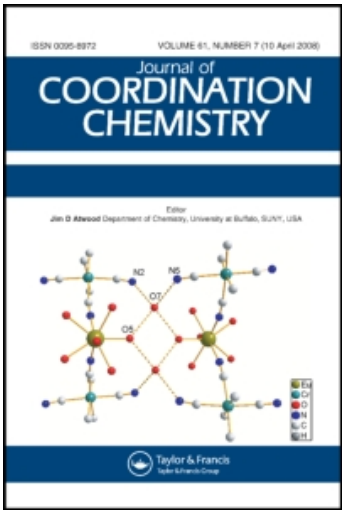

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structures, and fluorescence properties of (RS)-2-methylglutarato Zn(II), Cd(II) complexes

Yue-Qing Zheng[a]; Wen Liu[a]; Fang-Yang Yao[a]
[a] Faculty of Materials Science & Chemical Engineering, Institute of Solid Materials Chemistry, State Key Laboratory Base of Novel Functional Materials & Preparation Science, Ningbo University, Ningbo, 315211 P.R. China

To cite this Article Zheng, Yue-Qing , Liu, Wen and Yao, Fang-Yang(2009) 'Synthesis, crystal structures, and fluorescence properties of (RS)-2-methylglutarato Zn(II), Cd(II) complexes', Journal of Coordination Chemistry, 62: 15, 2497 — 2510
To link to this Article: DOI: 10.1080/00958970902852934
URL: http://dx.doi.org/10.1080/00958970902852934

Journal of Coordination Chemistry
Vol. 62, No. 15, 10 August 2009, 2497–2510

Taylor & Francis
Taylor & Francis Group

Synthesis, crystal structures, and fluorescence properties of (RS)-2-methylglutarato Zn(II), Cd(II) complexes

YUE-QING ZHENG*, WEN LIU and FANG-YANG YAO

Faculty of Materials Science & Chemical Engineering, Institute of Solid Materials Chemistry, State Key Laboratory Base of Novel Functional Materials & Preparation Science, Ningbo University, Ningbo, 315211 P.R. China

(*Received 6 November 2008; in final form 11 December 2008*)

Reactions of fresh $M(OH)_2$ ($M = Zn^{2+}$, Cd^{2+}) precipitate and (RS)-2-methylglutaric acid (H_2MGL), 2,2′-bipyridine (bipy), or 1,10-phenanthroline (phen) in aqueous solution at 50°C afforded four new metal–organic complexes $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ (**1**), $[Zn_2(phen)_2(H_2O)(MGL)_2]$ (**2**), $[Cd(bipy)(H_2O)(MGL)]\cdot 3H_2O$ (**3**), and $[Cd(phen)(H_2O)(MGL)]\cdot 2H_2O$ (**4**), which were characterized by single crystal X-ray diffraction, IR spectra, TG/DTA analysis as well as fluorescence spectra. In **1**, the $[Zn(bipy)(H_2O)]^{2+}$ moieties are linked by R- and S-2-methylglutarate anions to build up the centrosymmetric dinuclear $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ molecules. In **2**, the 1-D ribbon-like chains $[Zn_2(phen)_2(H_2O)(MGL)_2]_n$ can be visualized as from centrosymmetric dinuclear $[Zn_2(phen)_2(H_2O)_2(MGL)_2]$ units sharing common aqua ligands. Both **3** and **4** exhibit 1-D chains resulting from $[Cd(bipy)(H_2O)]^{2+}$ and $[Cd(phen)(H_2O)]^{2+}$, respectively, bridged alternately by R- and S-2-methylglutarate anions in *bis*-chelating fashion. The intermolecular and interchain $\pi\cdots\pi$ stacking interactions form supramolecular assemblies in **1** and 1-D chains in **2**–**4** into 2-D layers. The hydrogen bonded lattice H_2O molecules are sandwiched between 2-D layers in **3** and **4**. Fluorescence spectra of **1**–**4** exhibit LLCT $\pi \rightarrow \pi^*$ transitions.

Keywords: (RS)-2-methylglutaric acid; Zn(II) complexes; Cd(II) complexes; Supramolecular assembly; Fluorescence properties

1. Introduction

Metal-organic coordination polymers have been one of the most active subjects in coordination chemistry and materials science [1–5]. Judicious choice of metal ion and organic ligands are most important for rational design and synthesis of molecular-based materials with potential applications in non-linear optics, magnetism, and electric-optical devices [6–13]. Carboxylic acids have been widely used not only due to their abundant coordination modes but also to form neutral metal-organic frameworks [14–17]. Our lab has focused on exploration and utilization of saturated aliphatic α,ω-dicarboxylate ligands, leading to syntheses of a series of new coordination polymers not only with specific structures [18–23] but also with interesting properties; for

*Corresponding author. Email: zhengcm@nbu.edu.cn

ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902852934

example, Zn(II) succinate exhibits a significant non-linear optical effect [24]. In comparison with linear α,ω-dicarboxylic acids, branched α,ω-dicarboxylic acids such as 2-methyl glutaric acid (H_2MGL) has been seldom used to construct coordination polymers. Zn(II) and Cd(II) metal ions exhibit appealing structures and possess photoluminescent properties [25]. In this contribution, we report syntheses, crystal structures, and properties of four Zn(II) and Cd(II) coordination polymers, $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ (**1**), $[Zn_2(phen)_2(H_2O)(MGL)_2]$ (**2**), $[Cd(bipy)(H_2O)(MGL)]\cdot 3H_2O$ (**3**), and $[Cd(phen)(H_2O)(MGL)]\cdot 2H_2O$ (**4**), resulting from self-assembly of metal ions and racemic 2-methylglutaric acid (H_2MGL) in the presence of 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), in aqueous solution at 50°C. These are the first examples using (RS)-2-methylglutaric acid as bridging ligand to construct coordination polymers.

2. Experimental

2.1. *Materials and methods*

Chemicals of reagent grade were commercially available and used without purification. FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric measurements were carried out from room temperature to 800°C on pre-weighed samples in a nitrogen stream using a Seiko Exstar 6000 TG/DTA6300 apparatus with a heating rate of 10°C min^{-1}. The C, N, and H microanalyses were performed with a Heraeus Rapid–CHNO elemental analyzer. Diffraction data were collected by Rigaku Raxis-Rapid X-ray single crystal diffraction apparatus. The fluorescence spectra on solid samples were determined with a RF-5301PC spectrophotometer.

