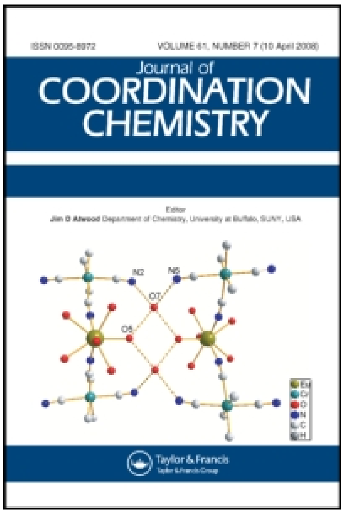

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structure, and thermal properties of 3-D coordination polymers constructed from asymmetrical carboxylates

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To cite this Article Xu, Xinxin , Liu, Xiaoxia , Sang, Xiaoguang and Wang, Enbo(2010) 'Synthesis, structure, and thermal properties of 3-D coordination polymers constructed from asymmetrical carboxylates', Journal of Coordination Chemistry, 63: 17, 3060 — 3070, First published on: 22 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.503961

URL: http://dx.doi.org/10.1080/00958972.2010.503961

Journal of Coordination Chemistry
Vol. 63, No. 17, 10 September 2010, 3060–3070

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Synthesis, structure, and thermal properties of 3-D coordination polymers constructed from asymmetrical carboxylates

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(*Received 1 February 2010; in final form 21 May 2010*)

Three new coordination polymers constructed from asymmetric ligands were synthesized under hydrothermal conditions and characterized with single crystal X-ray analysis, infrared, and thermal gravimetric methods. Complex **1** exhibits a 3-D network constructed from rod-shaped secondary building units. Pyrimidine-4-carboxylic acid (bpa) was used as the starting material, but under hydrothermal conditions bpa formed 2,2′-pyrimidine-4,4′-dicarboxylic acid (bpda) *in situ*, which further connected with Pb. 3-D two-fold interpenetration of complex **2** was obtained by the similar method as described for **1**, except that $Cd(NO_3)_2 \cdot 6H_2O$ was used instead of $Pb(NO_3)_2 \cdot 6H_2O$ to react with bpa. Complex **3** shows a three-connected 3-D network. Furthermore, the photoluminescence properties of **1** and **2** were studied.

Keywords: Coordination polymer; Asymmetrical carboxylates; 3-D network; Photoluminescence property

1. Introduction

Design and synthesis of coordination polymers has become a flourishing research area owing to novel topologies and potential applications in magnetism, ion exchange, catalysis, gas separation, and electrical conductivity [1–9]. For crystal engineering, coordination polymers with desired properties require careful selection of the organic ligands [10], with polymers possessing various physical properties and diverse structural features arising from different types of ligands [11, 12]. Carboxylates have been widely used for the construction of coordination polymers [13–16]. Despite many coordination polymers synthesized by symmetrical carboxylates, studies on asymmetrical carboxylates are less reported [17–19]. This may be because asymmetry of the ligand brings difficulty in crystallization [20]. Through careful controlling of the reaction conditions, coordination polymers with various structural features have been synthesized from asymmetrical carboxylates [21–24]. The aim of our research is to synthesize new

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.503961

coordination polymers from asymmetrical carboxylates. Among various asymmetrical carboxylates, pyrimidine-4-carboxylic acid (bpa) and pyrazine-3-carboxylic acid (pza) are good candidates for coordination polymer for several reasons: (1) The asymmetry allows prechiral or asymmetrical ligands providing an effective way to construct acentric materials. (2) They are rigid ligands with oxygen and nitrogen donors on opposite sides, enabling them to act as a linear bridge. (3) They are good candidates for developing molecular building blocks and may yield a new generation of coordination polymers with different topologies [25].

Due to their special electron configuration and radius, Pb(II), Cd(II), and Hg(I) exhibit variable coordination numbers and geometries [26–28]. There has been a growing interest in the coordination chemistry of Pb(II), Cd(II), and Hg(I), not only owing to their biological activities but also because they possess flexible coordination modes, which provide unique opportunities for the construction of coordination polymers [29]. Some coordination polymers possessing interesting photochemical and physical properties have been synthesized [30, 31].

