

# Construction of metal-organic frameworks through coordination and hydrogen bonding interactions: Syntheses, structures and photoluminescent properties of metal complexes with macrocyclic ligand

Xing-Mei Ouyang,<sup>a</sup> Zhen-Wu Li,<sup>a</sup> Taka-aki Okamura,<sup>b</sup> Yi-Zhi Li,<sup>a</sup> Wei-Yin Sun,<sup>a,\*</sup> Wen-Xia Tang,<sup>a</sup> and Norikazu Ueyama<sup>b</sup>

<sup>a</sup>State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, China

<sup>b</sup>Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received 29 May 2003; received in revised form 1 September 2003; accepted 3 September 2003

## Abstract

A macrocyclic ligand *L* with two diethylenetriamine units linked by two rigid biphenylene spacers was used as building block for construction of metal-organic frameworks. A silver(I) complex with macrocyclic and open-chain mix-type ligands [Ag<sub>2</sub>(*L*)(*L'*)](ClO<sub>4</sub>)<sub>2</sub> (**1**) [*L'* = 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diazahexane] was obtained by reaction of *L* and *L'* together with AgClO<sub>4</sub> · H<sub>2</sub>O. It is interesting that the open-chain tetradentate ligand *L'* only served as a bidentate ligand to bridge the Ag<sub>2</sub>*L* units into an infinite one-dimensional (1D) cationic chain. Neutral 1D chain coordination polymer [Cu<sub>2</sub>(*L*)(μ-SO<sub>4</sub>)<sub>2</sub>] · 3H<sub>2</sub>O · 3MeOH (**2**) is formed by sulfate bridges between the neighboring Cu<sub>2</sub>*L* units. When *L* reacted with nickel(II) sulfate instead of copper(II) sulfate, a monomacrocyclic molecular complex [Ni<sub>2</sub>(*L*)(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>] (**3**) was obtained in which the sulfate anion acts as monodentate ligands rather than as bridges. When Cd(II) salts were used for the reactions with *L*, another two neutral 1D coordination polymers, [Cd<sub>2</sub>(*L*)(μ-Cl)<sub>2</sub>Cl<sub>2</sub>] · 2H<sub>2</sub>O (**4**) and [Cd<sub>2</sub>(*L*)(μ-Br)<sub>2</sub>Br<sub>2</sub>] (**5**), with the same structure were isolated. All the synthesized complexes exhibit three-dimensional framework structures linked by various hydrogen bonds. The photoluminescent properties of the synthesized complexes were studied in the solid state at room temperature, and the Ag(I) and Cd(II) complexes were found to show strong blue luminescence.

© 2003 Elsevier Inc. All rights reserved.

**Keywords:** Macrocyclic ligand; Metal-organic frameworks; Metal complexes

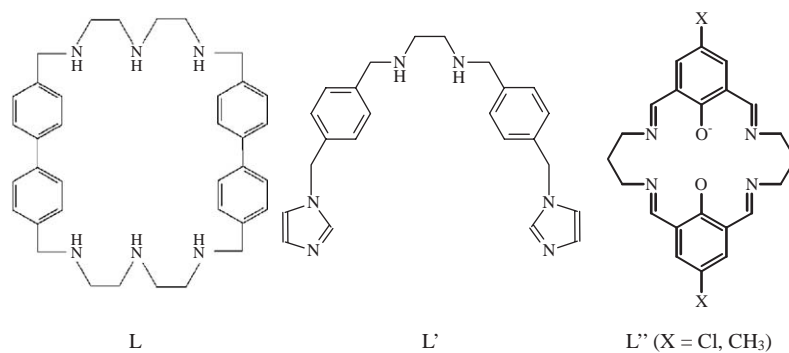
## 1. Introduction

Crystal engineering of metal-organic frameworks (MOFs) has been of great interest due to their novel structures with specific topology and promising properties [1–5]. Among them, the construction of coordination polymers from metal salts and open-chain multidentate organic ligands has achieved great progress in forming interesting and beautiful architectures [1,6,7] such as helix, rotaxane and catenane, which exhibit novel properties such as porosity [8,9], magnetism [10], fluorescence [11] and non-linear optical behaviors [12].

On the other hand, the coordination chemistry of macrocyclic ligands has been studied extensively during the last decades and their complexes were often used for the study of catalysis, metalloenzyme mechanisms and molecular recognition [13]. In addition, novel topological structures containing macrocyclic ligands were also explored. For example, relatively few mononuclear macrocyclic double helicate systems were obtained by using 34-membered macrocyclic Schiff-base ligands with N<sub>6</sub> donor set [14]. Sauvage et al. synthesized a series of [2] catenane and [2] rotaxane [15] with a conjugated rod threaded through pre-organized 30-membered rings containing 1,10-phenanthroline groups by means of the transition metal template technique. The investigations of macrocyclic ligands on the construction of

\*Corresponding author. Fax: +86253314502.

E-mail address: [sunwy@nju.edu.cn](mailto:sunwy@nju.edu.cn) (W.-Y. Sun).



Scheme 1.

coordination polymers are still limited compared with those of open-chain organic ligands. Macrocyclic monomeric complexes have been proved to be good building blocks for the construction of coordination polymers and multidimensional networks using aromatic polycarboxylate ligands, e.g., 1,2,4,5-benzenetetracarboxylic acid, as bridges [16]. However, coordination polymers with macrocyclic binuclear building blocks and bridging ligands are less explored up to now. Recently, a polymeric manganese complex was obtained with 26-membered binuclear macrocyclic moieties linked by  $[\text{MnCl}_4]^{2-}$  anions to form one-dimensional (1D) chain having a continuous  $-\text{Mn}-\text{Cl}-\text{Mn}-\text{Cl}-$  linkage [17]. Binuclear or tetranuclear palladium(II) complexes involving 30-membered macrocyclic ligand are connected into a 1D chain through hydrogen bonding interactions [18].

We are interested in the reactions of flexible multi-dentate ligands with various metal salts to investigate the construction, structure and property of MOFs [19]. Now we initiate to study reactions of metal salts with macrocyclic and linear mixed ligands. As shown in Scheme 1, an open-chain tetradentate ligand 1,6-bis(4-imidazol-1'-ylmethylphenyl)-2,5-diazahexane ( $L'$ ) was adopted in this study, together with a macrocyclic ligand  $L$  containing two identical diethylenetriamine moieties as coordination sites to metal atoms and two biphenylene groups as spacers to import rigidity to the macrocycle [20], to construct novel coordination polymers. We obtained a Ag(I) coordination polymer involving ligands  $L$  and  $L'$  and other four complexes only contain macrocyclic ligands. The Ag(I) coordination polymer  $[\text{Ag}_2(L)(L')](\text{ClO}_4)_2$  (**1**) exhibits 1D chain structure with  $\text{Ag}_2L$  units bridged by linear ligand  $L'$ , which is obtained from the reactions of macrocyclic ligand  $L$  and open-chain tetradentate ligand  $L'$  together with  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ . When copper(II) sulfate or nickel(II) sulfate was used for the reaction with ligand  $L$ , 1D coordination polymer  $[\text{Cu}_2(L)(\mu\text{-SO}_4)_2] \cdot 3\text{H}_2\text{O} \cdot 3\text{MeOH}$  (**2**) and monocyclic molecular complex  $[\text{Ni}_2(L)(\text{H}_2\text{O})_4(\text{SO}_4)_2]$  (**3**) are generated. Another two coordination polymers  $[\text{Cd}_2(L)(\mu\text{-Cl})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  (**4**) and

$[\text{Cd}_2(L)(\mu\text{-Br})_2\text{Br}_2]$  (**5**) are obtained by the reaction of ligand  $L$  with  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  or  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ . The synthesized complexes were characterized by X-ray crystal diffraction and luminescence spectral measurements.

## 2. Experimental

All commercially available chemicals were used as received without further purification. Ligand  $L'$  was prepared by the previously reported method [19a]. Solvents were purified according to standard methods. Elemental analyses for C, H and N were made on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University.  $^1\text{H}$  NMR spectra were measured on a Bruker DRX500 MHz NMR spectrometer at room temperature. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm. All the measurements were carried out under the same experimental conditions.

