

- Bianchi, A., Calabi, L., Ferrini, L., Losi, P., Fulvio Uggeri, F., and Valtancoli, B. (1996). "Thermodynamics of Gd(III) complexation by macrocyclic and acyclic polyamino carboxylates," Inorganica Chimica Acta, 249(1), 13-15.
- Bing, Z., Kou, H.-Z., Cui, A.-L. and Wang, R.-J. (2005). "Template syntheses and crystal structures of hexaaza macrocyclic complexes with C-methyl substituent," Chinese Journal of Structural Chemistry, 24(11), 1259-1263.
- Brandenburg, K. and Putz, H. (2005). DIAMOND. Releas 3.0c. Crystal Impact GbR, Bonn, Germany.
- Bruker. (2003). SAINT and SADABS. Version 6.0. Bruker AXS Inc. Madison Wisconsin, USA.
- Cenini, S., Cravotto, G., Giovenzana, G. B., Palmisano, G. and Tollari, S. (1999). "Polyoxygenated coumarins. Oxonium ylides *en route* to polyoxa-macrocyclic coumarins," Tetrahedron, 55(21), 6577-6584.
- Choi, K.-Y. (2002). "Two-dimensional nickel(II) tetraaza macrocyclic complex linked by hydrogen bonds," Journal of Chemical Crystallography, 32(12), 537-540.
- Choi, K.-Y., Park, J.-R. and Suh, I.-H. (1998). "Preparation and structure of macrocyclic zinc(II) complex with a chromate bridge," Polyhedron, 18 (3), 497-500.
- Grant, G. J., Jones, M. W., Loveday, K. D., Derveer, D. G., Pennington, W. T., Eagle, C. T. and Mehre, L. F. (2000). "Transition metal complexes with macrocyclic oxathiaethers," Inorganic Chimica Acta, 300-302, 250-263.
- Han, J. H., Cha, M. J., Kim, B. G., Kim, S. K. and Min, K. S. (2008). "Synthesis and characterization of macrocyclic nickel(II) complexes with α -methylbenzyl groups as chiral pendants," Inorganic Chemistry Communications, 11(7), 745-748.
- Han, S., Kim, T., Lough, A. J. and Kim, J. C. (2011). "Synthesis, structures and properties of macrocyclic nickel(II) supramolecules with imidazole pendants," Inorganica Chimica Acta, 370(1), 170-174.
- Husain, A., Moheman, A., Nami, S. A.A. and Siddiqi, K.S. (2012). "Fourteen membered hexaaza copper macrocyclic: Synthesis, characterization, crystal structures and the consequence of anion coordination," Inorganic Chimica Acta, 384, 309-317.
- Jeong, H. H., Min J. C., Bong G. K. and Kil S. M. (2008). "Synthesis and characterization of macrocyclic nickel(II) complexes with α -methylbenzylamine group as chiral pendants," Inorganic Chemistry Communication, 11(7), 745-748.

- Kim, J. C., Lough, A. J. and Jo, H. (2002). "Syntheses and X-ray crystal structures of 14-membered tetraaza macrocyclic copper(II) complexes with polycarboxylate ligands," Inorganic Chemistry Communications. 5 (8), 616–620
- Kou, H.-Z., Gao, S., Bu, W.-M., Liao, D.-Z., Ma, B.-Q., Jiang, Z.-H., Yan, S.-P., Fan, Y.-G. and Wang, G.-L. (1999). "Synthesis, crystal structure and metamagnetic properties of a two-dimensional honeycomb network based on ferricyanide and (3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)nickel(II) building blocks," Journal of the Chemical Society, Dalton Transactions. 15, 2477-2480.
- Kou, H.-Z., Jiang, Y.-B., Zhou, B. C. and Wang, R.-J. (2004). "Cyano-bridged 2D Cu^{II}-Cr^{III} coordination polymers: structural evidence for formation of a polymeric macrocyclic metallic compound," Inorganic Chemistry. 43(10), 3271-3276.
- Lampeka, Y. D, Gavriash, S. P., Maloshtan, I. M., Dalley, K., Lamb, J. D. and Nazarenko, A. Y. (1998). "New cyclam-type copper(II) complexes with amide molecularpadlock: synthesis, properties and crystal structure," Inorganica Chimica Acta. 282(2), 142-148.
- Li, Y. W., Xiang H., Lu, T.-B. and Ng S. W. (2004). "[1,8-Bis(2-benzyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(II) diperchlorate," Acta Crystallographic. 60(3), 309-311.
- Lim, I.-T., Choi, J. H. and Choi, K.-Y. (2006). "Two-dimension hydrogen-bonded polymer from nickel(II) tetraaza macrocyclic complex and succinate ligand," Journal of Chemical Crystallography. 41(8), 1169-1173.
- Lu, T., Xiang, H., Li, X., Mao, Z. and Ji, L. (2000). "Molecular architecture via hydrophobic interaction. Synthesis and structure of [NiL](ClO₄)₂ (L = 3,10-bis(2-phenylethyl)-1,3,5,8,10,12-hexaazacyclotetradecane)," Inorganic Chemistry Communications. 3(11), 597-599.
- Lu, T.-B., Ou, G.-C., Jiang, L., Feng, X.-L. and Ji, L.-N. (2005). "Further study of the effect of macrocyclic pendant groups on the supramolecular architecture: Synthesis and structures of macrocyclic nickel (II) complexes with *trans*-butene dicarboxylate," Inorganica Chimica Acta. 358(11), 3241–3245.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., Maccabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., Van de streek, J. and Wood, P. A. (2008). "Mercury CDS 2.0 New Feature for the Visualization and Investigation of Crystal Structures," Journal of Applied Crystallography. 41(2), 466-470.