2.2. *Synthesis of $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ (1)*

Dropwise addition of 1.0 mL NaOH (1.0 M) to a stirred aqueous solution of 0.148 g (0.5 mmol) $Zn(NO_3)_2\cdot 6H_2O$ in 4 mL H_2O produced white precipitate, which was then centrifuged and washed with doubly-distilled water several times, and subsequently added to a stirred solution of 0.073 g (0.5 mmol) (RS)-2-H_2MGL and 0.078 g (0.5 mmol) bipy in 40 mL H_2O. The resulting mixture was further stirred for 30 min and solid was filtered off. The colorless filtrate (pH = 4.73) was kept at 50°C in a constant temperature incubator and colorless block crystals formed in 1 week. Yield: 28% (60 mg) based on the initial $Zn(NO_3)_2\cdot 6H_2O$. The phase purity of the product was checked by powder X-ray diffraction pattern compared with the simulated PXRD based on the single crystal data (figure S1a). Anal. Calcd for $C_{32}H_{36}N_4O_{10}Zn_2$ (%): C, 50.1; H, 4.7; N, 7.3. Found: C, 50.2; H, 4.6; N, 7.4. IR data (cm^{-1}): 3421b, 3110w, 2961w, 1558vs, 1412s, 1317w, 1157w, 1022w, 764m, 632w. TG/DTA measurements (figure S2): the DTA curve exhibits three endothermic peaks at 143, 240, and 385°C, and the corresponding TG curve displays that **1**, when heated, underwent three continuous weight losses: 9.3% over 70–176°C, 11.4% over 176–260°C, and 58.6% over 260–465°C. The final residue is confirmed to be ZnO (Obs. 20.8%, Calcd 21.2%).

2.3. *Synthesis of [$Zn_2(phen)_2(H_2O)(MGL)_2$] (2)*

A synthetic procedure analogous to **1** was employed except that 0.099 g (0.5 mmol) phen was used instead of bipy. The resulting solution (pH = 5.24) was kept at 50°C, and slow evaporation afforded colorless block crystals. Yield: 30% (67 mg) based on the initial $Zn(NO_3)_2 \cdot 6H_2O$. The phase purity was checked according to powder X-ray diffraction pattern compared with the simulated PXRD based on the single crystal data (figure S1b). Anal. Calcd for $C_{36}H_{34}N_4O_9Zn_2$ (%): C, 54.3; H, 4.2; N, 7.0. Found: C, 54.1; H, 4.3; N, 7.1. IR data (cm^{-1}): 3421b, 3083w, 2912w, 1560vs, 1418s, 1338w, 1147w, 854vs, 729vs, 692m. TG/DTA measurements (figure S2): the DTA curve exhibits two endothermic peaks at 211 and 334°C, and the corresponding TG curve shows that dehydration of **2** takes place from 55 to 240°C with the observed weight loss of 2.5% in good agreement with the calculated value of 2.3%. Upon further heating, the anhydrous intermediate experiences gradual weight loss of 28.5% from 305 to 540°C.

2.4. *Synthesis of [$Cd(bipy)(H_2O)(MGL)] \cdot 3H_2O$ (3)*

A synthetic procedure analogous to **1** was employed except that 0.134 g (0.5 mmol) $Cd(Ac)_2 \cdot 2H_2O$ was used instead of $Zn(NO_3)_2 \cdot 6H_2O$. The resulting solution (pH = 4.33) was kept at 50°C, and slow evaporation yielded colorless block crystals. Yield: 78% (191 mg) based on the initial $Cd(Ac)_2 \cdot 2H_2O$. The phase purity of the product was checked by powder X-ray diffraction pattern compared with the simulated PXRD based on the single crystal data (figure S1c). Anal. Calcd for $C_{16}H_{24}CdN_2O_8$ (%): C, 39.6; H, 5.0; N, 5.8. Found: C, 39.5; H, 5.1; N, 5.7. IR data (cm^{-1}): 3420b, 2967w, 1556vs, 1439w, 1405s, 1315w, 1170w, 1016w, 771m, 649w. TG/DTA measurements (figure S2): the DTA curve exhibits four endothermic peaks at 80, 243, 261, and 364°C, and the corresponding TG curve shows that complete dehydration of **3** was observed in the temperature range 40–105°C with the observed weight loss of 14.6% in good agreement with the calculated value of 14.9%. The anhydrous intermediate is stable on further heating to 205°C, after which two successive weight losses of 21.3 and 59.4% in the temperature regions 205–280°C and 305–500°C, respectively, were observed. The final residue of 4.9% was assumed to be elemental carbon.

2.5. *Synthesis of [$Cd(phen)(H_2O)(MGL)] \cdot 2H_2O$ (4)*

A synthetic procedure analogous to **2** was employed except that 0.134 g (0.5 mmol) $Cd(Ac)_2 \cdot 2H_2O$ was used instead of $Zn(NO_3)_2 \cdot 6H_2O$. The resulting solution (pH = 4.14) was kept at 50°C, and slow evaporation led to colorless block crystals. Yield: 15% (37 mg) based on the initial $Cd(Ac)_2 \cdot 2H_2O$. The phase purity of the product was checked by powder X-ray diffraction pattern compared with the simulated PXRD based on the single crystal data (figure S1d). Anal. Calcd for $C_{18}H_{22}CdN_2O_7$ (%): C, 44.1; H, 4.5; N, 5.7. Found: C, 44.1; H, 4.6; N, 5.8. IR data (cm^{-1}): 3384b, 2964w, 2928w, 1558vs, 1414s, 1304w, 1143w, 856m, 729m, 575w. TG/DTA measurements (figure S2): the TG/DTA curves demonstrate one endothermic dehydration peak at 99°C with the observed weight loss of 12.1% corresponding to the calculated value of 11.0%.

The resulting dehydration intermediate is stable to 370°C; then, two successive endothermic decompositions with total weight loss of 51.0% up to 550°C occurred.

2.6. *X-ray crystallography*

Suitable single crystals were selected under a polarizing microscope and fixed with epoxy cement on glass fibers which were mounted on a Rigaku R-Axis Rapid IP X-ray diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection, operating at 50 kV and 40 mA. Data were collected from $3.1 \leq \theta \leq 27.5°$ at 295 K and corrected for *Lp* and absorption effects. SHELXS-97 and SHELXL-97 [26] were used for structure solution and refinement. The structures were solved by direct methods. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms associated with carbon atoms were geometrically generated, and the remaining hydrogens were located from successive difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares technique and hydrogen atoms with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in table 1.

Table 1. Summary of crystal data and structure refinement details for **1**–**4**.