### 2.1. Preparation of ligand $L$

The macrocyclic ligand  $L$  was synthesized by procedures reported previously [21]. The product was recrystallized from  $\text{CH}_3\text{OH}$ . Mp 183–185°C.  $^1\text{H}$  NMR [500 MHz, ( $\text{CDCl}_3$ ):  $\delta$  3.84 (s, 8H,  $-\text{CH}_2\text{Ph}$ ), 7.50 (d, 8H, Ph), 7.38 (d, 8H, Ph), 2.90 (m, 8H,  $-\text{CH}_2-$ ), 2.84 (m, 8H,  $-\text{CH}_2-$ ). Calc. elem. anal. for  $\text{C}_{36}\text{H}_{46}\text{N}_6$ : C 76.83; H 8.24; N 14.93. Found: C 76.65; H 8.20; N 14.89.

### 2.2. Syntheses of $[\text{Ag}_2(L)(L')](\text{ClO}_4)_2$ **1**

All procedures for synthesis and measurements of silver(I) complex were performed in the dark. The title complex was prepared by layering method. A buffer layer of solution (10 mL) of methanol and water (3:1) was carefully layered over an aqueous solution (5 mL) of

Table 1  
Crystallographic data for complexes 1–5

Complex	1	2	3	4	5
Empirical formula	C <sub>60</sub> H <sub>74</sub> N <sub>12</sub> Ag <sub>2</sub> Cl <sub>2</sub> O <sub>8</sub>	C <sub>39</sub> H <sub>64</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>14</sub> S <sub>2</sub>	C <sub>36</sub> H <sub>54</sub> N <sub>6</sub> Ni <sub>2</sub> O <sub>12</sub> S <sub>2</sub>	C <sub>36</sub> H <sub>50</sub> Cd <sub>2</sub> Cl <sub>4</sub> N <sub>6</sub> O <sub>2</sub>	C <sub>36</sub> H <sub>46</sub> N <sub>6</sub> Cd <sub>2</sub> Br <sub>4</sub>
Formula weight	1377.95	1032.16	944.39	965.37	1107.23
Crystal system	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P-4b2	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
<i>a</i> (Å)	15.672(15)	17.586(5)	14.1362(13)	31.121(3)	30.520(14)
<i>b</i> (Å)	16.168(19)	17.586(5)	10.2739(10)	8.6888(14)	8.984(4)
<i>c</i> (Å)	25.33(3)	31.301(11)	13.5879(13)	14.0893(16)	14.328(7)
$\alpha$ (deg.)	90.00	90.00	90.00	90.00	90.00
$\beta$ (deg.)	109.46(8)	90.00	97.271(2)	92.945(6)	98.44(4)
$\gamma$ (deg.)	90.00	90.00	90.00	90.00	90.00
<i>V</i> (Å <sup>3</sup> )	6051(11)	9680(5)	1957.6(3)	3804.8(9)	3886(3)
<i>Z</i>	4	8	2	4	4
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.513	1.416	1.602	1.676	1.893
$\mu$ (mm <sup>-1</sup> )	0.800	1.032	1.140	1.439	5.241
2 $\theta$ max (deg.)	54.96	54.94	50.0	54.98	54.76
Reflns. collected	29024	91169	9240	35194	35447
Independent reflns.	6918	11069	3417	8672	8732
<i>R</i> <sub>int</sub>	0.1052	0.1650	0.0497	0.1095	0.1247
Obsd. reflns. ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	2981	5321	3023	6077	4062
Parameters refined	398	569	262	461	433
<i>R</i> (obsd. data)	0.0607	0.0545	0.0433	0.0521	0.0469
<i>wR</i> (obsd. data)	0.1216 <sup>a</sup>	0.0896 <sup>b</sup>	0.1167 <sup>c</sup>	0.1208 <sup>d</sup>	0.0651 <sup>e</sup>
<i>R</i> (all data)	0.1564	0.1317	0.0476	0.0818	0.1262
<i>wR</i> <sub>2</sub> (all data)	0.1452	0.1036	0.1191	0.1360	0.0740
Goodness of fit	0.823	0.831	1.052	0.962	0.866
Residual electron density (e Å <sup>-3</sup> )	2.848; -0.520	0.482; -0.319	0.990; -0.519	1.349; -0.968	1.119; -0.872

<sup>a</sup>  $w = 1/[\sigma^2(F_o)^2 + (0.0698P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>b</sup>  $w = 1/[\sigma^2(F_o)^2 + (0.0380P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>c</sup>  $w = 1/[\sigma^2(F_o)^2 + (0.0636P)^2 + 2.3005P]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>d</sup>  $w = 1/[\sigma^2(F_o)^2 + (0.0762P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>e</sup>  $w = 1/[\sigma^2(F_o)^2 + (0.0086P)^2]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

AgClO<sub>4</sub>·H<sub>2</sub>O (6.8 mg, 0.03 mmol). Then a methanol solution (5 mL) of *L* (8.5 mg, 0.015 mmol) and *L'* (12.0 mg, 0.03 mmol) was layered over the buffer layer. Single crystals were obtained after several weeks. Yield: 21%. Calc. elem. anal. for C<sub>60</sub>H<sub>74</sub>N<sub>12</sub>Ag<sub>2</sub>Cl<sub>2</sub>O<sub>8</sub>: C 52.30; H 5.41; N 12.20. Found: C 52.27; H 5.31; N 12.09.

### 2.3. Syntheses of [Cu<sub>2</sub>(*L*)(μ-SO<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O·3MeOH **2**

Complex **2** was obtained by similar procedures to complex **1** using CuSO<sub>4</sub>·5H<sub>2</sub>O (7.5 mg, 0.03 mmol) instead of AgClO<sub>4</sub>·H<sub>2</sub>O to react with *L* (8.5 mg, 0.015 mmol) and *L'* (12.0 mg, 0.03 mmol) by layering method. Blue block crystals suitable for X-ray crystallographic analysis were obtained. Yield: 46%. Calc. elem. anal. for C<sub>39</sub>H<sub>64</sub>Cu<sub>2</sub>N<sub>6</sub>O<sub>14</sub>S<sub>2</sub>: C 45.38; H 6.25; N 8.14. Found: C 45.29; H 6.20; N 8.05.

### 2.4. Syntheses of [Ni<sub>2</sub>(*L*)(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>] **3**

Complex **3** was prepared by the solvothermal method. To 4 mL aqueous solution of NiSO<sub>4</sub>·7H<sub>2</sub>O (8.4 mg, 0.03 mmol), 8 mL methanol solution of *L* (8.5 mg,

0.015 mmol) was added and stirred for a while. Then the mixture was transferred and kept in a Teflon lined autoclave at 120°C for 3 days. After cooling to room temperature, pale blue block crystals were obtained and the yield is 46%. Calc. elem. anal. for C<sub>36</sub>H<sub>54</sub>Ni<sub>2</sub>N<sub>6</sub>O<sub>12</sub>S<sub>2</sub>: C 45.79; H 5.76; N 8.90. Found: C 45.70; H 5.71; N 8.87.

### 2.5. Syntheses of [Cd<sub>2</sub>(*L*)(μ-Cl)<sub>2</sub>(Cl)<sub>2</sub>]·2H<sub>2</sub>O **4** and [Cd<sub>2</sub>(*L*)(μ-Br)<sub>2</sub>(Br)<sub>2</sub>] **5**

Complexes **4** and **5** were prepared by the same method as complex **1** using CdCl<sub>2</sub>·2.5H<sub>2</sub>O (6.9 mg, 0.03 mmol) and CdBr<sub>2</sub>·4H<sub>2</sub>O (10.0 mg, 0.03 mmol) instead of AgClO<sub>4</sub>·H<sub>2</sub>O to react with *L* (8.5 mg, 0.015 mmol) and *L'* (12.0 mg, 0.03 mmol) by layering method, respectively. Colorless plate crystals were obtained after a week. Yield is 53% for complex **4** and 62% for complex **5**, respectively. Calc. elem. anal. for **4** C<sub>36</sub>H<sub>50</sub>Cd<sub>2</sub>Cl<sub>4</sub>N<sub>6</sub>O<sub>2</sub>: C 44.79; H 5.22; N 8.71. Found: C 45.06; H 5.21; N 8.72. Calc. elem. anal. for **5** C<sub>36</sub>H<sub>46</sub>Cd<sub>2</sub>N<sub>6</sub>Br<sub>4</sub>: C 39.05; H 4.19; N 7.59. Found: C 39.06; H 4.33; N 7.68.