Herein, we report the synthesis and characterization of three new 3-D coordination polymers $[Pb(bpdc)]_n$ (**1**), $[Cd(bpa)_2H_2O]_n$ (**2**), and $[Hg_2(pza)_2]_n$ (**3**) (bpdc = 2,2′-pyrimidine-4,4′-dicarboxylic acid, bpa = pyrimidine-4-carboxylic acid, pza = pyrazine-3-carboxylic acid). During the synthesis of **1**, with pyrimidine-4-carboxylic acid as the starting material, *in situ* reaction produced 2,2′-pyrimidine-4,4′-dicarboxylic acid, which further connected with Pb(II) ion. The photoluminescence properties of **1** and **2** are reported.

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were reagent grade and used without purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. FT/IR spectra were recorded from 4000 to 400 cm^{-1} on an Alpha Centaut FTIR spectrophotometer using KBr pellets. Thermal gravimetric analyses (TGA) were performed on Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10°C min^{-1}. Photoluminescence spectra were measured using a FL-2T2 instrument (SPEX, USA) with 450-W xenon lamp monochromated by double grating (1200 gr/mu^{-1}). All measurements were performed at room temperature.

2.2. *Preparation of* 1

Complex **1** was prepared from a mixture of $Pb(NO_3)_2 \cdot 6H_2O$ (0.109 g, 0.25 mmol), pyrimidine-4-carboxylic acid (0.062 g, 0.50 mmol), and 8 mL H_2O with pH adjusted to 5 with 1 mol L^{-1} NaOH. The mixture was stirred, then placed in a Teflon-lined stainless steel bomb and heated to 160°C under autogenous pressure for 5 days. The reaction system was then cooled to room temperature during 24 h. Yellow crystals of **1** were obtained. Yield: 55% (based on Pb). Elemental Anal. Calcd (%): C, 26.61; H, 0.89; N, 12.41. Found (%): C, 26.55; H, 0.91; N, 12.49. IR (cm^{-1}): 3201(w), 1605(w), 1538(s), 1482(s), 1398(s), 833(m), 735(w), 523(w).

2.3. *Preparation of* 2

Complex **2** was prepared from a mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (0.086 g, 0.25 mmol), pyrimidine-4-carboxylic acid (0.062 g, 0.50 mmol), and 8 mL H_2O with pH adjusted to 5 with 1 mol L^{-1} NaOH. The mixture was stirred, placed in a Teflon-lined stainless steel bomb, and heated to 160°C under autogenous pressure for 5 days. The reaction system was then cooled to room temperature during 24 h. Yellow crystals of **2** were obtained. Yield: 73% (based on Cd). Elemental Anal. Calcd (%): C, 31.89; H, 2.14; N, 14.88. Found (%): C, 31.75; H, 2.21; N, 14.79. IR (cm^{-1}): 3267(s), 3155(s), 1664(m), 1567(s), 1512(s), 1379(s), 841(m), 747(w), 655(w).

2.4. *Preparation of* 3

Complex **3** was prepared from a mixture of $Hg_2(NO_3)_2 \cdot H_2O$ (0.070 g, 0.25 mmol), pyrazine-3-carboxylic acid (0.062 g, 0.50 mmol) and 8 mL H_2O with pH adjusted to 4 with 1 mol L^{-1} NaOH. The mixture was stirred for 25 min, placed in a Teflon-lined stainless steel bomb, and heated to 150°C under autogenous pressure for 4 days. The reaction system was then cooled to room temperature during 24 h. Colorless crystals of **3** were obtained. Yield: 67% (based on Hg). Elemental Anal. Calcd (%): C, 18.55; H, 0.93; N, 8.65. Found (%): C, 18.66; H, 0.91; N, 8.72. IR (cm^{-1}): 3320(w), 1518(s), 1369(s), 1255(w), 1109(w), 866(m), 544(w), 413(w).

