

## Hydro/solvothermal synthesis, crystal structure, and thermal behaviour of piperazine-templated nickel(II) and cobalt(II) sulfates

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**Abstract :** Two piperazine-templated metal sulfate complexes,  $(C_4N_2H_{12})[Ni(H_2O)_6](SO_4)_2$ , **I** and  $(C_4N_2H_{12})[Co(H_2O)_6](SO_4)_2$ , **II**, have been synthesized by hydro/solvothermal reactions and their crystal structures analyzed by single crystal X-ray diffraction methods. Complex **I** crystallizes in the monoclinic system,  $P2_1/n$  space group,  $a=12.920(3)$ ,  $b=10.616(2)$ ,  $c=13.303(2)\text{\AA}$ ,  $\beta=114.09(1)^\circ$ ,  $Z=4$ ,  $R_1=0.030$  for 3683 reflections; **II**: monoclinic  $P2_1/n$ ,  $a=12.906(3)$ ,  $b=10.711(2)$ ,  $c=13.330(2)\text{\AA}$ ,  $\beta=114.10(2)^\circ$ ,  $Z=4$ ,  $R_1=0.032$  for 4010 reflections. The crystal structures of the piperazine-templated metal(II) sulfates demonstrate zero-dimensional compound constituted by diprotonated piperazine cations, metal(II) cations and sulfate anions. The structures of complex **I** and **II** are substantially isostructural to that of the previously reported our piperazine-templated copper(II) sulfate complex  $(C_4N_2H_{12})[Cu(H_2O)_6](SO_4)_2$ . The central metal(II) atoms are coordinated by six water molecules in the octahedral geometry. The crystal structures are stabilized by three-dimensional networks of the  $O_{\text{water}}-H\cdots O_{\text{sulfate}}$  and  $N_{\text{pip}}-H\cdots O_{\text{sulfate}}$  hydrogen bonds between the water molecules and sulfate anions and protonated piperazine cations. Based on the results of thermal analysis, the thermal decomposition reactions of the complex **I** was analyzed to have three distinctive stages whereas the complex **II** proceed through several stages.

**Key words :** Metal(II) sulfate, piperazine, organic template, hydro/solvothermal synthesis, crystal structure, thermal behaviour

### 1. Introduction

Inorganic open-framework materials<sup>1</sup> such as metal silicates,<sup>2</sup> phosphates,<sup>3</sup> carboxylates,<sup>4</sup> fluorides,<sup>5</sup> germanates,<sup>6</sup> arsenates,<sup>7</sup> and selenites<sup>8</sup> have been widely investigated during the past two decades. Among these materials, organically templated aluminosilicate zeolites and metal phosphates have been of the great interest in both academic research and indus-

trial applications owing to great structural diversity and desirable physical properties as catalysis, adsorption and ion exchange.<sup>1-3</sup>

Recently, there has been employed sulfate tetrahedron as a strategy for the design of new inorganic open-framework architectures.<sup>9-12</sup> The study of organically templated metal sulfates is of interest for several reasons.<sup>13</sup> First, the  $[SO_4]^{2-}$  tetrahedron is approximately the same size and shape compared

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with the  $[\text{PO}_4]^{3-}$  tetrahedron; S-O 1.49Å, P-O 1.53Å. However, the difference in charge between  $[\text{SO}_4]^{2-}$  and  $[\text{PO}_4]^{3-}$  moiety can result in the formation of new structural assemblies. Second, the majority of reports in the past five years deals with the preparation and structure of organically templated metal sulfates. Namely, metal sulfate chemistry is under-explored in comparison with extensively studied metal phosphate chemistry. Third, the small set of reported metal sulfates has exhibited in great structural diversity. Because of the sulfate ion act as a monodentate, chelating and/or bridging ligand.

Therefore, we undertook a comparative study of piperazine templated copper(II)-, nickel(II)- and cobalt(II)-sulfates with the original goal of producing structural analogue of the reported metal phosphates. Recently, our group reported the structural characterization and thermal property of piperazine templated copper(II)-sulfate complex.<sup>14</sup> In this article, we report the hydro/solvothermal synthesis, crystal structure and thermal behaviour of two piperazine-templated metal sulfate complexes,  $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ , **I** and  $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ , **II**.