- Masoud, S. N. and Amiri, A. (2006). "Synthesis and characterization of bis(macrocyclic) nickel(II) complexes containing aromatic nitrogen-nitrogen linkers produced by template condensation," Transition Metal Chemistry. 31(2), 157-162.
- Mohammad, S., Yasser, A., Hamida, T. N. C., Nishat, B., Poonam, C. and Mohammad, Y. S. (2006). "Synthesis, physic-chemical and antimicrobial screening studies on 14 and 16-membered hexaazamacrocyclic complexes bearing pendant amine groups," Journal of Brazilian Chemistry Society. 17(2), 272-278.
- Nelson, S. M. (1980). "Developments in the synthesis and coordination chemistry of macrocyclic schiff base ligands," Pure and Applied Chemistry. 1(52), 2461-2476.
- Raman, N., Dhaveethu Raja, J. and Sakthivel, A. (2008). "Template synthesis of novel 14-membered tetraazamacrocyclic transition metal complexes: DNA cleavage and antimicrobial studies," Journal of the Chilean Chemical Society. 53(3), 1568-1571.
- Reddy, M. R., Reddy, K. H. and Raju, K. M. (1998). "Axial ligational properties of macrocyclic cobalt complexes," Polyhedron. 17(8), 1355-1361.
- Salavati-Niasari, M. and Najafian, H. (2003). "One-pot template synthesis and properties of Ni(II) complexes of 16-membered hexaaza macrocycle," Polyhedron. 22(18), 2633-2638.
- Salavati-Niasaria, M. and Davar, F. (2006). "Synthesis, characterization and catalytic activity of copper(II) complexes of 14-membered macrocyclic ligand; 3,10-dialkyl-dibenzo-1,3,5,8,10,12-hexaazacyclo-tetradecane/zeolite encapsulated nanocomposite materials," Inorganic Chemistry Communications. 9(3), 304-309.
- Shakir, M., Mohamed, A. K., Varkey, S. P., Nasman, O. S. M. and Siddiqi, Z. A. (1995). "Preparation and structural characterization of 14-16-membered pendant arm macrocyclic complexes of transition metal ions," Polyhedron. 14(10), 1277-1282.
- Suh, M. P., Shim, B. Y. and Yoon, T.-S. (1994). "Template syntheses and crystal structures of nickel(II) complexes of hexaaza macrocyclic ligands with pendant functional groups: Formation of a coordination polymer," Inorganic Chemistry. 33(24), 5509-5514.
- Suh, M. P., Kim, I. S., Shim, B. Y., Hong, D. and Yoon, T.-S. (1996). "Extremely facile template synthesis of gold(III) complexes of a saturated azamacrocycle and crystal structure of a six-coordinate gold(III) complex," Inorganic Chemistry. 35(12), 3595-3598.

- Tongbu, L., Hua, X., Xiaoyan, L., Zongwan, M. and Liangnian, J. (2000). "Molecular architecture via hydrophobic interaction. Synthesis and structure of $[\text{NiL}](\text{ClO}_4)_2$ ($\text{L} = 3,10\text{-bis}(2\text{-phenylethyl})\text{-}1,3,5,8,10,12\text{-hexaazacyclotetradecane}$," *Inorganic Chemistry Communication*. 3(11), 597-599.
- Valencia, L., Bastida, R., Fernández-Fernández, M. D. C., Macías, A. and Vicente, M. (2005). "Co (II), Ni(II) and Cu(II) complexes with a new pendant armed macrocyclic ligand showing several π, π -interactions," *Inorganica Chimica Acta*. 358(9), 2618-2628.
- Yi, H., Kou, H. Z., Yong, L., Bei, C. Z., Ming, X. and Yadong, L. (2003). "One-pot template synthesis and crystal structure of two new polyaza copper(II) complexes," *Inorganic Chemistry Communication*. 6(1), 38-42.
- Yan, Z. and Li, T. (2009). "Crystal structure of (1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane)nickel(II) diperchlorate, $[\text{Ni}(\text{C}_{10}\text{H}_{26}\text{N}_6)](\text{ClO}_4)_2$," *Zeitschrift fuer Kristallographie - New Crystal Structures*. 224(3), 505-506.