Compounds	**1**	**2**	**3**	**4**
Empirical formula	$C_{32}H_{36}N_4O_{10}Zn_2$	$C_{36}H_{34}N_4O_9Zn_2$	$C_{16}H_{24}CdN_2O_8$,	$C_{18}H_{22}CdN_2O_7$
Formula weight	767.39	797.41	484.77	490.78
Color/Shape	Colorless/Block	Colorless/Platelet	Colorless/Prism	Colorless/Prism
Crystal size (mm)	$0.33 \times 0.25 \times 0.11$	$0.58 \times 0.48 \times 0.18$	$0.33 \times 0.31 \times 0.23$	$0.21 \times 0.20 \times 0.19$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell dimensions (Å, °)				
a	9.143(2)	23.559(5)	8.4052(17)	8.475(2)
b	10.981(2)	9.925(2)	19.788(4)	19.334(4)
c	16.391(3)	17.774(4)	11.992(2)	12.025(2)
β	91.84(3)	128.90(3)	99.23(3)	98.86(3)
V (Å^3)	1644.8(6)	3234.4(11)	1968.7(7)	1946.8(7)
Z	2	4	4	4
D_{Calcd} (g cm^{-3})	1.549	1.635	1.636	1.674
F(000)	792	1636	984	992
μ (mm^{-1})	1.52	1.55	1.15	1.16
θ range (°)	3.10–27.48	3.11–27.47	3.20–27.47	3.18–27.48
Total no. of data	15,858	15,241	18,787	18,726
Unique reflections	3770	3688	4475	4441
No. of obs. data [$I \geq 2\sigma(I)$][a]	2763	2886	3943	3671
Goodness-of-fit on F^2	1.043	1.099	1.122	1.065
R_1, wR_2	0.070, 0.092	0.056, 0.112	0.039, 0.071	0.040, 0.070
R_1, $wR_2[I \geq 2\ \sigma(I)]$[a]	0.044, 0.083	0.042, 0.107	0.033, 0.068	0.029, 0.059
Extinction	0.0000(4)	0.00000(15)	0.0000(2)	0.0000(2)
Number of variable	221	232	245	266
$\delta\rho_{max}$, $\delta\rho_{min}$ (e Å^{-3})	0.34, −0.29	0.70, −0.41	0.775, −0.375	0.42, −0.32

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, and $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. *Synthesis*

Freshly-prepared Zn(II) and Cd(II) hydroxides from reactions of NaOH with soluble Zn(II) and Cd(II) salts reacted with (RS)-2-methylglutaric acid in the presence of 2,2′-bipyridine or 1,10-phenanthroline in aqueous solution, yielding $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ (**1**), $[Zn_2(phen)_2(H_2O)(MGL)_2]$ (**2**), $[Cd(bipy)(H_2O)(MGL)]\cdot 3H_2O$ (**3**), and $[Cd(phen)(H_2O)(MGL)]\cdot 2H_2O$ (**4**), whose reactions could be expressed as follows:

$$2Zn(OH)_2 + 2bipy + 2H_2MGL = [Zn_2(bipy)_2(H_2O)_2(MGL)_2] + 2H_2O \quad (1)$$

$$2Zn(OH)_2 + 2phen + 2H_2MGL = [Zn_2(phen)_2(H_2O)(MGL)_2] + 3H_2O \quad (2)$$

$$Cd(OH)_2 + bipy + H_2MGL + 2H_2O = [Cd(bipy)(H_2O)(MGL)]\cdot 3H_2O \quad (3)$$

$$Cd(OH)_2 + phen + H_2MGL + H_2O = [Cd(phen)(H_2O)(MGL)]\cdot 2H_2O \quad (4)$$

Compounds **1**, **2**, and **4** are insoluble in water, methanol, and ethanol. Compound **3** is insoluble in water and ethanol, but loses its crystallinity in methanol.

3.2. *Structure descriptions*

3.2.1. $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ (1). The asymmetric unit of **1** consists of a Zn^{2+}, a 2-methylglutarate anion, an aqua ligand, and a 2,2′-bipyridine. As depicted in figure 1, the Zn atoms are octahedrally coordinated by two nitrogens of one bipy, and four oxygens of one aqua ligand and two 2-methylglutarato ligands to form a ZnN_2O_4 chromophore with d(Zn–N) = 2.111 and 2.160 Å and d(Zn–O) = 2.027–2.425 Å. Of the four coordinated oxygens, three (O1, O2, O3#1; #1 = $-x+1$, $-y+1$, $-z$) belong to R- and S-methylglutarate. The transoid and cisoid angles about the central Zn fall in the regions 156.3–168.0 and 76.3–117.6°, respectively (see the "Supplementary material": table 2), exhibiting significant deviations from a regular octahedron. The bonding values are normal in comparison with Zn(II) complexes with similar coordination geometry [27–29].

Both R- and S-2-methylglutarate anions are twisted with the terminal carboxylate groups chelating and monodentate, respectively, to bridge Zn, forming a centrosymmetric binuclear $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ whose centers are located at the crystallographic 2*b* sites (figure 1a). The Zn···Zn distance within the molecule is 7.946 Å. Along the [0 1 0] direction, molecules are arranged with mean interplanar distance between two closest antiparallel bipy ligands of adjacent dinuclear molecules of 3.43 Å, suggesting significant face-to-face $\pi\cdots\pi$ interactions. In addition, bipy of a complex molecule donates hydrogen to the chelating oxygen of an adjacent molecule to form weak C–H···O hydrogen bonds. The intermolecular $\pi\cdots\pi$ stacking and C–H···O hydrogen bonding interactions assemble the molecules into 1-D chains propagating infinitely in the [0 1 0] direction. The aqua ligand forms a strong intramolecular O–H···O hydrogen bond to the non-coordinating carboxylate O with d(O···O) = 2.589 Å. Nearly linear interchain hydrogen bonds between aqua ligands