Table 2  
Selected bond distances (Å) and angles (deg.) for **1–5**

<b>[Ag<sub>2</sub>(L)(L')](ClO<sub>4</sub>)<sub>2</sub> (1)</b>			
Ag(1)–N(5)	2.276(5)	Ag(1)–N(3)	2.315(9)
Ag(1)–N(1)	2.360(5)	Ag(1)–N(2)	2.456(4)
N(5)–Ag(1)–N(3)	107.9(3)	N(5)–Ag(1)–N(1)	118.06(18)
N(3)–Ag(1)–N(1)	134.0(3)	N(5)–Ag(1)–N(2)	130.96(17)
N(3)–Ag(1)–N(2)	77.1(2)	N(1)–Ag(1)–N(2)	74.33(16)
<b>[Cu<sub>2</sub>(L)(μ-SO<sub>4</sub>)<sub>2</sub>] · 3H<sub>2</sub>O · 3MeOH (2)</b>			
Cu(1)–O(11)	1.929(3)	Cu(1)–N(2)	1.972(4)
Cu(1)–N(3)	2.023(5)	Cu(1)–N(1)	2.043(4)
Cu(1)–O(23)	2.364(3)	Cu(2)–O(21)	1.928(4)
Cu(2)–N(5)	1.979(5)	Cu(2)–N(6)	2.017(4)
Cu(2)–N(4)	2.038(5)	Cu(2)–O(12)	2.434(4)
O(11)–Cu(1)–N(2)	166.91(16)	O(11)–Cu(1)–N(3)	93.60(17)
N(2)–Cu(1)–N(3)	85.0(2)	O(11)–Cu(1)–N(1)	97.72(17)
N(2)–Cu(1)–N(1)	84.9(2)	N(3)–Cu(1)–N(1)	167.93(16)
O(11)–Cu(1)–O(23)	101.76(13)	N(2)–Cu(1)–O(23)	91.32(15)
N(3)–Cu(1)–O(23)	93.95(19)	N(1)–Cu(1)–O(23)	79.67(16)
O(21)–Cu(2)–N(5)	168.19(17)	O(21)–Cu(2)–N(6)	94.70(16)
N(5)–Cu(2)–N(6)	84.6(2)	O(21)–Cu(2)–N(4)	96.75(17)
N(5)–Cu(2)–N(4)	84.53(19)	N(6)–Cu(2)–N(4)	168.46(19)
O(21)–Cu(2)–O(12)	100.98(14)	N(5)–Cu(2)–O(12)	90.81(18)
N(6)–Cu(2)–O(12)	90.39(17)	N(4)–Cu(2)–O(12)	86.04(17)
<b>[Ni<sub>2</sub>(L)(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>] (3)</b>			
Ni(1)–O(2)	2.051(2)	Ni(1)–N(2)	2.066(3)
Ni(1)–O(5)	2.085(2)	Ni(1)–N(1)	2.095(3)
Ni(1)–O(6)	2.193(2)	Ni(1)–N(3)	2.159(3)
O(1)–Ni(1)–N(2)	177.54(10)	O(1)–Ni(1)–O(5)	90.33(10)
N(2)–Ni(1)–O(5)	91.11(11)	O(1)–Ni(1)–N(1)	94.77(10)
N(2)–Ni(1)–N(1)	83.64(12)	O(5)–Ni(1)–N(1)	173.02(10)
O(1)–Ni(1)–N(3)	99.39(11)	N(2)–Ni(1)–N(3)	82.66(12)
O(5)–Ni(1)–N(3)	88.44(11)	N(1)–Ni(1)–N(3)	95.41(12)
O(1)–Ni(1)–O(6)	89.60(10)	N(2)–Ni(1)–O(6)	88.49(11)
O(5)–Ni(1)–O(6)	86.11(10)	N(1)–Ni(1)–O(6)	89.16(10)
N(3)–Ni(1)–O(6)	169.52(11)		
<b>[Cd<sub>2</sub>(L)(μ-Cl)<sub>2</sub>(Cl)<sub>2</sub>] · 2H<sub>2</sub>O (4)</b>			
Cd(1)–N(2)	2.350(4)	Cd(1)–N(1)	2.375(4)
Cd(1)–N(3)	2.457(4)	Cd(1)–Cl(2)	2.4507(13)
Cd(1)–Cl(1)	2.6772(12)	Cd(1)–Cl(1) <sup>a</sup>	2.6932(11)
Cd(2)–N(4)	2.478(4)	Cd(2)–N(5)	2.343(5)
Cd(2)–N(6)	2.379(4)	Cd(2)–Cl(3)	2.494(2)
Cd(2)–Cl(4)	2.7791(17)	Cd(2)–Cl(4) <sup>b</sup>	2.5610(16)
N(2)–Cd(1)–N(1)	76.07(13)	N(2)–Cd(1)–Cl(2)	176.40(10)
N(1)–Cd(1)–Cl(2)	100.46(10)	N(2)–Cd(1)–N(3)	74.47(13)
N(1)–Cd(1)–N(3)	95.69(12)	Cl(2)–Cd(1)–N(3)	105.17(9)
N(2)–Cd(1)–Cl(1)	81.89(10)	N(1)–Cd(1)–Cl(1)	91.75(9)
Cl(2)–Cd(1)–Cl(1)	99.28(5)	N(3)–Cd(1)–Cl(1)	152.63(9)
N(2)–Cd(1)–Cl(1) <sup>a</sup>	87.28(9)	N(1)–Cd(1)–Cl(1) <sup>a</sup>	163.28(9)
Cl(2)–Cd(1)–Cl(1) <sup>a</sup>	96.16(5)	N(3)–Cd(1)–Cl(1) <sup>a</sup>	78.04(9)
Cl(1)–Cd(1)–Cl(1) <sup>a</sup>	87.38(4)	N(5)–Cd(2)–N(6)	74.75(16)
N(5)–Cd(2)–N(4)	74.22(15)	N(6)–Cd(2)–N(4)	108.13(15)
N(5)–Cd(2)–Cl(3)	166.74(12)	N(6)–Cd(2)–Cl(3)	94.44(13)
N(4)–Cd(2)–Cl(3)	102.66(12)	N(5)–Cd(2)–Cl(4) <sup>b</sup>	90.78(12)
N(6)–Cd(2)–Cl(4) <sup>b</sup>	158.84(12)	N(4)–Cd(2)–Cl(4) <sup>b</sup>	81.84(10)
Cl(3)–Cd(2)–Cl(4) <sup>b</sup>	101.63(8)	N(5)–Cd(2)–Cl(4)	87.02(12)
N(6)–Cd(2)–Cl(4)	78.45(11)	N(4)–Cd(2)–Cl(4)	157.16(11)
Cl(3)–Cd(2)–Cl(4)	98.49(7)	Cl(4) <sup>b</sup> –Cd(2)–Cl(4)	85.58(5)
Cd(1)–Cl(1)–Cd(1) <sup>a</sup>	92.62(4)	Cd(2) <sup>b</sup> –Cl(4)–Cd(2)	94.42(5)
<b>[Cd<sub>2</sub>(L)(μ-Br)<sub>2</sub>(Br)<sub>2</sub>] (5)</b>			
Cd(1)–N(2)	2.328(5)	Cd(1)–N(3)	2.412(4)
Cd(1)–N(1)	2.486(5)	Cd(1)–Br(2)	2.5654(14)

Table 2 (continued)

Cd(1)–Br(1)	2.8353(15)	Cd(1) <sup>c</sup> –Br(1)	2.8712(14)
Br(1) <sup>c</sup> –Cd(1)	2.8711(14)	Cd(2)–N(5)	2.388(5)
Cd(2)–N(4)	2.391(5)	Cd(2)–N(6)	2.409(5)
Cd(2)–Br(4)	2.5816(13)	Cd(2)–Br(3)	2.6374(15)
N(2)–Cd(1)–N(3)	76.49(16)	N(2)–Cd(1)–N(1)	74.53(16)
N(3)–Cd(1)–N(1)	95.08(15)	N(3)–Cd(1)–Br(2)	97.48(12)
N(2)–Cd(1)–Br(2)	173.85(11)	N(1)–Cd(1)–Br(2)	105.11(12)
N(2)–Cd(1)–Br(1)	88.40(12)	N(3)–Cd(1)–Br(1)	164.89(11)
N(1)–Cd(1)–Br(1)	80.41(10)	Br(2)–Cd(1)–Br(1)	97.61(5)
N(2)–Cd(1)–Br(1) <sup>c</sup>	84.03(12)	N(3)–Cd(1)–Br(1) <sup>c</sup>	92.36(11)
N(1)–Cd(1)–Br(1) <sup>c</sup>	154.91(11)	Br(2)–Cd(1)–Br(1) <sup>c</sup>	97.59(4)
Br(1)–Cd(1)–Br(1) <sup>c</sup>	86.21(3)	Cd(1)–Br(1)–Cd(1) <sup>c</sup>	93.78(3)
N(5)–Cd(2)–N(4)	74.07(17)	N(5)–Cd(2)–N(6)	74.92(18)
N(4)–Cd(2)–N(6)	115.64(16)	N(5)–Cd(2)–Br(4)	171.49(12)
N(4)–Cd(2)–Br(4)	98.26(13)	N(6)–Cd(2)–Br(4)	105.93(13)
N(5)–Cd(2)–Br(3)	82.61(12)	N(4)–Cd(2)–Br(3)	122.93(12)
N(6)–Cd(2)–Br(3)	106.86(11)	Br(4)–Cd(2)–Br(3)	104.97(4)

<sup>a</sup> Equivalent atoms generated by 1–x, 1–y, 1–z.