บันทึกข้อความ

ส่วนราชการ สถาบันวิจัยและพัฒนา มหาวิทยาลัยทักษิณ วิทยาเขตพัทลุง โทร.7256
ที่ ศธ 64.26/0229 วันที่ 3 มีนาคม 2557

เรื่อง ตอบรับการนำเสนอผลงานวิจัยในงานประชุมวิชาการระดับชาติมหาวิทยาลัยทักษิณ

เรียน อาจารย์ ดร.อานอบ คันชะชา

ตามที่ท่านได้ลงทะเบียนเข้าร่วมเสนอผลงานวิจัยจัดงานประชุมวิชาการระดับชาติมหาวิทยาลัยทักษิณ ครั้งที่ 24 ประจำปี 2557 ในระหว่างวันที่ 21-24 พฤษภาคม 2557 บัดนี้ คณะกรรมการฝ่ายวิชาการฯ ได้พิจารณาผลงานวิจัยของท่านเรียบร้อยแล้ว และขอแจ้งให้ทราบว่าผลงานของท่าน เรื่อง “การยับยั้งเชื้อแบคทีเรียของสารประกอบโคออร์ดิเนชันบางชนิดที่มีลิแกนด์พอลิเอชวาวงใหญ่” ได้รับการพิจารณาให้นำเสนอใน ภาคโปสเตอร์ ทั้งนี้ ขอให้ท่านยืนยันการเข้าร่วมนำเสนอผลงานวิจัยตามแบบฟอร์มที่กำหนดและปรับแก้บทความตามข้อเสนอแนะของผู้ทรงคุณวุฒิ และส่งมายังฝ่ายวิชาการการจัดประชุมฯ (สถาบันวิจัยและพัฒนา มหาวิทยาลัยทักษิณ) โดยผ่านทาง E-mail: conference2014.tsu@gmail.com ภายในวันที่ 21 มีนาคม 2557 สำหรับกำหนดการประชุมและช่วงเวลานำเสนอผลงานท่านสามารถตรวจสอบได้ที่เว็บไซต์ <http://www.pt.tsu.ac.th/rdi/> ตั้งแต่วันที่ 1 พฤษภาคม 2557 เป็นต้นไป

จึงเรียนมาเพื่อทราบและดำเนินการ

(ผู้ช่วยศาสตราจารย์ ดร.พรพันธุ์ เขมคุณาคัย)

ผู้อำนวยการสถาบันวิจัยและพัฒนา

โทรศัพท์ 074-609600 ต่อ 7250-8 # และ 081-540-7304

โทรศัพท์/โทรสาร 074-673227 E-mail : conference2014.tsu@gmail.com

- หมายเหตุ:
1. ท่านจะต้องส่งแบบยืนยันและชำระค่าลงทะเบียนให้แล้วเสร็จภายในวันที่ 21 มีนาคม 2557 หากพ้นกำหนดเวลาดังกล่าวฝ่ายวิชาการจัดการประชุมจะถือว่าท่านสละสิทธิ์การเข้าร่วมประชุม
 2. ท่านจะต้องดาวน์โหลด QR code จากระบบลงทะเบียนและนำมาแสดงหน้างานเพื่อติดต่อขอรับใบเสร็จรับเงินในวันจัดประชุมวิชาการ

การยับยั้งเชื้อแบคทีเรียของสารประกอบโคออร์ดิเนชันคอปเปอร์(II) และนิกเกิล(II) ที่มีลิแกนด์
พอลิเอซาวงใหญ่

The Antibacterial Activity of Copper(II) and Nickel(II) Coordinated Compounds
Containing a Polyaza Macrocyclic Ligand