## 2. Experimental

### 2.1. Synthesis

In the hydro/solvothermal synthesis, distilled water and ethylene glycol (EG) were the mixture solvent, piperazine·6H<sub>2</sub>O (PIP) was the templating agent, and  $\text{M}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$  {M=Ni(II) or Co(II)} and H<sub>2</sub>SO<sub>4</sub> were the respective sources of the metal(II) and sulfate ions.

In a synthesis of complex **I**, 0.25 g (1 mmol) of  $\text{Ni}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$  was dissolved in a 4 mL of H<sub>2</sub>O solution under constant stirring. To this solution was added 0.1 mL (2 mmol) of H<sub>2</sub>SO<sub>4</sub> and 3 mL (50 mmol) of ethylene glycol. Finally, 0.78 g (4 mmol) of piperazine·6H<sub>2</sub>O was added to the mixture, and the mixture was stirred for 30 min to obtain a homogeneous gel. The final mixture with the composition of  $\text{Ni}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O} : 2\text{H}_2\text{SO}_4 : 4\text{PIP} : 50\text{EG} : 200\text{H}_2\text{O}$  was transferred into a 23-mL Teflon-lined stainless-steel autoclave and heated at 180°C for 4

days. The resulting product was green block-shaped crystals mixed with some amorphous materials.

In a synthesis of complex **II**, the final reaction mixture with the composition of  $\text{Co}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O} : 2\text{H}_2\text{SO}_4 : 4\text{PIP} : 50\text{EG} : 200\text{H}_2\text{O}$  was transferred into a 23-mL Teflon-lined stainless-steel autoclave and heated at 170°C for 5 days. The resulting product was red block-shaped crystals mixed with some amorphous materials. The single crystal was picked out and submitted to composition analysis and structure determination.

### 2.2. Characterization

The FT-IR spectra in the 4000~400 cm<sup>-1</sup> region for the complex **I** and **II** were obtained by the KBr pellet method on a BioRad Digilab FTS-165 infrared spectrophotometer at ambient temperature. Piperazine, sulfate ion and water molecule were assigned by the relevant IR absorption bands, respectively.<sup>15</sup> The EDS spectra obtained on a EDAX Phoenix energy dispersive X-ray spectrometer with Philips XL-30S FEG scanning electron microscope showed the presence of C, N, O, S, Ni or Co. The contents of the carbon, hydrogen, nitrogen, sulfur and oxygen were analyzed by a CE EA-1110 elemental analyzer. The content of the nickel or cobalt were analyzed by a Jobin-Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer.

The composition of the crystal for complex **I** and **II** were deduced from the elemental analyses; the formula of  $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Ni}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ , **I** and  $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ , **II**, are consistent with the results of X-ray single crystallography. For complex **I**, *Anal. Found*: C 10.97, H 5.46, N 6.56, S 14.38, Ni 13.2%. *Calc. for C<sub>4</sub>H<sub>24</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>Ni*: C 10.75, H 5.41, N 6.27, O 50.10, S 14.34, Ni 13.13%. For complex **II**, *Anal. Found*: C 11.15, H 5.48, N 6.57, S 14.31, Co 13.2%. *Calc. for C<sub>4</sub>H<sub>24</sub>N<sub>2</sub>O<sub>14</sub>S<sub>2</sub>Co*: C 10.74, H 5.41, N 6.26, O 50.08, S 14.34, Co 13.18%.

The thermal decomposition of the complex **I** and **II** were investigated on a TA Instruments 2960 SDT thermogravimetric analyzer/differential thermal analyzer. Samples were loaded into an alumina crucible and heated from ambient temperature to 800°C at

10°C/min under flowing nitrogen.