2.5. *X-ray crystallography*

Single crystals of **1–3** were glued on glass fibers. Data were collected on a Bruker AXS SMART APEX II CCD diffractometer at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL 97 crystallographic software package [32, 33]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogens were placed in geometrically calculated positions; oxygen-bound hydrogen atoms were located in the difference Fourier maps and kept in that position. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Structure description*

Single-crystal X-ray analysis reveals that **1** crystallizes in the orthorhombic system with $P\ mn2_1$ space group. There exists only one crystallographically independent Pb in the fundamental unit. Pb connects with two oxygens and two nitrogens from bpda with Pb–O distance of 2.379 Å and Pb–N distance of 2.690 Å. If weak Pb–O interactions in the range 2.830–2.924 Å are considered, Pb1 can be described as eight-coordinate as shown in figure 1(a) [34–36]. Lead coordination as holodirected refers to complexes in which the Pb–ligand bonds are directed throughout the surface of coordination sphere, while hemidirected refers to those in which Pb–ligand bonds are directed only to a part of the coordination sphere; Pb compounds are hemidirected for low

Table 1. Crystal data and structure refinement for **1**–**3**.

	1	**2**	**3**
Formula	$C_{10}H_4N_4O_4Pb$	$C_{10}H_8N_4O_5Cd$	$C_{10}H_6N_4O_4Hg_2$
Formula weight	451.36	376.60	647.37
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P mn2₁*	*P bca*	*C c*
Unit cell dimensions (Å, °)			
a	13.619(3)	11.483(2)	9.2022(18)
b	4.2558(9)	12.083(2)	10.793(2)
c	10.323(2)	17.512(4)	14.815(3)
β	90	90	90.17(3)
Volume (Å^3), *Z*	598.3(2), 2	2429.9(8), 8	1471.4(5), 4
Calculated density (g cm^{-3})	2.505	2.059	2.922
F(000)	412	1472	1144
Reflections collected	5483	22,067	5043
Reflections unique	1434	2765	2168
R (int)	0.0502	0.0376	0.0380
Completeness	99.7%	98.9%	95.6%
S	1.047	1.015	1.039
R_1 [$I > 2\sigma(I)$]	0.0318	0.0287	0.0441
wR_2 [$I > 2\sigma(I)$]	0.0873	0.1122	0.1240
R_1 (all data)	0.0333	0.0341	0.0464
wR_2 (all data)	0.0896	0.1212	0.1270

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

1			
Pb(1)–O(1)#1	2.379(8)	Pb(1)–O(1)#2	2.379(8)
Pb(1)–N(2)	2.690(10)	Pb(1)–N(2)#3	2.690(10)
O(1)#1–Pb(1)–O(1)#2	80.0(4)	O(1)#1–Pb(1)–N(2)	74.5(3)
O(1)#1–Pb(1)–N(2)#3	108.0(3)	O(1)#2–Pb(1)–N(2)	108.0(3)
O(1)#2–Pb(1)–N(2)#3	74.5(3)	N(2)#3–Pb(1)–N(2)	53.2(5)
2			
Cd(1)–O(1)#1	2.640(3)	Cd(1)–O(2)#1	2.278(3)
Cd(1)–O(4)	2.247(2)	Cd(1)–OW1	2.381(3)
Cd(1)–N(2)	2.358(3)	Cd(1)–N(4)#2	2.310(3)
O(2)#1–Cd(1)–N(2)	96.78(10)	O(2)#1–Cd(1)–N(4)#2	147.54(9)
O(2)#1–Cd(1)–O(1)#1	52.87(9)	O(4)–Cd(1)–O(1)#1	133.21(9)
O(4)–Cd(1)–O(2)#1	80.55(9)	O(4)–Cd(1)–N(2)	102.93(11)
O(4)–Cd(1)–N(4)#2	127.58(10)	O(4)–Cd(1)–OW1	91.40(10)
N(2)–Cd(1)–O(1)#1	88.32(10)	N(2)–Cd(1)–OW1	165.63(10)
N(4)#2–Cd(1)–OW1	77.97(10)	N(4)#2–Cd(1)–N(2)	92.21(10)
N(4)#2–Cd(1)–O(1)#1	96.52(9)	OW1–Cd(1)–O(1)#1	82.47(10)
3			
Hg(1)–O(1)	2.704(16)	Hg(1)–N(1)	2.007(16)
Hg(1)–N(4)#1	2.136(15)	Hg(2)–O(2)#2	2.699(15)
Hg(2)–N(2)	2.053(16)	Hg(2)–N(3)	2.070(15)
O(1)–Hg(1)–N(1)	78.5(7)	O(1)–Hg(1)–N(4)#1	101.5(7)
N(1)–Hg(1)–N(4)#1	179.1(6)	O(2)#2–Hg(2)–N(2)	72.8(5)
O(2)#2–Hg(2)–N(3)	109.3(6)	N(2)–Hg(2)–N(3)	176.7(8)