อานอบ คันทะชา^{1*}
Anob Kantacha^{1*}

บทคัดย่อ

สารประกอบ $[\text{CuL}](\text{ClO}_4)_2$ (1) และ $[\text{NiL}](\text{ClO}_4)_2$ (2) เตรียมได้จากการทำปฏิกิริยาของ 1,2-ไดอะมิโนโพรเพน แอลฟา-เมทิลเบนซิลลามีน และฟอร์มัลดีไฮด์ เมื่อ L คือ 6,13-ไดเมทิล-3,10-บิส(1-ฟีนิลเอทิล)-1,3,5,8,10,12-เฮกซะอะซาไซโคลเตตราเดเคน ได้ยืนยันโครงสร้างสารประกอบโคออร์ดิเนชัน 1 และ 2 โดยเทคนิคทาง สเปกโทรสโกปี คือ การวิเคราะห์ปริมาณธาตุ อินฟราเรด ลิกควิดโครมาโทกราฟี-แมสสเปกโทรเมตรี และยูวี-วิสิเบิล สเปกโทรสโกปี พบว่า สารประกอบ 1 และ 2 ประกอบด้วยไอออนหลัก ๆ คือ $[\text{ML}]^{2+}$ จำนวน 1 ไอออน และเปอร์คลอเรตจำนวน 2 ไอออน อะตอมไนโตรเจน 4 อะตอมของลิแกนด์พอลิเอซาวงใหญ่ได้สร้างพันธะโคออร์ดิเนตโคเวเลนต์กับโลหะ(II) ไอออนอะตอม กลางมีรูปร่างเป็นสี่เหลี่ยมแบนราบ สารประกอบโคออร์ดิเนชันทั้งสองมีประสิทธิภาพในการยับยั้งเชื้อแบคทีเรีย *Escherichia coli* และ *Staphylococcus aureus*

คำสำคัญ: สารประกอบโคออร์ดิเนชัน พอลิเอซา แอลฟา-เมทิลเบนซิลลามีน เทคนิคทางสเปกโทรสโกปี

Abstract

$[\text{CuL}](\text{ClO}_4)_2$ (1) and $[\text{NiL}](\text{ClO}_4)_2$ (2) compounds containing a polyaza macrocyclic ligand have been prepared via the reaction of 1,2-diaminopropane, α -methylbenzylamine and formaldehyde in the presence of metal(II) ions, where L = 6,13-dimethyl-3,10-bis(1-phenylethyl)-1,3,5,8,10,12-hexaazacyclotetradecane. The compound 1 and 2 have been characterized by elemental analysis, IR, LC-MS and UV-Vis spectroscopy. The essential structure of two compounds consist of $[\text{ML}]^{2+}$ ($M = \text{Cu}^{2+}$ and Ni^{2+}) cation and two perchlorate anions. Metal-ion center, which is Ni(II) and Cu(II), in each compound is coordinated by four secondary amine nitrogen donors of the macrocyclic ligand and has a square-planar geometry forming five- and six-membered rings. The investigation on the antibacterial activity of newly synthesized Ni(II) and Cu(II) compounds were found to be active against the tested antibacterial of *Escherichia coli* and *Staphylococcus aureus*.

Keywords: Coordination compounds, Polyaza, α -methylbenzylamine, Spectroscopy techniques

¹ อ.ดร., สาขาวิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยทักษิณ สงขลา 90000

* Corresponding author: e-mail: k_anob@hotmail.com Tel. 083-1931922

Introduction

Coordination compounds containing polyaza macrocyclic ligand have attracted much attention in chemistry, material science and the chemical industry because of their applications for catalytic activity (Salavati-Niasari, M. et al, 2006), antimicrobial activity (Husain, A. et al, 2011) and magnetic properties (Kou, H.-Z. et al, 2004). However, primary amine was side chain the most and it has been long chain of alkane group, such as methylamine (Yan, Z. et al, 2009), benzylamine (Husain, A. et al, 2011) and 1-(3-aminopropyl)imidazole (Han, S. et al, 2011).

Recently, it has been found the synthesized method of coordination compounds containing polyaza macrocyclic ligand simple route, convenient and high percent yield. There has been called "One pot template condensation reaction". Typical methods of condensation reaction consist of transition metals salt, formaldehyde and primary amine with reflux.

The applications of coordination compounds containing polyaza macrocyclic ligand in the international journals showed that coordination compound can be used practically. Most of the tested microorganisms, such as bacteria are an inhibit *E. coli*, *P. aeruginosa*, *B. thuringiensis* and *S. typhimurium* etc., fungi including *P. chrysogenum*, *C. albicans* and *C. neoformans* (Shakir, M. et al, 2006). The present is found that the many of antibiotic resistance, which is adjustment to the drug by various methods in order to eliminate or reduce the effectiveness of antibiotic resistance. The drug resistant may be naturally having microorganisms that may occur under the pressure of antibiotics (Luvira, V. 2006).

In this work, coordination compounds containing polyaza macrocyclic ligand using copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate, formaldehyde and α -methylbenzylamine were synthesized as side chains in which N-donor atom coordinated to metal(II) center. In addition, these coordination compounds were studied for the antibacterial activity of *Escherchia coli* as gram negative and *Staphylococcus aureus* as gram positive by measuring of clear zone (millimeter) and comparing with tetracycline as standard drug.

Experimental

Materials and Method

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 1,2-diaminopropane, formaldehyde, α -methylbenzylamine and perchloric acid were all purchased from commercial source and used as received. *Caution!* Perchlorate salts of metal complexes are potentially explosive. Only a small amount material should be prepared, and it should be handled with care. The IR spectra ($4000\text{-}400\text{ cm}^{-1}$) were recorded with FT-IR spectrometer as a KBr disk and visible absorption spectra were recorded with a Shimadzu Lambda-1600 UV-Vis spectrophotometer in DMSO. The CHN-O elemental analysis was analyzed by dynamic flash combustion technique and Liquid Chromatograph-Mass Spectrometer (LC-MS) and it was recorded with Electron Spray Ionization Positive mode (ESI^+) in acetonitrile.