### 2.3. X-ray crystallography

A crystal of the complex **I** and **II** were coated with epoxy glue in order to prevent spontaneous liberation of water molecules from the specimen under ambient conditions. The epoxy-coated crystals were mounted on a Siemens P4 four-circle X-ray diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ). The intensity data were collected in the  $\theta$ - $2\theta$  scan mode with operating 50 kV, 30 mA at a temperature  $295 \pm 2$  K. Three standard reflections were measured every 97 reflections: no remarkable decays were observed throughout data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the psi-scans was applied.<sup>16</sup>

All calculations were carried out using the Siemens SHELXTL crystallographic software programs.<sup>17</sup> The space group was assigned based on the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure

was solved by the direct method<sup>18</sup> and refined by successive full-matrix least-squares method followed by difference Fourier maps. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at the calculated positions with the isotropic thermal parameters were included in the final structure factor calculations. Final difference of electron density maps contained no significant features.

## 3. Results and Discussion

As shown in *Fig. 1*, the FT-IR spectra of complex **I** and **II** are virtually identical. The spectra are dominated by the characteristic bands of water molecules and sulfate groups, whereas the vibration modes arising from the diprotonated piperazinium cations are systematically weak. A broad strong absorption bands observed in the 2900~3600  $\text{cm}^{-1}$  region are due to the OH and NH stretching, together with CH stretching. The strong absorption bands in the 1090 and 610  $\text{cm}^{-1}$  regions can be attributed to sulfate groups. The typical sharp peaks in the 900~1600

Table 1. Crystallographic and experimental data for complex **I** and **II**

	<b>I</b>	<b>II</b>
Formula	C <sub>4</sub> H <sub>24</sub> N <sub>2</sub> O <sub>14</sub> S <sub>2</sub> Ni	C <sub>4</sub> H <sub>24</sub> N <sub>2</sub> O <sub>14</sub> S <sub>2</sub> Co
Formula weight	447.08	447.30
Crystal system	monoclinic	monoclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	12.920(3)	12.906(3)
<i>b</i> (Å)	10.616(2)	10.711(2)
<i>c</i> (Å)	13.303(2)	13.330(2)
$\beta$ (°)	114.09(1)	114.10(2)
<i>V</i> (Å <sup>3</sup> )	1665.6(5)	1682.1(5)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.783	1.766
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.486	1.339
<i>F</i> (000)	936	932
$\theta$ range for data collection (°)	1.9~26.5	1.9~26.5
Index range	-16 ≤ <i>h</i> ≤ 1 -13 ≤ <i>k</i> ≤ 1 -15 ≤ <i>l</i> ≤ 16	-1 ≤ <i>h</i> ≤ 16 -1 ≤ <i>k</i> ≤ 13 -16 ≤ <i>l</i> ≤ 15
Reflections collected	3683	4010
Independent reflections	3012 [ <i>R</i> <sub>int</sub> = 0.0293]	3208 [ <i>R</i> <sub>int</sub> = 0.0272]
Data/restraints/parameters	3012/0/257	3208/0/257
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.071	1.051
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.030, <i>wR</i> <sub>2</sub> = 0.080	<i>R</i> <sub>1</sub> = 0.032, <i>wR</i> <sub>2</sub> = 0.083