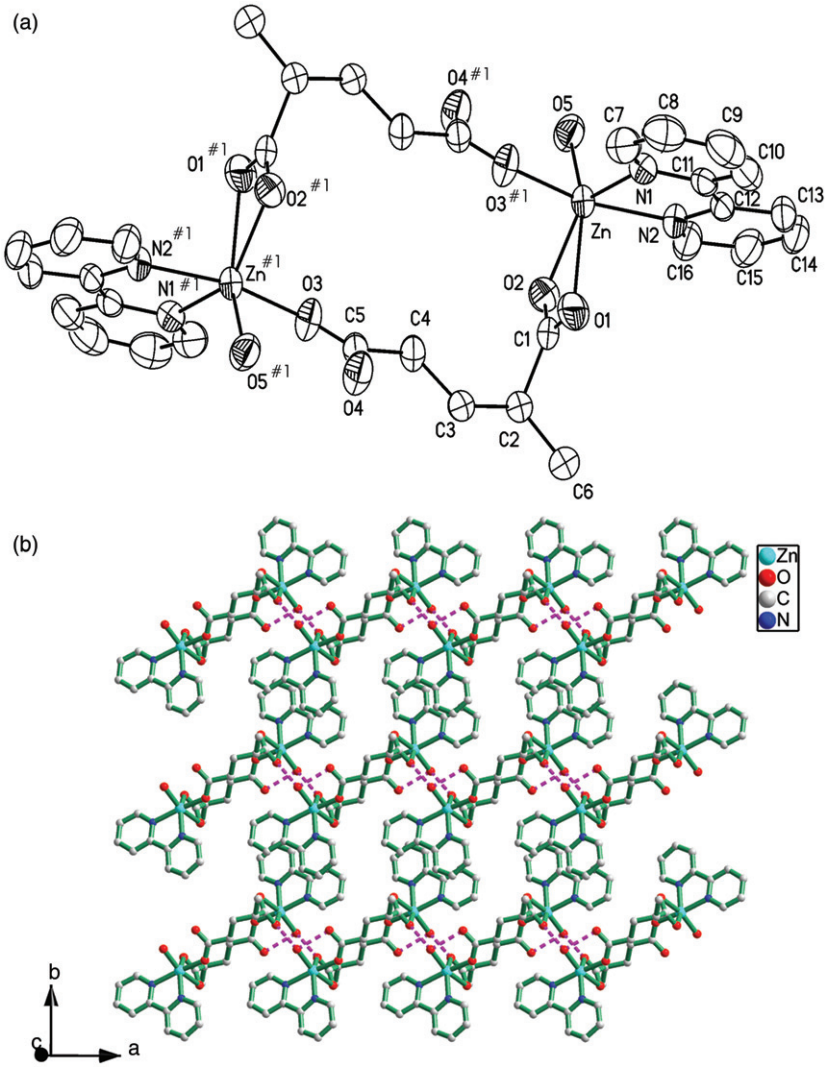

Figure 1. (a) The ORTEP view of coordination of Zn along with the bridging of 2-methylglutarato and atomic labeling for **1**. The thermal ellipsoids are drawn at 45% probability (symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z$). (b) Supramolecular assembly of dinuclear $[Zn_2(H_2O)_2(2,2'\text{-bipy})_2(2\text{-MGL})_2]$ molecules via intermolecular $\pi\cdots\pi$ interaction and hydrogen bonding interactions (pink dashed lines).

and chelating O atoms hold the resulting chains together to generate 2-D layers parallel to (0 0 1), as illustrated in figure 1(b). The crystal structure is stabilized by weak interlayer C–H$\cdots\pi$ interactions from MGL to bipy.

3.2.2. $[Zn_2(phen)_2(H_2O)(MGL)_2]$ (2). The asymmetric unit of **2** contains one Zn^{2+}, one 2-methylglutarate anion, half an aqua ligand, and one 1,10-phenanthroline. As shown in figure 2(a), Zns are severely distorted octahedra defined by two nitrogens of one 1,10-phenanthroline and four oxygens from one water and three carboxylate

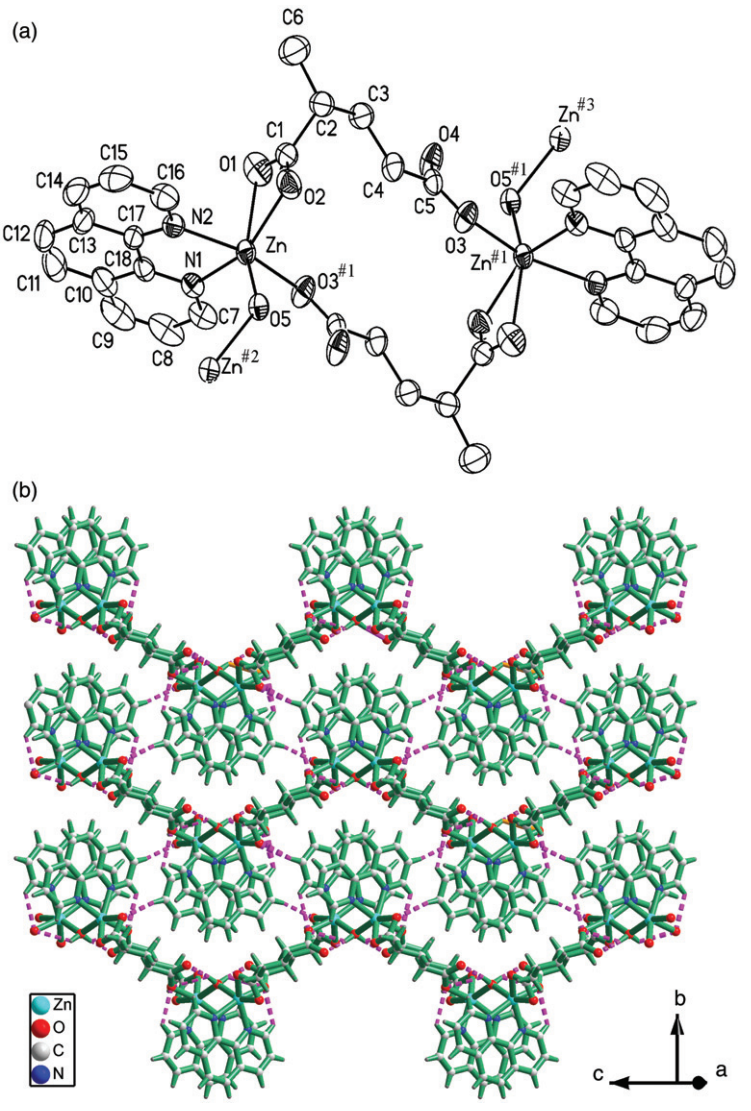

Figure 2. (a) The ORTEP view of the coordination environment of Zn along with the bridging of 2-methylglutarato and atomic labeling for **2**. The thermal ellipsoids are drawn at 45% probability (symmetry transformations used to generate equivalent atoms: #1: $-x, -y, -z$; #2: $-x, y, -z+1/2$, #3: $x, -y, z-1/2$). (b) Supramolecular assembly of the dinuclear $[Zn_2(H_2O)(phen)_2(2\text{-MGL})_2]$ *via* inter- and intramolecular hydrogen bonding (pink dashed lines).

