CHAPTER 2

EXPERIMENTAL

2.1 Hydrothermal Crystal Growth of Nickel-Vanadate-Organodiamine Hybrid Frameworks (Ni-POVs)

Single crystals of Ni-POVs-X, where X = Cl^- (Ni-POV-Cl), Br^- (Ni-POV-Br) and I^- (Ni-POV-I) were synthesized and grown from the reaction mixtures prepared from vanadium oxide (V_2O_5; Fluka, 99%), nickel halide (NiX) and ethylenediamine ($C_2H_8N_2$, en; Carlo Erba, 98%) in an aqueous solution with a molar ratio of 1:1:3:250 for V_2O_5:NiX:en:H_2O. pH of some of the mixtures were adjusted by few drops of nitric acid (HNO_3; Carlo Erba, 65%) as indicated in Table 2.1. Three different nickel halides, including nickel(II) chloride ($NiCl_2 \cdot 6H_2O$; Univar, 99%), nickel(II) bromide ($NiBr_2$; Aldrich, 98%) and nickel(II) iodide (NiI_2; Aldrich, 99%) were used in the synthesis of Ni-POV-Cl, Ni-POV-Br and Ni-POV-I, respectively. The detail volume of the mixtures was listed in Table 2.1.

The reactions were conducted in a closed Teflon-lined autoclave, subjected to the temperature of 200°C for 3 days before being cooled to room temperature with a cooling rate of $0.1°C \cdot min^{-1}$. Dark green crystals were obtained from every reaction irrespective of different nickel halide reagent, and the pH of the mixtures after the completion of the reactions was close to 9 in every experiment. The crystals were separated from the supernatant by decantation, and washed with distilled water followed by ethanol.

Table 2.1 Synthetic conditions employed in the syntheses of Ni-POV-Cl, Ni-POV-Br and Ni-POV-I.

	V_2O_5	NiX	en*	H_2O	HNO_3	pH
Ni-POV-Cl	0.1413 g (0.77 mmol)	0.1843 g (0.78 mmol)	0.1558 cm^3 (2.33 mmol)	3.5 cm^3 (193.84 mmol)	0.05 cm^3	8
Ni-POV-Br	0.1410 g (0.77 mmol)	0.1694 g (0.78 mmol)	0.1555 cm^3 (2.33 mmol)	3.5 cm^3 (193.84 mmol)	0.00 cm^3	8
Ni-POV-I	0.1410 g (0.77 mmol)	0.2423 g (0.78 mmol)	0.1555 cm^3 (2.33 mmol)	3.5 cm^3 (193.84 mmol)	0.01 cm^3	8

* en = ethylenediamine ($C_2H_8N_2$)

2.2 Crystal Structures Determination

Powder X-ray diffractometer (Bruker D8 Advance, CuK_α, Ni filter, λ = 1.540558 Å, 48 kV, 30 mA) was used to identify the crystalline phase(s) of the bulk samples, whereas the energy dispersive X-ray microanalyzer (SEM-EDS) equipped by scanning electron microscope (FESEM, JEOL JSM – 6335F) was used to semi-quantify elemental composition of the crystals. The amounts of carbon, hydrogen and nitrogen were then determined using a CHNS/O analyzer (Perkin Elmer Series II 2400), and the presence of en was confirmed by Fourier transform infrared spectroscopy (FT-IR; Bruker Tensor 27, 4000-400 cm^{-1} and Nicolet Magna 500, 4000-400 cm^{-1}, resolution 0.5 cm^{-1}) using KBr pellets prepared from ground crystals. Absorption spectra of crystal compounds were performed by UV-vis spectrometer (Perkin Elmer UV LAMDA 25, 200-800 nm).

Suitable single crystals of Ni-POV-Cl, Ni-POV-Br and Ni-POV-I were chosen for data collection using the high flux D8 3-circle single crystal X-ray diffractometer equipped with Bruker-Nonius APEXII charge coupled device (CCD) area detector, with synchrotron radiation source (λ = 0.7977 Å) at station 16.2 smx, synchrotron Radiation Source, CCLRC Daresbury Laboratory, England. The structures were then solved using SHELXS-97 [63], and refined by full-matrix least squares analysis against F^2 using the SHELXL-97 [64] *via* the WinGX [65] program interface. Structural illustrations were depicted using DIAMOND 3.1 [66], based on the refined single crystal structures.

2.3 Study of Thermal Stability and Magnetic Properties

Thermal behavior of the crystals was studied using thermal gravimetric/differential thermal analyser (TG/DTA; Mettler Toledo TGA/SDTA 851^e) in a temperature range of 30-1100 °C with a heating rate of 10 °C/min under the flow of N_2. The magnetic properties of the ground samples were examined at 298 K in a magnetic field range of ±10kOe, using vibrating sample magnetometer (VSM; Lake Shore VSM 7403) facilitated by Department of Chemistry, Faculty of Science, Khon Kean University.

2.4 Study of Vanadium Valences

Vanadium valences were investigated and confirmed by both experimental and theoretical approaches *via* manganometric titration and computational chemistry, respectively. Manganometric titration used sulfuric acid (H_2SO_4; MERCK, 95-97%)

1 $mol \cdot dm^{-3}$ solution of compounds titrating against standardized potassium permanganate ($KMnO_4$; BDH, 99%) solution. The back titration with SO_2 (from sodium sulfite (Na_2SO_3; AJAX, 98.0%)) was again performed to investigate the number of all vanadium.

For computational calculation, the various methods of BLYP, PBE and PW91 with double numerical plus a polarization *d*-function were employed in the generalized gradient approximation to obtain the Mulliken population analysis using $DMol^3$ module of Accelrys' Materials Studio version 4.2.