<sup>b</sup> Equivalent atoms generated by –x, 1–y, –z.

<sup>c</sup> Equivalent atoms generated by 2–x, 1–y, 1–z.

## 2.6. X-ray crystal structure determinations

The data collections for complexes **1**, **2**, **4** and **5** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.7107$  Å) at 200 K. The data collection for **3** was performed on a Smart Apex CCD diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. The structures were solved by direct method with SIR92 and expanded using Fourier techniques [22]. The absorption correction for all complexes was performed by multiscan method. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on  $F^2$  using SHELXL-97 [23]. The hydrogen atoms of coordinated water molecules in **3** were found from the difference map directly and refined using a riding model, while the ones of non-coordinated water molecules in **2** and **4** and the ones of hydroxyl group of methanol molecules in **2** were not added since they could not be found from the difference map. The other hydrogen atoms were generated geometrically assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic  $U$  of the atoms to which they are attached and allowed to ride on their respective parent atoms. In complex **1**, atoms N3 and C4 are disordered into two positions with site occupancy factors (SOF) of 0.603(11) and 0.397(11), respectively. In complex **4**, a solvent water molecule is disordered and atom O1 is located at two positions with SOF of 0.688(14) and 0.312(14), respectively. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure corporation [24].

Details of the crystal parameters, data collection and refinement for complexes **1–5** are summarized in

Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2. Further details are provided in the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-211540 (**1**), CCDC-211541 (**2**), CCDC-211542 (**3**), CCDC-211543 (**4**) and CCDC-211544 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

### 3. Results and discussion

#### 3.1. Crystal structure of $[Ag_2(L)(L')](ClO_4)_2$ **1**

The crystal structure of complex **1** is shown in Fig. 1a. Each Ag(I) atom is coordinated by three N atoms from ligand *L* and one N atom from the ethylenediamine unit of ligand *L'* with heavy distorted tetrahedral geometry since the coordination angles vary from  $74.33(16)^\circ$  to  $134.0(3)^\circ$  (Table 2). It is noted that, as shown in Fig. 1a, two phenylene ring planes of the biphenylene group involving C(21) is not coplanar and the dihedral angle between them is  $50.8^\circ$ . While the corresponding dihedral angle between the two phenylene ring planes of the biphenylene group involving C(11) is  $45.9^\circ$ . Additionally, the two biphenylene groups within one macrocyclic *L* ligand are almost perpendicular to each other since the dihedral angle between them is  $87.5^\circ$ . It can be seen from Fig. 1a that the Ag(1) and Ag(1A) atoms lie above and below the average plane of two biphenylene groups of *L*, respectively, i.e., the macrocyclic ligand *L* is adopting a slight chair-like conformation in **1**.

As illustrated in Fig. 1b, two Ag(I) atoms binding to the same macrocyclic ligand *L* are coordinated by two ethylenediamine N atoms from two different ligands *L'*, and in turn each *L'* ligand using its two ethylenediamine N atoms connects two Ag(I) atoms from two different  $Ag_2L$  units. Such coordination mode leads to the formation of 1D chain-like structure of **1**. It is surprising that the imidazole N atoms of ligand *L'* do not participate in the coordination with metal atoms, that is to say, each ligand *L'* in fact only serves as a bidentate ligand to link two neighboring macrocyclic moieties. While in the previous reported silver(I) complex with *L'*,  $[Ag_3(L')_2](ClO_4)_3$ , both ethylenediamine and imidazole N atoms coordinated with the Ag(I) atoms [19a]. It has been reported that 4,4'-bipyridine ligands linked neighboring binuclear units with macrocyclic ligand *L''* (prepared from 1,3-diaminopropane and sodium 2,6-diformyl-4-methylphenolate, see Scheme 1) into 1D ladder coordination polymer [25], which is topologically

different from complex **1** as schematically shown in Scheme 2.

The 1D chains of **1** are further linked together by perchlorate anions through hydrogen bonds to give a three-dimensional (3D) framework as shown in Fig. 1c. The hydrogen bonding data are summarized in Table 3. Each  $ClO_4^-$  anion formed five hydrogen bonds: three (*L'*) C–H...O (perchlorate) and two (*L*, *L'*) N–H...O (perchlorate).

#### 3.2. Crystal structure of $[Cu_2(L)(\mu-SO_4)_2] \cdot 3H_2O \cdot 3MeOH$ **2**

When the reaction of ligands *L* and *L'* was carried out with  $CuSO_4 \cdot 5H_2O$  instead of  $AgClO_4 \cdot H_2O$  under the same condition as for preparation of **1**, compound **2** was isolated. However, the result of crystallographic analysis showed that no ligand *L'* was found in **2**. The repeat unit of complex **2** is shown in Fig. 2a. It is clear that each Cu(II) atom has a  $N_3O_2$  coordination environment, in which three N atoms are from a triamine unit of the macrocyclic ligand and two O atoms from two sulfate anions. The Cu(II) atoms are almost at the equatorial plane since the deviation of Cu(1) from the plane containing N(1), N(2), N(3) and O(11) is  $0.12 \text{ \AA}$  and the one of Cu(2) from the plane formed by N(4), N(5), N(6) and O(21) is  $0.13 \text{ \AA}$ . Therefore, the coordination geometry of each Cu(II) atom is a distorted tetragonal pyramid. The atoms O(23) and O(12) occupy the apical positions of Cu(1) and Cu(2), respectively, with elongated bond lengths as listed in Table 2. Each sulfate anion bridges two copper(II) atoms from two different macrocyclic ligands to produce an infinite 1D chain structure as exhibited in Fig. 2b. In contrast to the chair-like conformation in complex **1**, the macrocyclic ligand *L* in complex **2** exhibits a boat-like conformation and the boats are arranged in alternating “up” and “down” conformations in the 1D chain (Fig. 2b). Two coordination planes formed by N(1), N(2), N(3), O(11) and N(1A), N(2A), N(3A), O(11A) with a dihedral angle of  $1.1^\circ$  are near perpendicular to the two biphenylene groups within one *L* ligand. In addition, the two phenylene ring planes from a biphenylene group of ligand *L* in **2** are near coplanar since the dihedral angle between them is  $10.3^\circ$  which is smaller than those in **1** ( $45.9^\circ$  and  $50.8^\circ$ ). The dihedral angle between the two biphenylene groups within one ligand *L* in **2** is  $120.9^\circ$ , rather than near perpendicular as observed in **1**.

The crystal packing diagram of **2** is shown in Fig. 2c in which the hydrogen bonds are indicated by dashed lines. There are solvent methanol and water molecules in complex **2**, which can act as donors and acceptors for hydrogen bonds in addition to the sulfate O atoms (acceptors). The water and methanol molecules locate at the vacancy among the 1D chains and hold the 1D chains together through N–H...O, C–H...O and