Symmetry transformations used to generate equivalent atoms for **1**: 1: $-x+3/2$, $-y+1$, $z-1/2$; #2: $x+1/2$, $-y+1$, $z-1/2$; #3: $-x+2$, y, z; for **2**: #1: $-x$, $y+1/2$, $-z+1/2$; #2: $x+1/2$, $-y+3/2$, $-z$; for **3**: #1: $x-1$, $-y+1$, $z-1/2$; #2: $x+1/2$, $y+1/2$, z.

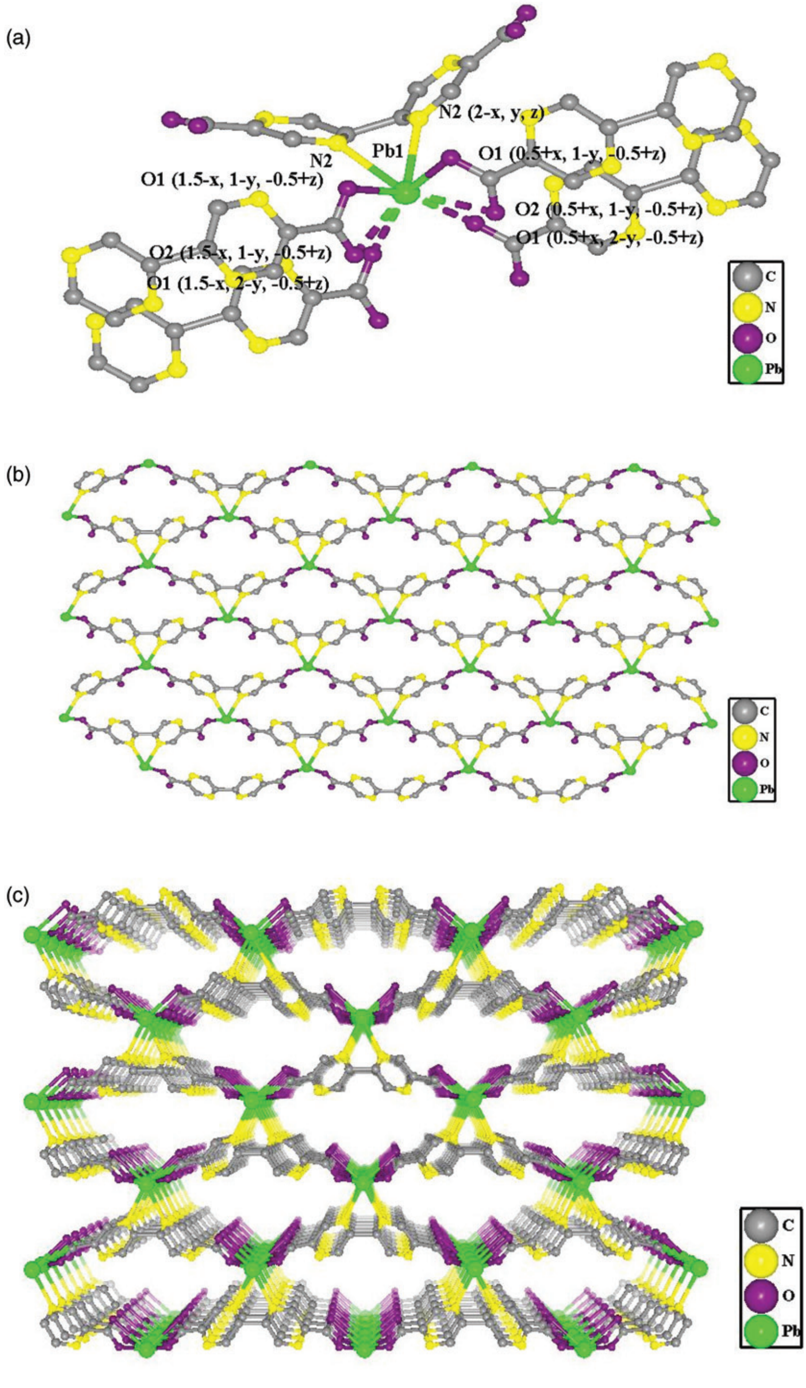

Figure 1. (a) The fundamental unit of **1**. (b) The 2-D layer structure of **1**. (c) The 3-D network of **1**.