oxygens (O1, O2, O3#1; #1 = $-x, -y, -z$) of a pair of MGL anions assuming R- and S-configurations. Zn–O bond distances fall in the range 2.046–2.330 Å, averaged to 2.153 Å, a little longer than the Zn–N bond distance (average: 2.148 Å). The *trans* and *cis* angles about Zn are from 150.5 to 166.0° and 58.0 to 113.2°, respectively (see the "Supplementary material": table 3). The bonding values are similar to those observed in **1**. The MGL anions exhibit the same coordination configurations and modes as in **1**. A pair of MGL anions in R- and S-configurations bridge two Zns to form a centrosymmetric binuclear complex with a rhombus ring (figure 2a), and the binuclear

units form 1-D zigzag chain formulated as $^{1}_{\infty}$[Zn(phen)$(H_2O)_{2/2}$$(MGL)_{2/2}$] by sharing aqua ligands, each of which is crystallographically imposed by C_2 symmetry. The Zn···Zn distance separated by sharing aqua is 3.834 Å, and the Zn···Zn distance bridged by (RS)-2-MGL is 7.876 Å, shorter than the corresponding value in **1**. Comparison with **1** indicates that substitution of phen for bipy results in partial loss of aqua ligands in dinuclear units from **1** to **2**, and condensation of dinuclear molecules in **1** to 1-D chains in **2**. The phen ligands on two Zns sharing the aqua ligand orient parallel due to crystallographic imposition of a two-fold axis, and the mean interplanar distance of 3.36 Å suggests substantial intrachain $\pi\cdots\pi$ stacking interactions [30]. Aqua donates hydrogen to O4 to form intrachain hydrogen bonds. The resulting chains extend infinitely along the [0 0 1] direction and assemble into 2-D layers parallel to (1 0 0) (figure 2b) due to weak C–H···O hydrogen bonds between phen ligands and chelating carboxylate oxygens. The 2-D layers are closely-packed in ABAB··· sequence so that each layer is shifted by $(1/2)(\vec{b} + \vec{c})$ with respect to the neighbor, which is advantageous for interlayer $\pi\cdots\pi$ stacking of adjacent phen ligands from different layers.

3.2.3. [Cd(bipy)(H_2O)(MGL)]·3H_2O (3). The asymmetric unit of **3** contains one Cd^{2+}, one bipy, one aqua, one 2-methylglutarate, and three lattice waters. As demonstrated in figure 3(a), the Cd is seven-coordinate by two nitrogens of bpy and five oxygens of one aqua and a pair of MGL anions in R- and S-configuration. The coordination geometry around Cd is a distorted monocapped octahedron. The Cd–O bond distances range from 2.291 to 2.589 Å (average: 2.388 Å), and the Cd–N bond distances are 2.342 and 2.349 Å. The O–Cd–O and O–Cd–N angles fall in the range 51.41–167.10° and 70.24–157.20° (see the "Supplementary material": table 4). Different from **1** and **2**, each carboxylate of twisted MGL anions in **3** chelates one metal ion as a *bis*-chelating ligand. The R- and S-conformational MGL ligands alternatively bridge the CdN_2O_5 polyhedra to generate polymeric chains formulated as $^{1}_{\infty}$[Cd(bipy)$(H_2O)$$(MGL)_{2/2}$] along the direction of [1 0 $\bar{1}$] with 2,2′-bipyridine located at both sides with distance of the adjacent Cd atoms 8.575 Å. The 2,2′-bipyridines have interchain $\pi\cdots\pi$ stacking interactions (mean interplanar bipy-to-bipy distance: 3.48 Å), assembling the 1-D chains into 2-D layers parallel to (1 0 1) as shown in figure 3(b). The layers are stacked along the [0 1 0] direction and shifted by $(1/2)\vec{b}$ with respect to the neighbors, and arranged alternately in ABAB··· sequence. The lattice H_2O molecules are sandwiched between the resulting supramolecular layers. There exist three kinds of O–H···O hydrogen bonds (see the "Supplementary material": table 4): (1) the aqua ligand (O5) donates hydrogen to lattice H_2O molecules O7#1 and O8#3, (2) lattice water O7 is a hydrogen donor to O6, and (3) lattice water molecules are engaged in hydrogen bonds to carboxylate oxygen. Coordinated O5 and lattice water O6, O7, and O8 form a discrete "Z"-shaped tetrameric water cluster $(H_2O)_4$ *via* O–H···O hydrogen bonds with notation as D4 according to Infantes' classification [31]. Extensive hydrogen bonds make significant contribution to the stability of the structure.

3.2.4. [Cd(phen)(H_2O)(MGL)]·2H_2O (4). Complex **4** features 1-D polymeric coordination chain formulated as $^{1}_{\infty}$[Cd(phen)$(H_2O)$$(MGL)_{2/2}$], extremely similar to **3** with 1,10-phenanthroline instead of 2,2′-bipyridine. A pair of twisted MGL anions in both