Table 2. Selected bond lengths (Å) and angles (°) for complex I

Ni-O(1)	2.077(2)	Ni-O(2)	2.036(2)
Ni-O(3)	2.082(2)	Ni-O(4)	2.060(2)
Ni-O(5)	2.058(2)	Ni-O(6)	2.026(2)
S(10)-O(11)	1.453(2)	S(10)-O(12)	1.472(2)
S(10)-O(13)	1.465(2)	S(10)-O(14)	1.457(2)
S(20)-O(21)	1.477(2)	S(20)-O(22)	1.451(2)
S(20)-O(23)	1.468(2)	S(20)-O(24)	1.468(2)
N(11)-C(12)	1.484(3)	C(12)-C(13) <sup>i</sup>	1.496(4)
N(11)-C(13)	1.473(4)	N(21)-C(22)	1.488(3)
C(22)-C(23) <sup>i</sup>	1.504(4)	N(21)-C(23)	1.489(3)
O(1)-Ni-O(2)	87.30(8)	O(1)-Ni-O(3)	89.18(9)
O(1)-Ni-O(4)	177.88(9)	O(1)-Ni-O(5)	93.10(8)
O(1)-Ni-O(6)	92.96(9)	O(2)-Ni-O(3)	94.28(8)
O(2)-Ni-O(4)	93.50(8)	O(2)-Ni-O(5)	179.39(8)
O(2)-Ni-O(6)	87.34(8)	O(3)-Ni-O(4)	92.71(9)
O(3)-Ni-O(5)	85.27(8)	O(3)-Ni-O(6)	177.38(8)
O(4)-Ni-O(5)	86.12(8)	O(4)-Ni-O(6)	85.12(9)
O(5)-Ni-O(6)	93.09(8)	O(11)-S(10)-O(12)	107.7(1)
O(11)-S(10)-O(13)	109.5(1)	O(11)-S(10)-O(14)	109.9(2)
O(12)-S(10)-O(13)	110.1(1)	O(12)-S(10)-O(14)	111.1(1)
O(13)-S(10)-O(14)	108.5(1)	O(21)-S(20)-O(22)	109.7(1)
O(21)-S(20)-O(23)	107.4(1)	O(21)-S(20)-O(24)	108.0(1)
O(22)-S(20)-O(23)	110.5(1)	O(22)-S(20)-O(24)	109.8(1)
O(23)-S(20)-O(24)	111.3(1)	N(11)-C(12)-C(13) <sup>i</sup>	109.8(2)
N(11)-C(13)-C(12) <sup>i</sup>	110.7(2)	C(12)-N(11)-C(13)	112.2(2)
N(21)-C(22)-C(23) <sup>ii</sup>	110.2(2)	N(21)-C(23)-C(22) <sup>ii</sup>	110.7(2)
C(22)-N(21)-C(23)	111.9(2)		

Symmetry transformations used to generate equivalent atoms: <sup>i</sup>-x+2, -y-1, -z, <sup>ii</sup>-x+2, -y+1, -z+1.

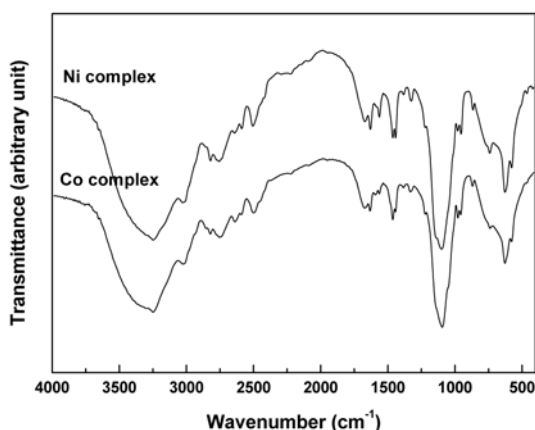


Fig. 1. Infrared spectra of Ni(II) complex I and Co(II) complex II.

$\text{cm}^{-1}$  region are used to confirm the presence of the piperazine template.

The crystallographic and experimental data for the complex I and II are summarized in Table 1. The selected bond lengths and bond angles for the complex I are listed in Table 2. Fig. 2 shows the molecular structures with atomic numbering and the perspective views of the complex I.

As shown in Fig. 2, the complex I consists of diprotonated piperazine cation, hexahydrated nickel (II) cation and two sulfate anions. The nickel(II) metal ion lies on an inversion center and is six-coordinated by water molecules with no direct bonding to the sulfate groups. Its structural coordination feature can be described as an octahedral arrangement. Diprotonated piperazine cation take a chair conformation. Bond lengths and angles of this piperazine cation are not unusual as listed in Table 2. The structures of complex I and II are substantially isostruc-