Synthesis of [CuL](ClO₄)₂ (1)

To a 99% absolute ethanol (10 mL) of Cu(CH₃COO)₂·H₂O (1.9970 g, 10 mmol) were added 98% 1,2-diaminopropane (1.3 mL, 20 mmol) in 99% absolute ethanol (10 mL). After the mixture was completely clear purple solution, then 37% formaldehyde (2.2 mL, 40 mmol) was added with stirring until the mixture was completely dark blue solution and then α -methylbenzylamine (1.27 mL, 20 mmol) was added with continuous stirring. The mixture of reactants was refluxed for 48 hours and the purple - red solution was cooled to room temperature and with filtering to remove any insoluble solids. After the amount of concentrated perchloric acid was added dropwise to the mixture, it was filtered and stored at room temperature to form purple-red solids. Yield: \approx 57%. *Anal. Calc.* for C₂₆H₄₂N₆Cl₂O₈Cu: C, 43.46; H, 5.87; N, 12.01; O, 23.09. Found: C, 43.30; H, 5.83; N, 12.04; O, 23.05%.

Synthesis of [NiL](ClO₄)₂ (2)

The yellow solids of compound 2 were prepared by a similar procedure of complex 1 with an proximate yield of 27% but using Ni(CH₃COO)₂·4H₂O instead of Cu(CH₃COO)₂·H₂O. *Anal. Calc.* for C₂₆H₄₂N₆Cl₂O₈Ni: C, 44.91; H, 6.08; N, 12.08; O, 20.09. Found: C, 44.89; H, 6.05; N, 12.06; O, 20.05%.

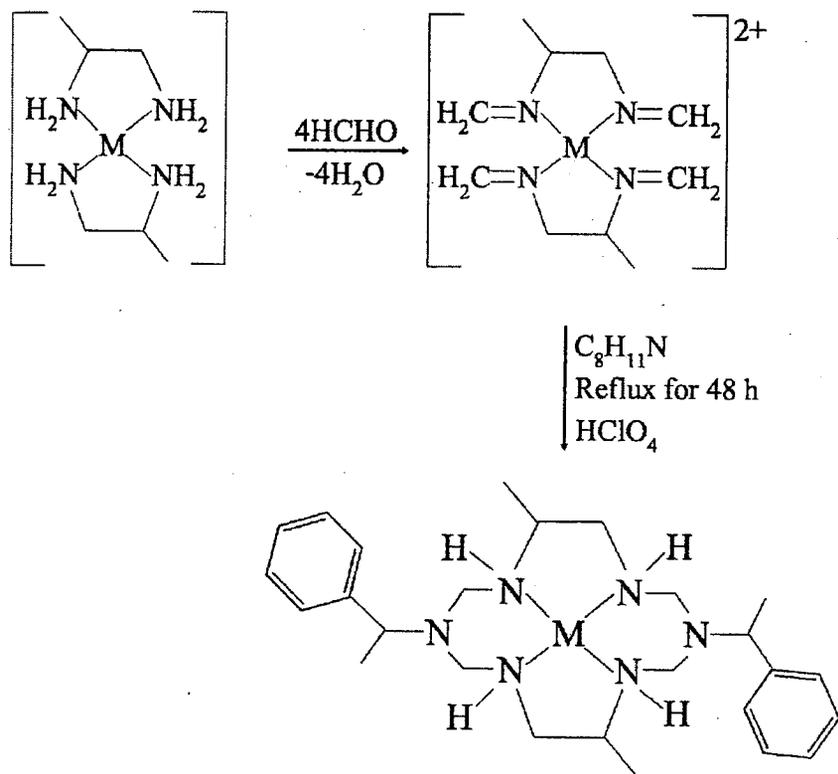
In *vitro* antibacterial assays

The agar diffusion method was followed for antibacterial test. Plates were prepared by pouring 20 mL of Nutrient Agar (NA), and allowed to solidify. These agar plates were inoculated with 0.1 mL of a McFaland standardized bacterial suspension (10⁻⁵-10⁻⁷ cells/mL) and uniformly spread. A 6 mm paper disc was placed on agar plate in the center and the well was filled with a solution of the 1 and 2 compounds at three concentration (25, 50 and 100 mg/10 mL). The diameter of the clear zone observed around the well was measured for each bacterium. After 24 h of incubation at 37 °C about 24 hours, a well was filled with DMSO solvent to serve as a control and compared with standard drug as tetracycline.