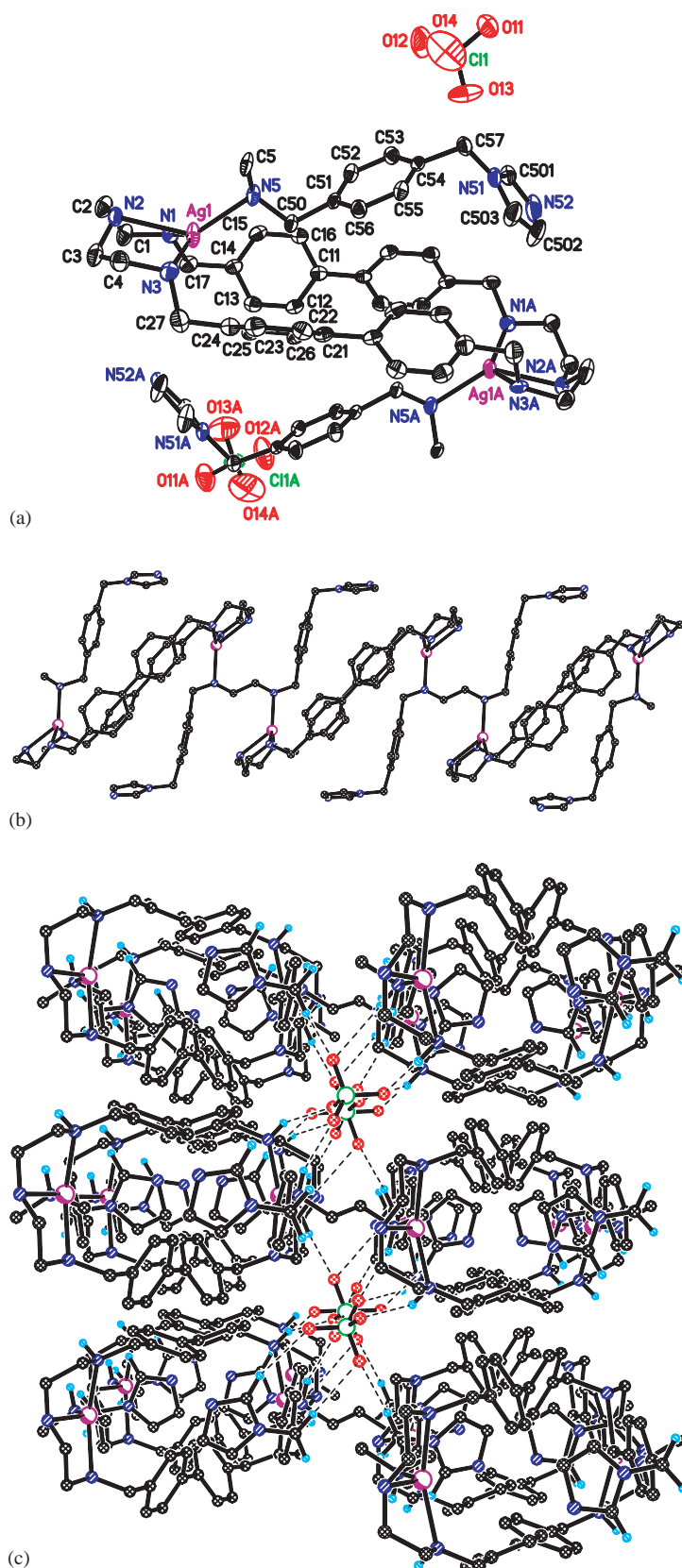
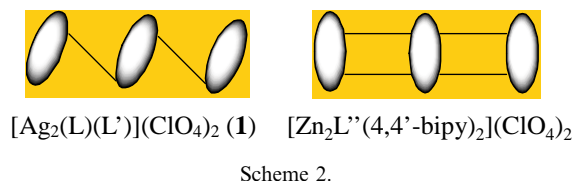


Fig. 1. (a) Crystal structure of  $[\text{Ag}_2(\text{L})(\text{L}')](\text{ClO}_4)_2$  (**1**), hydrogen atoms were omitted for clarity. The thermal ellipsoids are drawn at 30% probability. (b) An infinite zigzag chain structure of **1** linked by  $\text{L}'$  bridging ligands. (c) 3D structure of **1** through hydrogen bonding interactions indicated by dashed lines.

O–H...O hydrogen bonds (Table 3) to generate a 3D architecture. The distances ranging from 2.39(2) to 3.575(8) Å between two O atoms of methanol, water molecules and/or sulfate anions as listed in Table 3 indicate the existence of O–H...O hydrogen bonds although the hydrogen atoms of water molecules and hydroxyl group of methanol could not be found from the difference map.



### 3.3. Crystal structure of [Ni<sub>2</sub>(L)(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>] **3**

When NiSO<sub>4</sub>·7H<sub>2</sub>O, instead of CuSO<sub>4</sub>·5H<sub>2</sub>O, was employed to react with the ligands *L* and *L'* by the same method used for preparations of **1** and **2**, unfortunately, neither complex with *L* and *L'* mix-type ligands like **1** nor one with only ligand *L* as in **2** was obtained. After several attempts, when the ligand *L* reacts with NiSO<sub>4</sub>·7H<sub>2</sub>O in the mixed solvents of methanol and water (*v:v* = 1:2) under the solvothermal condition, compound **3** was obtained and its structure was determined by X-ray single crystal structure analysis. As exhibited in Fig. 3a along with the atom numbering scheme, it is clear that complex **3** is a binuclear molecular complex, rather than an infinite 1D chain-like structure of complex **2**. The remarkable difference between complexes **2** and **3** is the different coordination

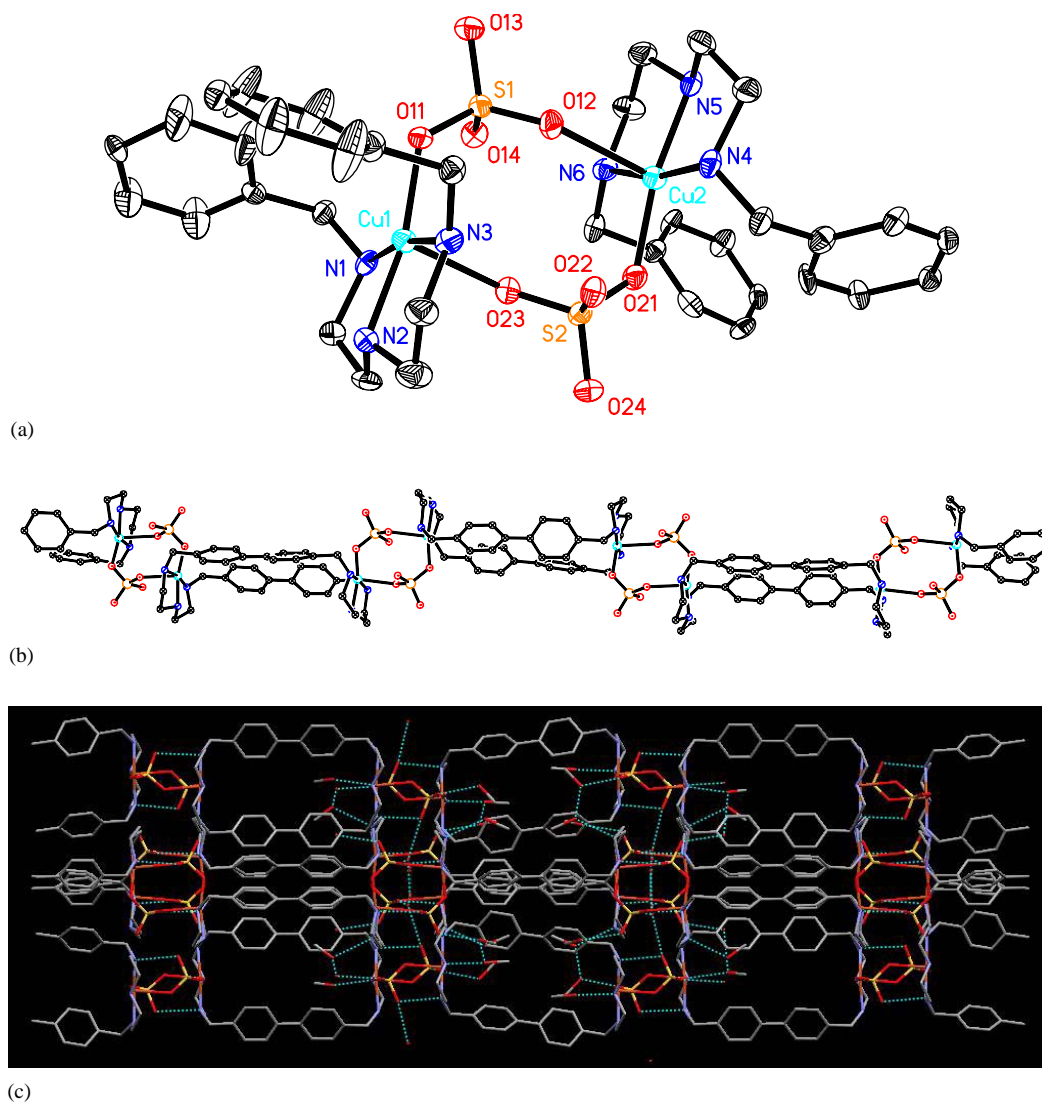


Fig. 2. (a) The repeat unit structure of [Cu<sub>2</sub>(L)(μ-SO<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O·3MeOH (**2**), hydrogen atoms and solvent molecules were omitted for clarity. The thermal ellipsoids are drawn at 30% probability. (b) An infinite chain structure in **2** through SO<sub>4</sub><sup>2-</sup> anion bridges. (c) 3D architecture of **2** produced by hydrogen bonds from interactions of coordinated sulfate anions, solvent water and methanol molecules among the chains.