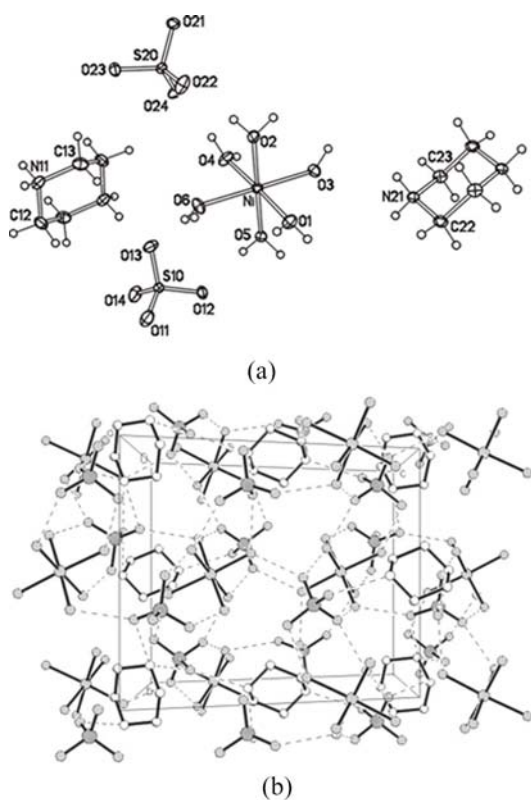


Fig. 2. The molecular structure and perspective view of Ni(II) complex I; hydrogen bonds are shown by broken lines.

tural to that of the previously reported our piperazine-templated copper(II) sulfate complex ( $C_4N_2H_{12}$ ) [ $Cu(H_2O)_6](SO_4)_2$ .<sup>14</sup>

The Ni-O<sub>water</sub> bond lengths range from 2.026(2) to 2.082(2) Å. The O<sub>water</sub>-Ni-O<sub>water</sub> bond angles from 85.12(9) to 93.50(8)°, and from 177.38(8) to 179.39(8)°. Whereas, the Co-O<sub>water</sub> bond lengths are 2.062(2)–2.126(2) Å. The O<sub>water</sub>-Co-O<sub>water</sub> bond angles are 84.86(9)–94.04(8)° and 177.21(9)–178.83(8)°. The S-O<sub>sulfate</sub> bond lengths in the sulfate anion range from 1.451(2) to 1.478(2) Å and the O<sub>sulfate</sub>-S-O<sub>sulfate</sub> bond angles from 107.4(1) to 111.3(1)°. The bond lengths, and angles of the sulfate anion are similar to those of the previously reported results.<sup>9,14,19</sup>

The piperazine templated Ni(II)-sulfate complex I or Co(II)-sulfate complex II are demonstrate zero-dimensional structure constituted by diprotonated piperazine cations, hexahydrated metal(II) cations

and sulfate anions. The crystal structure is stabilized by three-dimensional networks of the intermolecular O<sub>water</sub>-H $\cdots$ O<sub>sulfate</sub> and N<sub>pip</sub>-H $\cdots$ O<sub>sulfate</sub> hydrogen bonds between the water molecules and sulfate anions and protonated piperazine cations. The piperazine cations, sulfate anions and metal cations are linked together in -PIP-SO<sub>4</sub>-M(H<sub>2</sub>O)<sub>6</sub>-SO<sub>4</sub>-PIP-hydrogen bonding chains along the *b* direction by the N<sub>pip</sub>-H $\cdots$ O<sub>sulfate</sub> and O<sub>water</sub>-H $\cdots$ O<sub>sulfate</sub> bonds. The sulfate anions and metal cations are linked together in -SO<sub>4</sub>-M(H<sub>2</sub>O)<sub>6</sub>-hydrogen bonding chains along the *c* direction by the O<sub>water</sub>-H $\cdots$ O<sub>sulfate</sub> bonds. These hydrogen bonding planes are inter-linked along the *a* direction *via* another hydrogen bonds.

The detailed hydrogen bonding interactions between the sulfate anions and coordinated water molecules and piperazine nitrogen atoms in the Ni(II) complex I are described in follows: O(1)-H(1a) $\cdots$ O(12), 2.734(3) Å, 178(3)°; O(1)-H(1b) $\cdots$ O(23), 2.923(3) Å, 169(3)°; O(2)-H(2a) $\cdots$ O(24), 2.724(3) Å, 175(3)°; O(2)-H(2b) $\cdots$ O(22), 2.707(3) Å, 170(3)°; O(3)-H(3a) $\cdots$ O(23), 2.819(3) Å, 171(3)°; O(3)-H(3b) $\cdots$ O(14), 3.087(3) Å, 147(4)°; O(3)-H(3b) $\cdots$ O(11), 3.232(4) Å, 150(4)°; O(4)-H(4a) $\cdots$ O(24), 2.753(3) Å, 174(3)°; O(4)-H(4b) $\cdots$ O(11), 2.691(3) Å, 162(3)°; O(5)-H(5a) $\cdots$ O(12), 2.761(3) Å, 173(4)°; O(5)-H(5b) $\cdots$ O(14), 2.722(3) Å, 171(4)°; O(6)-H(6a) $\cdots$ O(13), 2.711(3) Å, 173(4)°; O(6)-H(6b) $\cdots$ O(22), 2.689(3) Å, 172(4)°; N(11)-H(11a) $\cdots$ O(13), 2.727(3) Å, 170.2°; N(11)-H(11b) $\cdots$ O(21), 2.731(3) Å, 169.9°; N(21)-H(21a) $\cdots$ O(21), 2.763(3) Å, 163.1°; N(21)-H(21b) $\cdots$ O(11), 2.765(3) Å, 150.9°; N(21)-H(21b) $\cdots$ O(12), 3.226(3) Å, 135.4°.