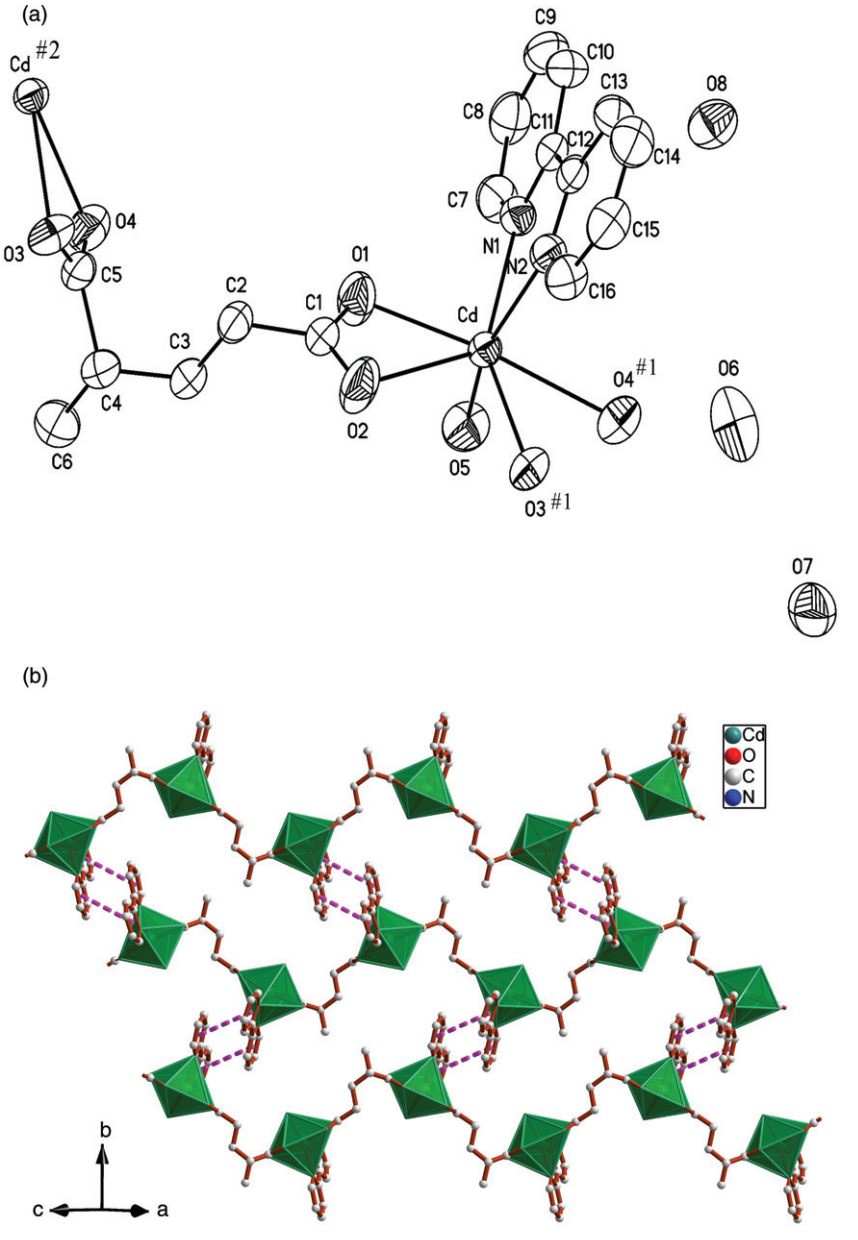

Figure 3. (a) The ORTEP view of coordination environments of Cd with the bridging of 2-methylglutarato and atomic labeling for **3**. The thermal ellipsoids are drawn at 45% probability (symmetry transformations used to generate equivalent atoms: #1: $-1/2+x$, $1/2-y$, $1/2+z$; #2: $1/2+x$, $1/2-y$, $-1/2+z$). (b) The 2-D layer of **3** is comprised by 1-D zigzag chains and $\pi\cdots\pi$ stacking interactions (pink dashed lines).

R- and S-configurations are *bis*-chelating ligands alternately bridging Cd^{2+} at 8.582 Å, almost equal to the corresponding value in **3**. The Cd in **4** is coordinated by two nitrogens of 1,10-phenanthroline and five oxygens of one aqua ligand and a pair of MGL anions (figure 4a). The coordination sphere about Cd is a distorted monocapped octahedral geometry with Cd–N bond distances of 2.373 and 2.354 Å, slightly longer

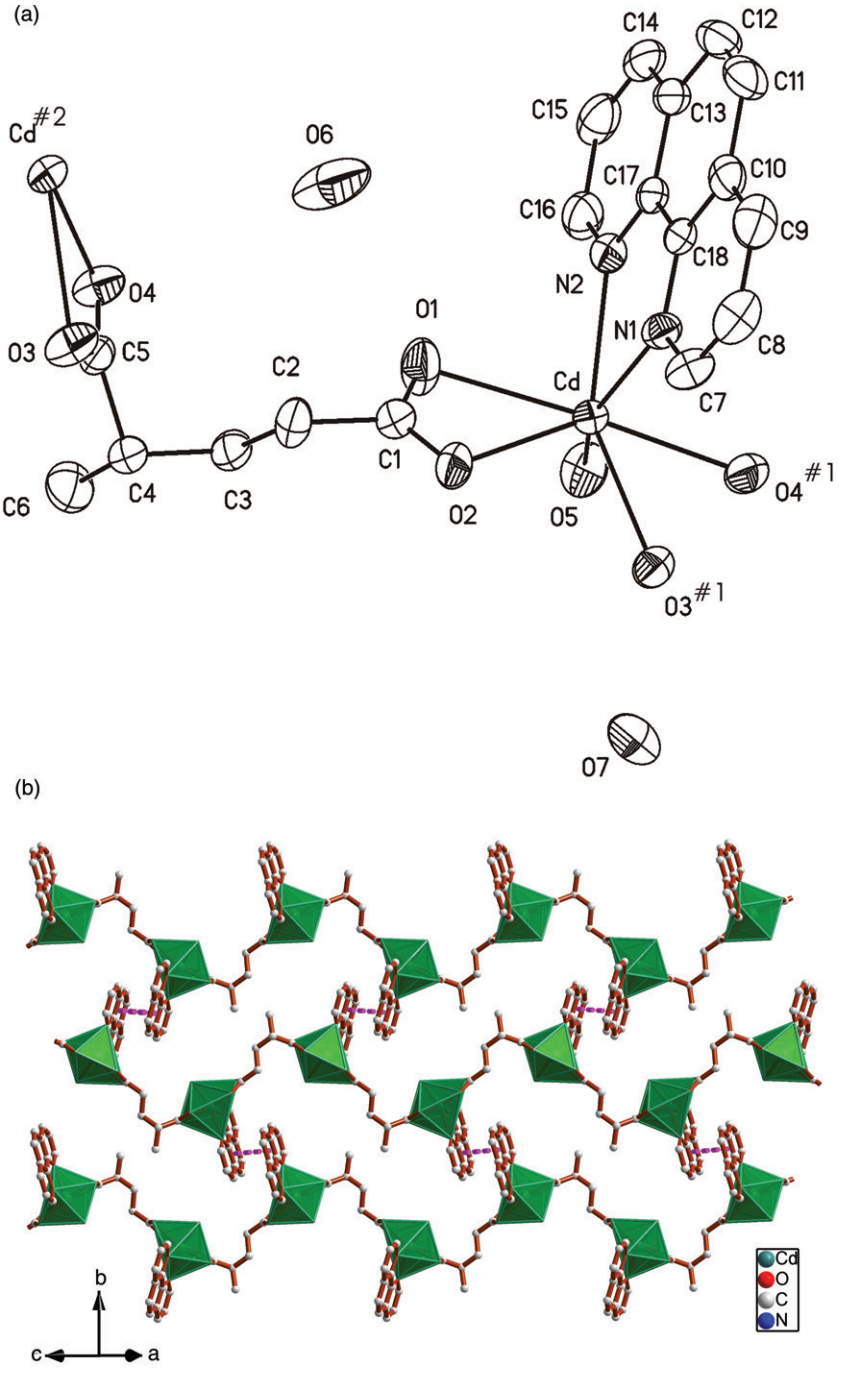

Figure 4. (a) The ORTEP view of coordination of Cd with the bridging of 2-methylglutarato and the atomic labeling for **4**. The thermal ellipsoids are drawn at 45% probability (symmetry transformations used to generate equivalent atoms: #1: $-1/2+x$, $1/2-y$, $1/2+z$, #2: $1/2+x$, $1/2-y$, $-1/2+z$). (b) The 2-D layer of **4** is comprised by chains along the direction of [1 0 $\bar{1}$] and $\pi\cdots\pi$ stacking interactions (pink dashed lines).

than the corresponding values in **3**. The Cd–O distances fall in the range 2.306–2.603 Å and O–Cd–O and O–Cd–N angles are 52.06–159.10 and 77.73–150.92°, respectively (see the "Supplementary material": table 5), normal, as reported [31, 32]. The 1-D polymeric chains $^{1}_{\infty}$[Cd(phen)(H_2O)($MGL)_{2/2}$] run parallel to [1 0 $\bar{1}$] with $\pi\cdots\pi$ stacking interactions (mean interplanar phen-to-phen distance: 3.37 Å) between the closest 1,10-phenanthroline ligands of neighboring chains (figure 4b). Such $\pi\cdots\pi$ stacking interactions are responsible for supramolecular assembly of the polymeric chains into 2-D layers parallel to (1 0 1). Similar to **3**, the layers are stacked along the [010] direction and shifted by $(1/2)\vec{b}$ with respect to the neighbor, and arranged alternately in ABAB$\cdots$ sequence along the direction of [1 0 1]. The two crystallographically distinct lattice water molecules are located between the layers and serve as hydrogen bond acceptors from the aqua ligand, and simultaneously as H donors to carboxylate oxygen (see the "Supplementary material": table 5); the intermolecular hydrogen bonds contribute to stabilizing the 3-D architecture.