mode of sulfate anion and different coordination geometry of copper(II) atom in **2** and nickel(II) atom in **3**. Each sulfate anion only coordinates to one Ni(II) atom in monodentate fashion in **3** while the one in **2** connects two copper(II) atoms in bidentate mode. In addition, the Cu(II) atom in **2** is five-coordinated with distorted tetragonal pyramidal geometry, while the Ni(II) atom in **3** has a distorted octahedral geometry with N<sub>3</sub>O<sub>3</sub> binding set. Two N atoms [N(1), N(2)] from ligand *L* and two O atoms [O(1), O(5)] from sulfate anion and water molecule, respectively, form the equatorial plane while N(3) atom from ligand *L* and O(6) atom from water molecule locate at the axial positions with slight longer bond distances compared with those at equatorial plane as tabulated in Table 2. On one hand, the macrocyclic ligand *L* exhibits a chair-like conformation in complex **3** which is similar to that in complex **1**, but different from the boat-like conformation of ligand *L* in complex **2**. On the other hand,

Table 3  
Hydrogen bonds data for complexes **1–5**

D–H...A	Distance of D...A (Å)	Angle of D–H–A (deg.)
<b>[Ag<sub>2</sub>(L)(L')](ClO<sub>4</sub>)<sub>2</sub> (1)</b>		
N(1)–H(1)...O(11) <sup>a</sup>	3.212(9)	153
N(5)–H(4)...O(12) <sup>a</sup>	3.084(9)	163
C(57)–H(33)...O(14)	3.543(11)	164
C(57)–H(34)...O(14) <sup>b</sup>	3.303(11)	167
C(501)–H(35)...O(13)	3.384(11)	160
<b>[Cu<sub>2</sub>(L)(μ-SO<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O·3MeOH (2)</b>		
N(2)–H(2)...O(101) <sup>c</sup>	2.907(9)	160
N(3)–H(3)...O(22)	2.908(7)	162
N(4)–H(4)...O(106) <sup>d</sup>	3.254(13)	130
N(5)–H(5)...O(102)	2.816(9)	162
N(6)–H(6)...O(14)	2.807(6)	171
C(2)–H(9)...O(13) <sup>c</sup>	3.152(6)	127
C(3)–H(12)...O(13) <sup>c</sup>	3.194(8)	123
C(4)–H(14)...O(14) <sup>c</sup>	3.549(7)	162
C(6)–H(17)...O(12)	3.179(7)	121
C(6)–H(18)...O(24) <sup>d</sup>	3.558(7)	169
C(8)–H(21)...O(22) <sup>f</sup>	3.561(7)	175
C(15)–H(25)...O(11)	3.313(8)	149
C(17)–H(27)...O(14)	3.279(7)	135
C(23)–H(30)...O(11)	3.299(7)	144
C(35)–H(37)...O(21)	3.240(7)	148
C(37)–H(39)...O(22)	3.260(7)	132
O(22)...O(105) <sup>e</sup>	2.778(6)	
O(24)...O(103) <sup>c</sup>	2.703(7)	
O(101)...O(101) <sup>g</sup>	2.87(2)	
O(106)...O(106) <sup>h</sup>	2.39(2)	
O(21)...O(103) <sup>c</sup>	3.575(8)	
O(105)...O(106) <sup>h</sup>	2.87(1)	
<b>[Ni<sub>2</sub>(L)(H<sub>2</sub>O)<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>] (3)</b>		
N(1)–H(1A)...O(2) <sup>i</sup>	2.854(4)	151
N(2)–H(2A)...O(4) <sup>j</sup>	3.029(4)	159
O(5)–H(5A)...O(4)	2.735(4)	153
O(5)–H(5B)...O(3) <sup>j</sup>	2.730(4)	162

Table 3 (continued)

D–H...A	Distance of D...A (Å)	Angle of D–H–A (deg.)
O(6)–H(6A)...O(4) <sup>i</sup>	2.865(4)	136
O(6)–H(6B)...O(3) <sup>j</sup>	2.784(4)	156
C(5)–H(5)...O(2)	3.420(5)	151
<b>[Cd<sub>2</sub>(L)(μ-Cl)<sub>2</sub>(Cl)<sub>2</sub>]·2H<sub>2</sub>O (4)</b>		
N(5)–H(5)...O(2) <sup>d</sup>	3.027(10)	149
N(6)–H(6)...O(1)	3.041(10)	151
C(4)–H(13)...Cl(1) <sup>k</sup>	3.695(5)	158
C(17)–H(28)...Cl(1)	3.443(5)	121
C(27)–H(34)...O(1) <sup>l</sup>	3.048(10)	131
Cl(3)–O(2)	3.027(10)	
Cl(4)–O(1B)	3.47(2)	
<b>[Cd<sub>2</sub>(L)(μ-Br)<sub>2</sub>(Br)<sub>2</sub>] (5)</b>		
N(4)–H(4)...Br(3) <sup>m</sup>	3.470(5)	167
N(5)–H(5)...Br(3) <sup>n</sup>	3.466(5)	119
C(1)–H(7)...Br(1) <sup>o</sup>	3.840(7)	160
C(27)–H(34)...Br(3) <sup>p</sup>	3.612(6)	137

<sup>a</sup> Equivalent atoms generated by 0.5–*x*, 0.5–*y*, 1–*z*.

<sup>b</sup> Equivalent atoms generated by –*x*, –*y*, 1–*z*.

<sup>c</sup> Equivalent atoms generated by 0.5 + *x*, 0.5–*y*, *z*.

<sup>d</sup> Equivalent atoms generated by –0.5 + *x*, 0.5–*y*, *z*.

<sup>e</sup> Equivalent atoms generated by 0.5–*x*, –0.5 + *y*, *z*.

<sup>f</sup> Equivalent atoms generated by 0.5–*x*, 0.5 + *y*, *z*.

<sup>g</sup> Equivalent atoms generated by –*x*, –*y* + 1, *z*.

<sup>h</sup> Equivalent atoms generated by 1–*x*, 1–*y*, *z*.

<sup>i</sup> Equivalent atoms generated by *x*, 1.5–*y*, 0.5 + *z*.

<sup>j</sup> Equivalent atoms generated by 1–*x*, 0.5 + *y*, 0.5–*z*.

<sup>k</sup> Equivalent atoms generated by *x*, –1 + *y*, *z*.

<sup>l</sup> Equivalent atoms generated by –0.5 + *x*, 1.5–*y*, *z*.

<sup>m</sup> Equivalent atoms generated by 1–*x*, 1–*y*, –*z*.

<sup>n</sup> Equivalent atoms generated by 0.5–*x*, –0.5 + *y*, –*z*.

<sup>o</sup> Equivalent atoms generated by 2–*x*, –*y*, 1–*z*.

<sup>p</sup> Equivalent atoms generated by 0.5–*x*, 0.5 + *y*, –*z*.

the dihedral angle between two phenylene ring planes from a biphenylene group is 19.0°, which is larger than the one in complex **2** (10.3°). In addition, the dihedral angle between the phenylene containing the C(16) atom and the one containing the C(1) atom within one ligand *L* is also 19.0°.

There are two intermolecular (ligand *L*) N–H...O (sulfate anion) and three intermolecular (coordinated water) O–H...O (sulfate anion) hydrogen bonds, in addition to the intra-molecular O–H...O and C–H...O ones (Table 3). Thus a 3D structure of complex **3** is formed by connections of binuclear molecules via these hydrogen bonds as illustrated in Fig. 3b.

The results showed that metal ions have important influences on the construction of MOFs with macrocyclic ligand. Due to the different coordination geometric requirement of metal ions, coordination compounds **2** and **3** have different structures and the macrocyclic ligand *L* exhibits diverse conformations in these complexes as mentioned above.