As shown in Fig. 3, the thermal decomposition reaction of the Ni(II) complex I would proceed through three stages under our experimental condition: the desorption and dehydration of water molecules, the decomposition of piperazine and sulfate group, and the formation of metal oxide. The first step of desorption and dehydration is the loss of adsorbed and coordinated six water molecules in the temperature of room temperature to 220°C. The weight loss of 24.1% exactly matches with the theoretical calculation for the loss of six water molecules

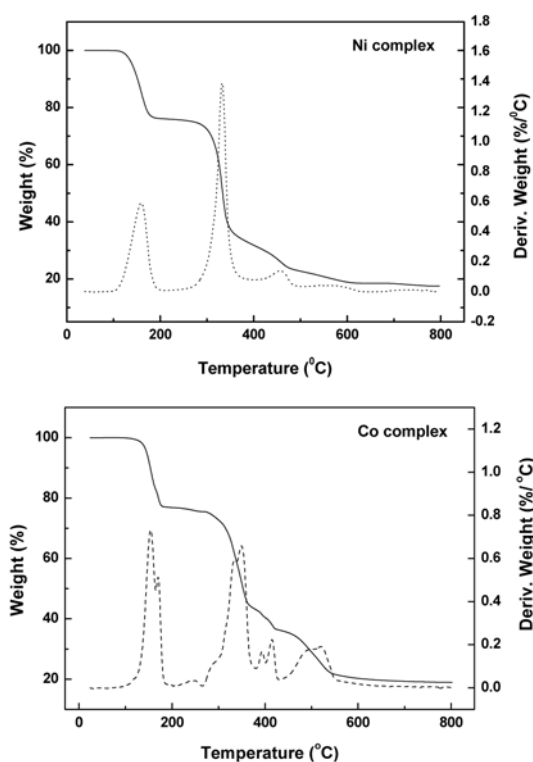


Fig. 3. Thermogravimetric and differential thermal analysis curves for Ni(II) complex **I** and Co(II) complex **II**.

from Ni(II) complex **I**. The second step occurs from 220 to 401°C and proceeds through two stages. The sharp weight loss of 44.2% due to the loss of piperazine molecule and sulfate ions. The high decomposition temperature of piperazine molecule is not surprising compare with boiling point 145~146°C, due to the fact that the molecule is strongly hydrogen bonded to sulfate ions.<sup>20</sup> The final stage of the decomposition starts at 401°C and the weight loss is 14.3%. This step leads to the metal oxide formation of NiO and the weight percentage of metal oxide is 17.4%. The total weight loss of three decomposition stages is 82.6%.

The thermal decomposition reaction of the Co(II) complex **II** would proceed through several stages. The first step occurs from room temperature to 206°C, and proceeds through two stages. The weight loss of 23.2% due to the loss of adsorbed and coordinated six water molecules. The second step occurs from 206 to 432°C and proceeds through five stages.

The weight loss of 40.6% due to the loss of piperazine molecule and sulfate ions. The final stage of the decomposition starts at 432°C and the weight loss is 17.3%. This step leads to the metal oxide formation of CoO and the weight percentage of metal oxide is 16.8%. The total weight loss of three decomposition stages is 81.1%.

**Supplementary Material:** Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-616481-616483). The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel: +44 1223 336031; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; home page: <http://www.ccdc.cam.ac.uk>).

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