3.3. *IR spectra*

Infrared spectra of **1**–**4** (figure S3) show characteristic broad bands centered at 3421, 3421, 3384, and 3420 cm^{-1}, respectively, due to OH stretch of water [33]. In comparison to IR spectrum of (RS)-2-methylglutaric acid (H_2MGL) (figure 5), weak absorptions in the range 2960–2967 cm^{-1} could be attributed to stretch of methyl of the dicarboxylate. The asymmetric stretch of $-CO_2$ is at 1558, 1556, 1558, and 1556 cm^{-1}, respectively, for **1**–**4**, and the symmetric stretching vibration at 1417, 1413, 1421, and 1405 cm^{-1}. The differences $\Delta\nu = [\nu(CO_2)_{asym} - \nu(CO_2)_{sym}]$ of 141, 143, 137, and 151 cm^{-1}, respectively, are clearly different from those expected based on carboxylate coordination modes derived from single X-ray crystal structure analyses [33]. The absorption bands at 766, 854, 771, and 727 cm^{-1}, respectively, are from out-of-plane C–H bending of aromatic rings of 2,2′-bipyridine and 1,10-phenanthroline.

3.4. *Fluorescent properties*

Figure 5 shows emission spectra of **1**–**4** in solid state at room temperature. Upon excitation at 247 nm, **1** displays intense photoluminescence with an emission maximum at *ca* 364 nm, and **2** at 377 and 391 nm. When illuminated at 245 and 244 nm, **3** exhibits an emission peak at 366 nm with a shoulder at 384 nm and **4** shows an emission at 383 nm. Zn(II) and Cd(II) coordination complexes exhibit ligand-to-ligand charge-transfer (LLCT) and ligand-to-metal charge-transfer (LMCT) [34]. The emission bands for **1** and **3** are similar to those for bipy [35, 36], but the emission intensity is stronger, suggesting that coordination enhances the fluorescent emission of bipy. Accordingly, the fluorescent emission bands can be assigned to a $\pi \rightarrow \pi^*$ transition of bipy as a LLCT [34–37]. In comparison with emission bands at 365 and 388 nm for free phen [38], the intensity of fluorescent emissions for **2** and **4** are much stronger for the LLCT due to the $\pi \rightarrow \pi^*$ transition on phen. The redshift of emission bands is possibly due to $\pi\cdots\pi$ stacking interactions between phen ligands, decreasing the energy gap between HOMO and LUMO [34].

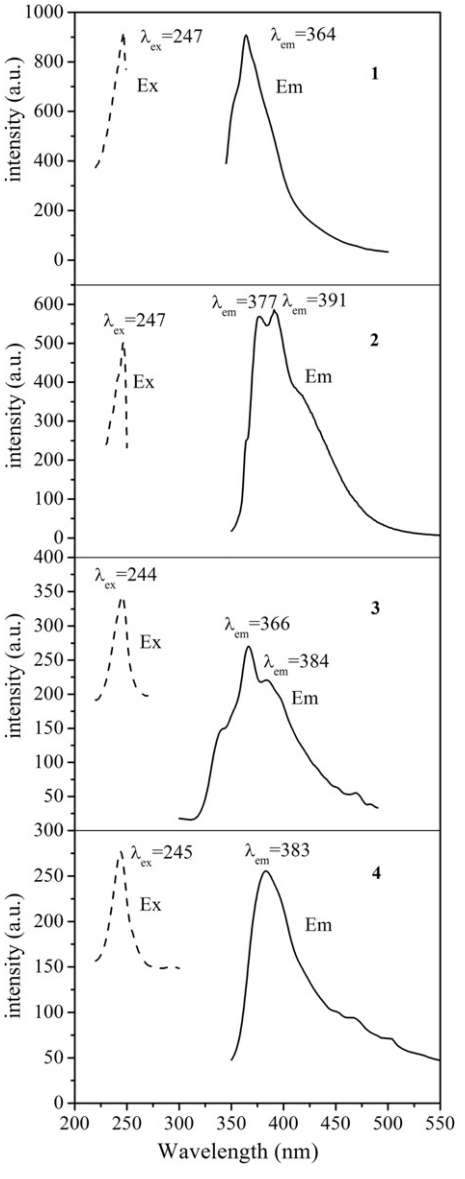

Figure 5. Solid-state emission spectra of the complexes at room temperature.

4. Conclusions

Self-assembly of Zn(II) and Cd(II), racemic (RS)-2-methylglutarate (MGL) in the presence of 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) in aqueous solution at 50°C produced $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ (**1**), $[Zn_2(phen)_2(H_2O)(MGL)_2]$ (**2**), $[Cd(bipy)(H_2O)(MGL)]\cdot 3H_2O$ (**3**), and $[Cd(phen)(H_2O)(MGL)]\cdot 2H_2O$ (**4**). The racemic (RS)-2-methylglutarato bridged dinuclear $[Zn_2(bipy)_2(H_2O)_2(MGL)_2]$ molecules in **1**, ribbon-like zigzag chains $^1_\infty[Zn(phen)(H_2O)_{2/2}(MGL)_{2/2}]$ in **2**, polymeric chains $^1_\infty[Cd(bipy)(H_2O)(MGL)_{2/2}]$ and $^1_\infty[Cd(phen)(H_2O)(MGL)_{2/2}]$ in **3** and **4**, which

assemble *via* $\pi\cdots\pi$ stacking interactions to supramolecular architectures. Comparing the structures of **1** and **2** show neutral ligands may have a significant effect on dimensionality of the resulting structures. Complexes **3** and **4** have similar structures due to the coordination mode of (RS)-2-methylglutarate. These complexes are the first examples using the (RS)-2-methylglutaric acid as bridging ligand to build coordination polymers. The fluorescence spectra of **1**–**4** exhibit substantial LLCT $\pi \rightarrow \pi^*$ transitions.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC 700178 ($C_{32}H_{36}N_4O_{10}Zn_2$), CCDC 700177 ($C_{36}H_{34}N_4O_9Zn_2$), CCDC 700180 ($C_{16}H_{24}CdN_2O_8$), and CCDC 700179 ($C_{18}H_{22}CdN_2O_7$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk). The XRD powder diffraction pattern, IR spectrum, TG–DTA curves, and additional crystallographic data of **1**, **2**, **3**, and **4** are available free of charge *via* the internet at http://www.tandf.co.uk

Acknowledgments

This project was supported by the Expert Project of Key Basic Research of the Ministry of Science and Technology of China (grant No. 2003CCA00800), Science and Technology Department of Zhejiang Province (grant No. 2006C21105), Education Department of Zhejiang Province, and the Ningbo Municipal Natural Science Foundation (grant No. 2006A610061). Honest thanks are also extended to K.C. Wong Magna Fund in Ningbo University.