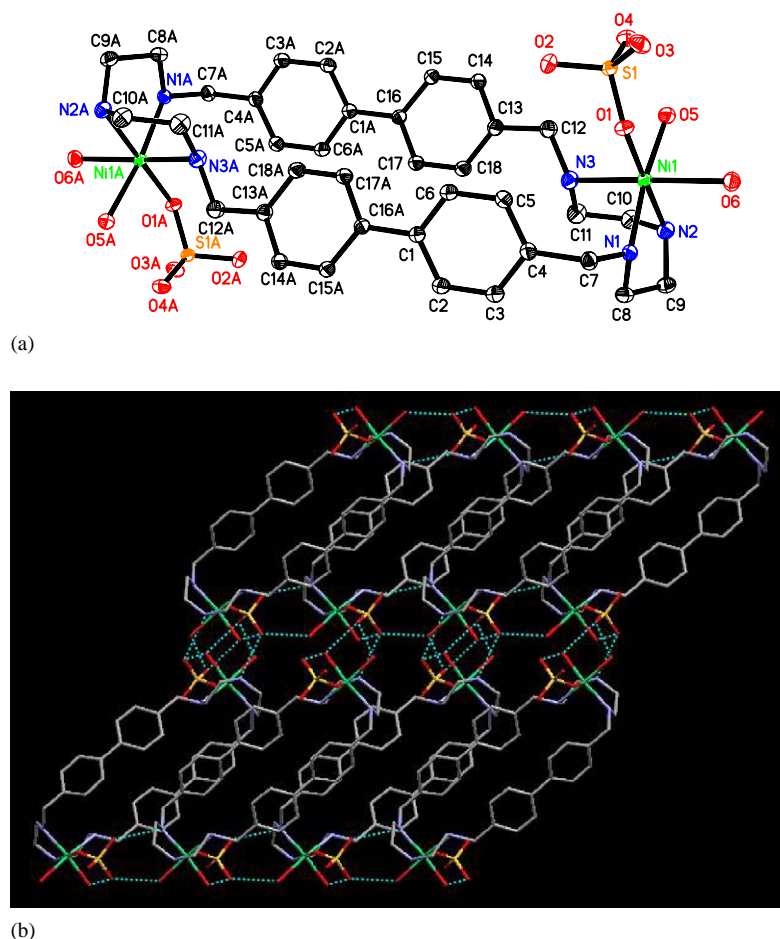


Fig. 3. (a) The crystal structure of  $[\text{Ni}_2(\text{L})(\text{H}_2\text{O})_4(\text{SO}_4)_2]$  (**3**), hydrogen atoms were omitted for clarity. The thermal ellipsoids are drawn at 30% probability. (b) 3D structure of **3** formed by hydrogen bonds.

### 3.4. Crystal structures of $[\text{Cd}_2(\text{L})(\mu\text{-Cl})_2(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$ **4** and $[\text{Cd}_2(\text{L})(\mu\text{-Br})_2(\text{Br})_2]$ **5**

The results of crystallographic analysis revealed that complexes **4** and **5** crystallize in the same monoclinic space group  $P2_1/c$ . As listed in Table 1, similar cell parameters of **4** and **5** indicate that the two compounds are isomorphous and isostructural, implying the  $\text{Cl}^-$  and  $\text{Br}^-$  anions have no obvious influence on the structure of the complexes. Thus as an example, the structure of complex **4** is described here. As shown in Fig. 4a, the coordination environment around the Cd(II) atom can be described as a distorted octahedral geometry with  $\text{N}_3\text{Cl}_3$  donor set. The equatorial planes consist of N(1), N(3), Cl(1A), Cl(1) with mean deviation of 0.094 Å and N(4), N(6), Cl(4), Cl(4A) with mean deviation of 0.059 Å. The metal atoms of Cd(1) and Cd(2) deviated from the corresponding equatorial plane 0.46 and 0.41 Å, respectively. Virtually six-coordinated environment of the Cd(II) atoms is achieved by bridged chloride atoms [e.g., Cl(1A) and Cl(4A) in Fig. 4b]. Namely, one of three chloride atoms coordinated to one Cd(II) atom is as a terminal ligand and the other two are

as bridging ligands to link two Cd(II) atoms (Fig. 4b). Two different rhombic planes with a dihedral angle of  $34.1^\circ$  are formed, each formed by two Cd(II) centers and two chloride bridges (Fig. 4b). On the other hand, in one macrocyclic ligand (Fig. 4a), the dihedral angle between two phenylene ring planes of a biphenylene group containing C(41) and C(31) ring planes is  $32.8^\circ$  and the one containing C(11) and C(21) ring planes is  $48.0^\circ$ . The dihedral angle between two biphenylene groups in one ligand *L* containing C(41) ring and C(21) ring is  $26.6^\circ$  and the one containing C(31) ring and C(11) ring is  $58.5^\circ$ .

As shown in Fig. 4b, two chloride atoms bridge two Cd(II) atoms from two different macrocyclic ligands with boat-like conformation to result in an infinite chain. The 1D chains are further linked into 3D framework by hydrogen bonds among water molecules, chloride atoms and ligand *L* as shown in Fig. 4c in which the hydrogen bonds indicated by dash lines.

The present study showed that, in addition to the role of metal atoms (vide supra), counter anions with different shape, coordination and bridging ability also have remarkable impact on the structure of MOFs, e.g.,

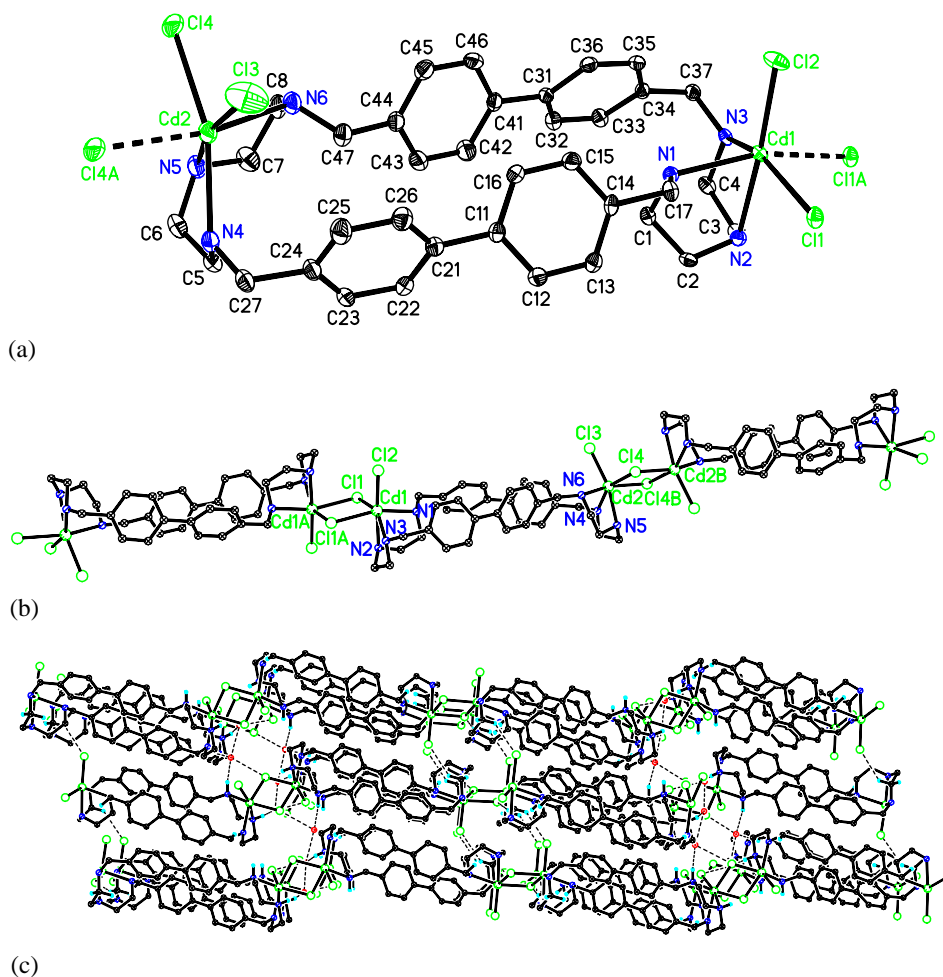


Fig. 4. (a) The coordination environment around Cd(II) atoms in  $[\text{Cd}_2(\text{L})(\mu\text{-Cl})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  (**4**), hydrogen atoms were omitted for clarity. The thermal ellipsoids are drawn at 30% probability. (b) An infinite chain structure formed by  $\mu$ -chloro bridges in **4**. (c) 3D structure of complex **4** with hydrogen bonds indicated by dashed lines.