Results and Discussion

The synthesis route of coordination compounds with polyazamacrocyclic ligand

The coordination compounds with polyaza macrocyclic ligand were synthesized in a one – pot reaction involving both nickel acetate tetrahydrate and copper acetate monohydrate, 1,2-diaminopropane, formaldehyde and α -methylbenzylamine as shown in Scheme 1. In the begining, the metal ion (Cu²⁺ or Ni²⁺) coordinated to 1,2-diaminopropane for the formation of complex then reacted with formaldehyde to form an imine. The imine formation was attacked by the α -methylbenzylamine of 1,2-diaminopropane to obtained a *gem*-diamine, then the condensation of other imines was formed to have the first six-membered ring. Consequently, the imine can be attacked by the α -methylbenzylamine of a free 1,2-diaminopropane in the solution to obtain a *gem*-diamine. Finally, the second six-membered ring was formed through imine condensation and the compound 1 and 2 are obtained and they are similar to previously reported (He, Y. et al, 2003).



Scheme 1. Reaction scheme for the formation of compound 1 and 2, where M = Cu(II) and Ni(II).

Compound 1 and 2 are stable in air and insoluble in water but they are soluble in some polar solvents, such as MeCN, DMF and DMSO. The analytical data for compound 1 and 2 with some physical properties are summarized in Table 1.

Table 1. Physical properties and analytical data for compound 1 and 2 containing polyaza macrocyclic ligand.

Compounds	Reaction	Melting point (°C)	Color
[CuL](ClO ₄) ₂ (1)	Cu(CH ₃ COO) ₂ ·H ₂ O + 2C ₃ H ₁₀ N ₂ + 4CH ₂ O + 2C ₈ H ₁₁ N	~ 259	Purple - red
[NiL](ClO ₄) ₂ (2)	Ni(CH ₃ COO) ₂ ·4H ₂ O + 2C ₃ H ₁₀ N ₂ + 4CH ₂ O + 2C ₈ H ₁₁ N	~ 277	Yellow

Infrared spectra

The preliminary identification of compound 1 and 2 has been characterized by IR spectroscopy. The main infrared spectra of both compounds are presented in Table 2. The IR data reveal the spectra of compound 1 and 2 are shown the presence of sharp band in the range 3206-3239 cm⁻¹ which are assigned to the coordination of secondary amine stretching mode. The absence of a band in the regions 1720-1740 cm⁻¹, which are characteristic V(C=O) carbonyl of aldehyde moiety, further confirms occurring condensation. The V(C-N) and V(C-H) modes are found in

the range 1283-1452 and 2975-2976 cm^{-1} , respectively. In addition, it is apparent that there is considerable broadening and splitting in the region centered around 1100 cm^{-1} with two peaks at 1062 and 1111 cm^{-1} in which these regions are assigned to perchlorate ions. An important feature is the appearance of a new band of peak intensity in the range 467-511 cm^{-1} which is attributable to $\nu(\text{M-N})$ is that assigned to aza-nitrogen as coordinate with metal ions. In polyaza macrocyclic ligand, similar spectra of IR were also observed and it was reported by Kongchoo, S. et al, 2012.

Table 2. IR spectra data (cm^{-1}) for the compound 1 and 2.

Compounds	$\nu(\text{N-H})$	$\nu(\text{C-N})$	$\nu(\text{C-H})$	$\nu(\text{Cl-O})$	$\delta(\text{Cl-O})$	$\delta(\text{aromatic ring})$	$\nu(\text{M-N})$
$[\text{CuL}](\text{ClO}_4)_2$ (1)	3209(s)	1283(w)	2975(m)	1111(s)	624(vs)	750(m)	467(w)
$[\text{NiL}](\text{ClO}_4)_2$ (2)	3206(s)	1289(w)	2976(m)	1091(s)	624(vs)	752(m)	511(w)

vs very strong; s strong; m medium; w weak

ESI mass spectra

The electron spray ionization mass spectra of compound 1 and 2 were studied in positive mode and the m/z values are shown in Table 3. The most abundant ion observed in the compound 1 and 2 shows an intense signal corresponding to $[\text{M-anion}]^+$ at m/z 595.3 and m/z 600.3, respectively. The proposed formula of compound 1 and 2 were confirmed by ESI mass spectrum. The different fragments of compound 1 and 2 give peaks with various intensities at different m/z values. The mass spectrum data of compound 1 and 2 are given in Table 3.

Table 3. Mass spectrum data for compound 1 and 2.

Compounds	Precursor ion	Mass (m/z)		Fragment ions (m/z)
		Theoretical	Observed	
$[\text{CuL}](\text{ClO}_4)_2$ (1)	$[\text{M-ClO}_4]^+$	597.3	595.3	495.3, 362.2, 229.1, 185.1
$[\text{NiL}](\text{ClO}_4)_2$ (2)	$[\text{M-ClO}_4]^+$	602.3	600.3	500.3, 367.2, 190.1

Visible absorption data

The electronic absorption data (Figure 1.) of compound 1 (violet-red) and 2 (yellow) measured in dimethyl sulfoxide shows one $d-d$ transition band with absorption maxima (λ_{max}) at 516 and 450 nm, respectively and is comparable with those reported for square-planar Cu(II) and Ni(II) complexes. (Kang, S.-G. et al, 2002.)