References

[1] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[2] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
[3] H.D. Selby, B.K. Roland, Z. Zheng. *Acc. Chem. Res.*, **36**, 933 (2003).
[4] S. Leininger, B. Olenyuk, P.J. Stang. *Chem. Rev.*, **100**, 853 (2000).
[5] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **425**, 705 (2003).
[6] N.J. Long. *Angew. Chem. Int. Ed. Engl.*, **34**, 21 (1995).
[7] Y.-T. Wang, H.-H. Fan, H.-Z. Wang, X.-M. Chen. *Inorg. Chem.*, **44**, 4148 (2005).
[8] S.D. Bella, I. Fragalà, I. Ledoux, M.A. Diaz-Garcia, T.J. Marks. *J. Am. Chem. Soc.*, **119**, 9550 (1997).
[9] L. Cheng, W.-X. Zhang, B.-H. Ye, J.-B. Lin, X.-M. Chen. *Eur. J. Inorg. Chem.*, 2668 (2007).
[10] A.M. Kirillov, Y.Y. Karabach, M. Haukka, M.F.C. Guedes da Silva, J. Sanchiz, M.N. Kopylovich, A.J.L. Pombeiro. *Inorg. Chem.*, **47**, 162 (2008).
[11] D.-W. Fu, Y.-M. Song, G.-X. Wang, Q. Ye, R.-G. Xiong, T. Akutagawa, T. Nakamura, P.W.H. Chan, S.D. Huang. *J. Am. Chem. Soc.*, **129**, 5346 (2007).
[12] Y.-Z. Tang, X.-F. Huang, Y.-M. Song, P.W.H. Chan, R.-G. Xiong. *Inorg. Chem.*, **45**, 4868 (2006).
[13] D.-W. Fu, W. Zhang, R.-G. Xiong. *Dalton Trans.*, 3946 (2008).
[14] M.-H. Zeng, M.-C. Wu, H. Liang, Y.-L. Zhou, X.-M. Chen, S.-W. Ng. *Inorg. Chem.*, **46**, 7241 (2007).

[15] N. Hao, E.-H. Shen, Y.-G. Li, E.-B. Wang, C.-W. Hu, L. Xu. *Eur. J. Inorg. Chem.*, 4102 (2004).
[16] Y.-Y. Liu, J.-F. Ma, J. Yang, J.-C. Ma, Z.-M. Su. *Cryst. Eng. Comm.*, **10**, 894 (2008).
[17] K. Hanson, N. Calin, D. Bugaris, M. Scancella, S.C. Sevov. *J. Am. Chem. Soc.*, **126**, 10502 (2004).
[18] Y.-Q. Zheng, Z.-P. Kong. *J. Solid State Chem.*, **166**, 279 (2002).
[19] Y.-Q. Zheng, J. Sun, J.-L. Lin. *Z. Anorg. Allg. Chem.*, **628**, 1397 (2002).
[20] Y.-Q. Zheng, J.-L. Lin, Z.-P. Kong. *Inorg. Chem.*, **43**, 2590 (2004).
[21] E.-B. Ying, Y.-Q. Zheng, H.-J. Zhang. *J. Mol. Struct.*, **693**, 73 (2004).
[22] Y.-Q. Zheng, W.-H. Liu, J.-L. Lin. *Z. Anorg. Allg. Chem.*, **628**, 620 (2005).
[23] Y.-Q. Zheng, E.-B. Ying. *Polyhedron*, **24**, 397 (2005).
[24] J.-G. Pan, G.-J. Zhang, Y.-Q. Zheng, J.L. Lin, W. Xu. *J. Cryst. Growth*, **308**, 89 (2007).
[25] C. Qin, X.-L. Wang, E.-B. Wang, C.-W. Hu, L. Xu. *Inorg. Chim. Acta*, **357**, 3683 (2004).
[26] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Refinement, and SHELXL-97, Program for Crystal Structure Solution*, Göttingen University, Germany (1997).
[27] D.-Y. Wei, Y.-Q. Zheng, J.-L. Lin. *Z. Anorg. Allg. Chem.*, **628**, 2005 (2002).
[28] Y.-Q. Zheng, W.-H. Liu, J.-L. Lin, L.-Y. Gu. *Z. Anorg. Allg. Chem.*, **628**, 829 (2002).
[29] Y.-Q. Zheng, W.-H. Liu, J.-L. Lin. *Z. Kristallgr. NCS.*, **217**, 199 (2002).
[30] C. Janiak. *J. Chem. Soc., Dalton Trans.*, 3885 (2000).
[31] X.-X. Xu, Y. Lu, E. Wang, Y. Ma, X. Bai. *Inorg. Chim. Acta.*, **360**, 455 (2007).
[32] Y.-S. Song, B. Yan, Z.-X. Chen. *J. Solid State Chem.*, **179**, 4037 (2006).
[33] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, John Wiley & Sons, New York (1986).
[34] S.-L. Zheng, X.-M. Chen. *Aust. J. Chem.*, **57**, 703 (2004).
[35] K.-Y. Ho, W.-Y. Yu, K.-K. Cheung, C.-M. Che. *Chem. Commun.*, 2101 (1998).
[36] R.-X. Yuan, R.-G. Xiong, Y.-L. Xie, X.-Z. You. *Inorg. Chem. Commun.*, **4**, 384 (2001).
[37] K.-Y. Ho, W.-Y. Yu, K.-K. Cheung, C.-M. Che. *J. Chem. Soc., Dalton Trans.*, 1581 (1999).
[38] X. Shi, G.-S. Zhu, Q.-R. Fang, G. Wu, G. Tian, R.-W. Wang, D.-L. Zhang, M. Xue, S.-L. Qiu. *Eur. J. Inorg. Chem.*, 185 (2004).