2D framework (Fig. 4 and S3). There are $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions between layers, with Ag(1)⋯Ag(2)^{*i*} distance of 3.2551 (3) Å, and the bond angles of C(26)–Ag(1)–C(17) (174.02(9)°) and C(8)–Ag(2)–C(9) (172.00(9)°) deviate slightly from linearity which could be due to the presence of these argentophilic interactions. The double 2D sheets show face-to-face π - π interactions between the five-membered ring (Cg1) of benzim ligands in $[(\text{benzim})\text{Ag}^{\text{I}}(\text{CN})]$ units of the first layer and six-membered ring (Cg2) of monodentate benzim ligands coordinated to the Mn^{II} of a second layer, with centroid⋯centroid distance (Cg(1)⋯Cg(2)^{*i*}) of 3.6298 Å [symmetry code: *i* = 1/2 + *x*, *y*, 1/2 – *z*]. Moreover, these double-layer 2D networks of compound **2** are further linked

**Fig. 4** Intra-double-layer π - π and $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions ($\text{Ag}(1)\cdots\text{Ag}(2)^i$, symmetry code *i* = 1/2 + *x*, *y*, 1/2 – *z*) of compound **2**. Hydrogen atoms, some coordinated benzim ligands and water molecules are omitted for clarity

to the others by π - π interactions between the coordinated benzim ligands which coordinate to Mn^{II} along the *c* axis, leading to a three-dimensional framework (Figure S4).

Infrared spectra

The IR spectra display strong peaks at 2,159 and 2,151 cm^{-1} for compounds **1** and **2**, respectively, which can be assigned to the CN groups in both $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ and $[\text{Ag}_2^{\text{I}}(\text{CN})_3]^-$ units which act as bidentate bridging ligands. These peaks are at higher wavenumbers than that of free $[\text{Ag}(\text{CN})_2]^-$ (2,135 cm^{-1}) at room temperature [5]. The IR spectrum of compound **1** also exhibits strong and sharp peaks at 3,494 and 3,380 cm^{-1} corresponding to the $\nu(\text{O}-\text{H})$ vibration of an aqua ligand and $\nu(\text{N}-\text{H})$ vibration of an amino group in the ampyz ligand. That of compound **2** displays a broad band at $\sim 3,500 \text{ cm}^{-1}$ which can be assigned to the $\nu(\text{O}-\text{H})$ vibration of a lattice water molecule, together with a strong and sharp peak at 3,328 cm^{-1} , corresponding to the $\nu(\text{N}-\text{H})$ vibration of a N–H group in the benzim ligand.

Conclusion

Two new multiple-layer two-dimensional network heterometallic $\text{Mn}^{\text{II}}-\text{Ag}^{\text{I}}$ coordination polymers have been prepared and structurally characterized. The crystal structure of compound **1** reveals a 3D structure consisting of a multiple-layer 2D network constructed by strong hexanuclear

argentophilic interactions, while compound **2** reveals a self-assembly of double-layer 2D networks by interlayer $\text{Ag}^{\text{I}} \cdots \text{Ag}^{\text{I}}$ and π – π interactions to give a 3D framework. Compounds **1** and **2** are the first examples of multiple-layer 2D network heterometallic Mn^{II} – Ag^{I} coordination polymers having different coordination network architectures based on the intermolecular interactions of $[\text{Ag}^{\text{I}}(\text{CN})_3]^-$ and $[\text{Ag}^{\text{I}}(\text{CN})_2]^-$ units. The results of this study may help the further design and development of such coordination polymers.

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Appendix: Supplementary material

CCDC numbers 844687 and 844688 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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