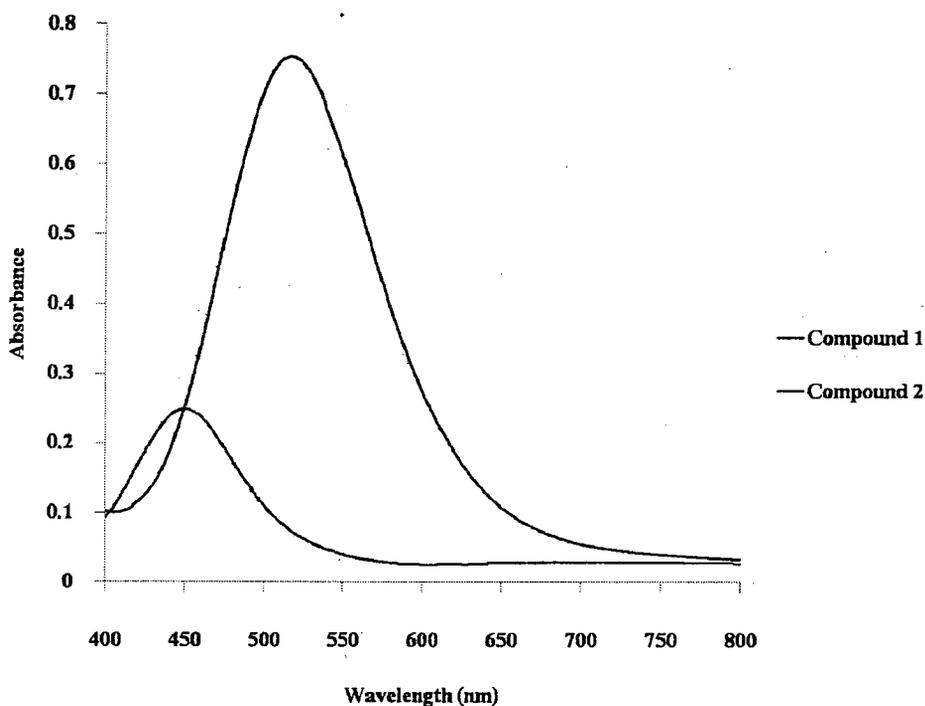


Figure 1. The visible spectra for compound 1 and 2.

In vitro Antibacterial activity

Antibacterial activities of the synthesized compound 1 and 2 were tested by the agar diffusion method using nutrient agar. The compounds were tested against the bacterial, viz., gram positive *Staphylococcus aureus* and gram negative *Escherichia coli*. The *in vitro* antibacterial activities are expressed as diameter of clear zones and compared to the tetracycline standard drug. The growth of the colony was recorded on completion of the incubation, and the average diameter for each compound at a concentration of 25, 50 and 100 mg/10 mL was recorded. DMSO and standard tetracycline were used as a control. The average of clear zone values, which was the investigated compounds, is summarized in Table 4 and 5.

Table 4. Antibacterial screening data for compound 1 and 2 as tested against the *Escherichia coli*.

Compounds	Zone of inhibition (mm) \pm SD.			
	25 mg/10mL	50 mg/10mL	100 mg/10mL	Tetracycline
[CuL](ClO ₄) ₂ (1)	19.50 \pm 0.58	24.07 \pm 0.58	27.00 \pm 0.00	30.00 \pm 0.00
[NiL](ClO ₄) ₂ (2)	18.70 \pm 0.58	23.67 \pm 0.58	25.00 \pm 0.00	30.00 \pm 0.00

Table 5. Antibacterial screening data for compound **1** and **2** as tested against the *Staphylococcus aureus*.

Compounds	Zone of inhibition (mm) \pm SD.			
	25 mg/10mL	50 mg/10mL	100 mg/10mL	Tetracycline
[CuL](ClO ₄) ₂ (1)	16.00 \pm 0.21	22.12 \pm 0.15	25.00 \pm 0.40	30.00 \pm 0.00
[NiL](ClO ₄) ₂ (2)	14.70 \pm 0.08	20.67 \pm 0.50	22.00 \pm 0.00	30.00 \pm 0.00

Antibacterial activity of the compound **1** and **2** were against selected bacteria both *Escherichia coli* and *Staphylococcus aureus*. It was found that compound **1** showed better antibacterial against compound **2**. They however showed less antibacterial activity than standard drug, tetracycline. According to Tweedy's chelation theory (Tweedy, B. G. 1964.) the lipid membrane, which surrounds the cell, favors the passage of only the lipid-soluble materials owing to liposolubility is an important factor that controls the antibacterial activity. Coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system of a polyaza macrocyclic ligand formed in the period of coordination. This system increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the microorganism thus destroying them more aggressively.