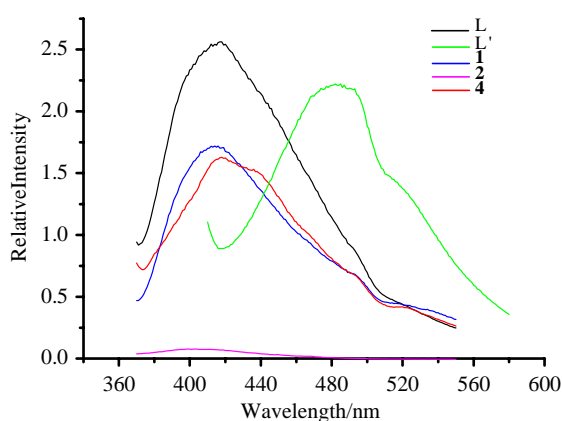


Fig. 5. The emission spectra of ligand *L* (black), ligand *L'* (green), complex **1** (blue), complex **2** (magenta), and complex **4** (red) in the solid state at room temperature with  $\lambda_{\text{exc}} = 350 \text{ nm}$ .

complexes **3** and **4** (**5**) with sulfate and chloride (bromide) anions have different structures, though both Ni(II) and Cd(II) are the same six-coordinated with

octahedral geometry. It is noteworthy that in complexes **1** and **3**, ligand *L* has a chair-like conformation, while in the anion-bridged coordination polymers **2**, **4** and **5**, macrocyclic ligand *L* showed boat-like conformation. In addition, the different conformation of ligand *L* has different linkage mode of macrocyclic metal units to form 1D chain. In complex **1**, the head-to-tail chain structure is generated by binding of open-chain ligand *L'* with the chair-like macrocyclic *L*. While, in complexes **2**, **4** and **5**, the head-to-head chains are obtained since the macrocyclic ligand *L* adopts boat-like conformation [18].

### 3.5. Fluorescent properties of complexes

The photoluminescent properties of the synthesized coordination polymers **1**, **2** and **4** were studied in the solid state at room temperature. As illustrated in Fig. 5, 1D coordination polymer **1** with mix-type ligands exhibits a fluorescent emission at 413 nm upon excitation at 350 nm, which is quite similar to that of ligand *L* (emission maximum at 417 nm) and a blue-shift occurs

compared to that of ligand  $L'$  (emission maximum at 485 nm) under the same conditions. Thus, the emission observed in complex **1** is mostly predominated by the intra-macrocyclic ligand fluorescence. It is not well-known that silver(I) complexes can emit photoluminescence at room temperature [19a]. In the case of 1D chain Cu(II) coordination polymer **2**, a broad blue shifted photoluminescence was observed with the maximum emission around 400 nm and with much weaker intensity compared with those of **1** and  $L$  ligand. The luminescence of complex **2** may probably be quenched by the Cu(II) ion [26]. It is known that the Ni(II) ion may also quench the luminescence of its complex, thus the photoluminescent measurement for complex **3** was not carried out [26]. Cd(II) complex **4** exhibits similar emission to complex **1** with the maximum emission around 416 nm, which can also be assigned to the intra-macrocyclic ligand fluorescence.

### Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant No. 20231020).

### References

- [1] (a) S.R. Batten, R. Robson, *Angew. Chem. Int. Ed.* 37 (1998) 1460;  
(b) S.A. Barnett, A.J. Blake, N.R. Champness, J.E.B. Nicolson, C. Wilson, *J. Chem. Soc. Dalton Trans.* (2001) 567;  
(c) S.R. Batten, *Cryst. Eng. Commun.* 18 (2001) 1.
- [2] P.J. Stang, B. Olenyuk, *Acc. Chem. Res.* 30 (1997) 502.
- [3] S. Leininger, B. Olenyuk, P.J. Stang, *Chem. Rev.* 100 (2000) 853.
- [4] M.J. Zaworotko, *Angew. Chem. Int. Ed.* 39 (2000) 3052.
- [5] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629.
- [6] D.B. Amabilino, J.F. Stoddart, *Chem. Rev.* 95 (1995) 2725.
- [7] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* 97 (1997) 2005.
- [8] S. Noro, S. Kitazawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed.* 39 (2000) 2082.
- [9] L. Pan, E.B. Woodlock, X. Wang, *Inorg. Chem.* 39 (2000) 4174.
- [10] (a) O. Kahn, C.J. Martinez, *Science* 279 (1998) 44;  
(b) O. Kahn, *Acc. Chem. Res.* 33 (2000) 647.
- [11] P.N.W. Baxter, *Chem. Eur. J.* 22 (2002) 5250.
- [12] (a) O.R. Evans, R. Xiong, Z. Wang, G.K. Wong, W. Lin, *Angew. Chem. Int. Ed.* 38 (1999) 536;  
(b) W. Lin, Z. Wang, L. Ma, *J. Am. Chem. Soc.* 121 (1999) 11249.
- [13] (a) P. Guerriero, S. Tamburini, P.A. Vigato, *Coord. Chem. Rev.* 139 (1995) 17;  
(b) T. Koike, M. Inoue, E. Kimura, M. Shiro, *J. Am. Chem. Soc.* 118 (1996) 3091;
- (c) C. Bazzicalupi, A. Bencini, A. Bianchi, M. Cecchi, B. Escuder, V. Fusi, E. Garcia-España, C. Giorgi, S.V. Luis, G. Maccagni, V. Marcelino, P. Paoletti, B. Valtancoli, *J. Am. Chem. Soc.* 121 (1999) 6807;
- (d) E. Ross, R.J. Motekaitis, A.E. Martell, *Inorg. Chim. Acta.* 286 (1999) 55.
- [14] (a) D.E. Fenton, R.W. Matthews, M. McPartlin, B.P. Murphy, I.J. Scowen, P.A. Tasker, *J. Chem. Soc. Chem. Commun.* (1994) 1391;  
(b) R.W. Matthews, M. Mcpartlin, I.J. Scowen, *J. Chem. Soc. Dalton Trans.* (1997) 2861.
- [15] D.J. Cárdenas, P. Gaviña, J.-P. Sauvage, *J. Am. Chem. Soc.* 119 (1997) 2656.
- [16] (a) H.J. Choi, M.P. Suh, *Inorg. Chem.* 38 (1999) 6309;  
(b) K.-Y. Choi, K.M. Chun, I.-L. Suh, *Polyhedron* 20 (2001) 57.
- [17] V.C. Gibson, S. McTavish, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, *Dalton Trans.* (2003) 221.
- [18] W. He, F. Liu, C. Duan, Z. Guo, S. Zhou, Y. Liu, L. Zhu, *Inorg. Chem.* 40 (2001) 1712.
- [19] (a) X.-M. Ouyang, D.J. Liu, T.-A. Okamura, H.-W. Bu, W.-Y. Sun, W.-X. Tang, N. Ueyama, *J. Chem. Soc. Dalton Trans.* (2003) 1836;  
(b) B.-L. Fei, W.-Y. Sun, K.-B. Yu, W.-X. Tang, *J. Chem. Soc. Dalton Trans.* (2000) 805;  
(c) B.-L. Fei, W.-Y. Sun, T.-a. Okamura, W.-X. Tang, N. Ueyama, *New J. Chem.* 25 (2001) 210;  
(d) X.-M. Ouyang, B.-L. Fei, T.-A. Okamura, H.-W. Bu, W.-Y. Sun, W.-X. Tang, N. Ueyama, *Eur. J. Inorg. Chem.* (2003) 618.
- [20] (a) M. Leivers, R. Breslow, *Bioorg. Chem.* 29 (2001) 345;  
(b) K. Li, M. Fernandez-Saiz, C. Ted Rigl, A. Kumar, K.G. Ragunathan, A.W. McConnaughie, D.W. Boykin, H.-J. Schneider, W.D. Wilson, *Bioorg. Med. Chem.* 5 (1997) 1157.
- [21] (a) S.-A. Li, J. Xia, D.-X. Yang, Y. Xu, M.-F. Wu, W.-X. Tang, *Inorg. Chem.* 41 (2002) 1807;  
(b) K.G. Ragunathan, H.-J. Schneider, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1219.
- [22] (a) SIR92: A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Cryst.* 27 (1994) 435;  
(b) DIRDIF94: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- [23] G.M. Sheldrick, SHELX1-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
- [24] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, 1999.
- [25] W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun, Q. Meng, *Inorg. Chem.* 40 (2001) 1712.
- [26] (a) D.H. Pierre, F. Daniel, *Coord. Chem. Rev.* 171 (1998) 351;  
(b) L. Prodi, F. Bolletta, M. Montalti, N. Zaccaroni, *Coord. Chem. Rev.* 205 (2000) 59.