Conclusion

In this work, a newly synthesized of coordination compounds containing a polyaza macrocyclic ligand has been synthesized in a one – pot reaction by reflux method. The characterizations of the proposed structures have been studied by spectroscopic technique containing elemental analysis, IR, LC-MS and Visible spectroscopy. The antibacterial activity revealed that the coordination compounds exhibited an inhibitory effect against *Escherichia coli*, gram negative bacteria tested and *Staphylococcus aureus* as gram positive bacteria tested. Compound **1** and **2** showed less antibacterial activity than standard drug.

Acknowledge

This paper was supported by the research funding of Thaksin University for the budget in 2012, and Department of Chemistry. The author is also thankful to the Chairman, Department of Biological Faculty of Science and Thaksin University for providing *in vitro* screening facilities for the compounds.

References

- Gurumoorthy, P., Ravichandran, J., Karthikeyan, N., Palani, P. and Rahiman, A. K. (2012). "Template synthesis of polyaza macrocyclic copper(II) and nickel(II) complexes: Spectral characterization and antimicrobial studies," *The Bulletin of the Korean Chemical Society*. 33(7), 2279-2286.

- Han, S., Kim, T., Lough, A. J. and Kim, J. C. (2011). "Synthesis, structures and properties of macrocyclic nickel(II) supramolecules with imidazole pendants," *Inorganic Chimica Acta*. 370(1), 170-174.
- He, Y., Kou, H.-Z., Li, Y., Zhou, B. C., Xiong, M. and Li, Y. (2003). "One-pot template synthesis and crystal structure of two new polyaza copper(II) complexes," *Inorganic Chemistry Communications*. 6(1), 38-42.
- Husain, A., Nami, S. A. A. and Siddiqi, K. S. (2011). "The synthesis, crystal structures and antimicrobial studies of C-methyl-substituted hexaaza macrocycle of Cu(II) having aromatic pendant arm," *Applied Organometallic Chemistry*. 25(10), 761-768.
- Kang, S.-G., Song, J. and Jeong, J. H. (2002). "Synthesis and characterization of new polyaza macrocyclic nickel(II) and copper(II) complexes containing to nitrile or imidate ester pendant arms: metal-mediated hydrolysis and alcoholysis of the nitrile groups," *Bulletin of Korean Chemical Society*. 23(6), 824-828.
- Kongchoo, S., Pakawatchai, C. and Kantacha, A. (2012). "Synthesis and crystal structure of nickel(II) complex with 14-membered tetraaza macrocyclic ligand," In *the 22nd National Conference : Thai ASEAN : Path of Collaboration*, (pages 70-78). 23-26 May 2012 The 60th Anniversary of His Majesty the King's Accession to the Throne International Convention Center. Songkhla : Thaksin University.
- Kou, H.-Z., Liang, Y.-B., Zhou, B. C. and Wang, R.-J. (2004). "Cyano-bridged 2D Cu^{II}-Cr^{III} coordination polymers: Structure evidence for formation of a polymeric macrocyclic metallic compound," *Inorganic Chemistry*. 43(1), 3271-3276.
- Luvira, V. (2006). "Overveiw of antibiotic resistance," *Songklanagarind Medical Journal*. 24(5), 453-459.
- Salavati-Niasari, M. and Davar, F. (2006). "In situ one-pot template synthesis (IOPTS) and characterization of copper(II) complexes of 14-membered hexaaza macrocyclic ligand "3,10-dialkyl-dibenzo-1,3,5,8,10,12-hexaazacyclotetradecane"," *Inorganic Chemistry Communications*. 9(2), 175-179.
- Shakir, M., Azim, Y., Chishti, H. T. N., Begum, N., Chingsubam, P. and Siddiqi, M. Y. (2006). "Synthesis, physico-chemical and antibacterial screening studied on 14 and 16-membered hexaazamacrocyclic complexes bearing pendant amine group," *Journal of the Brazilian Chemical Society*. 17(2), 272-278.
- Sujatha, S., Balasubramanian, S. and Varghese, B. (2009). " Synthesis, structural, spectral, electrochemical and spin equilibrium studies of hexaaza macrotricyclic complexes," *Polyhedron*. 28(17), 3723-3730.
- Tweedy, B. G. (1964). "Phytopathology," 55, 910.
- Yan, Z. and Li, T. (2009). "Crystal structure of (1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane)nickel(II) diperchlorate, [Ni(C₁₀H₂₆N₆)] [ClO₄]₂," *Zeitschrift für Kristallographie - New Crystal Structures*. 224(3), 505-506.