coordination numbers (2–5) and holodirected for high coordination numbers (8–10). Complex **1** is hemidirected Pb coordinates with the coordination number of eight [37]. Two carboxylates and two nitrogens both connect with Pb. Based on such linking, Pb connects with four bpda ligands resulting in 2-D (4,4) type topology layer structure of **1** as shown in figure 1(b). Adjacent Pb's are connected by carboxylates from bpda and form 1-D "rod-shaped" secondary building units (SBUs). Furthermore, the organic ligands link the neighboring "rod-shaped" SBUs together resulting in the 3-D network as shown in figure 1(c).

The structure of **2** has also been established. There exists only one crystallographically independent Cd in the fundamental unit. Cd(1) is ligated to three carboxylate oxygens and two nitrogens from bpa ligands, the last coordination site is occupied by water resulting in octahedral coordination (figure 2a). There exist two kinds of bpa ligands in **2**, in the first type, the carboxylate chelates while in the second type, the carboxylate group is monodentate. Cd links with four bpa ligands as a four connected knot. Adjacent Cd's are connected by bpa ligands forming a 3-D network with diamond topology as shown in figure 2(b). The most interesting feature of **2** is that two such individual 3-D networks are connected and form a two-fold interpenetration framework as shown in figure 2(c).

In synthesis of **1**, bpa *in situ* reaction formed bpda. If $Cd(NO_3)_2 \cdot 6H_2O$ was used instead of $Pb(NO_3)_2 \cdot 6H_2O$ to react with bpa, we got **2** with bpa coordinating to Cd. This kind of *in situ* carbon–carbon coupling reaction had been reported and can be attributed to the catalysis of metal ions [38, 39].

Complex **3** also exhibits a 3-D network with two crystallographically independent Hg's and two paz ligands in the fundamental unit (figure 3a). Two crystallographically independent paz ligands adopt the same coordination. The carboxylate of paz bridges and two nitrogens from the pyrazine ring coordinate with Hg. Hg(1) connects with two carboxylate oxygens and two nitrogens from pyrazine-3-carboxylate with Hg(1)–O(1) = 2.708 Å, Hg(1)–O(4) = 2.862 Å, Hg(1)–N(1) = 2.007 Å, Hg(1)–N(4) = 2.136 Å. Hg(2) adopts the same kind of coordination as Hg(1), but with different bond lengths and angles (Hg(2)–O(2) = 2.699 Å, Hg(2)–O(3) = 2.638 Å, Hg(2)–N(2) = 2.053 Å, Hg(2)–N(3) = 2.070 Å). Hg(1) connects with two paz ligands forming $Hg(paz)_2$, and $Hg(paz)_2$ connects with three Hg(2); at the same time, each Hg(2) connects with three $Hg(paz)_2$ units, defining two kinds of three-connected nodes. Each three-connected node is further linked to three nearest neighbors, resulting in a unique three-connected, 3-D framework as shown in figure 3(b) and (c). Inner molecular π–π interactions exist along the *b*-axis, with the distances of neighboring pyrazine rings from 3.59 to 3.67 Å.

3.2. *IR spectroscopy*

For **1**, absorption peaks at 1538 cm^{-1} and 1482, 1398 cm^{-1} display the asymmetric and symmetric vibrations, respectively; the separations (Δ) between γ_{asym} (CO_2) and γ_{sym} (CO_2) of 84 and 140 cm^{-1} indicate the presence of chelating and bridging coordination. The IR spectrum of **2** shows the absorption peaks at 1567 cm^{-1} and 1512, 1379 cm^{-1} with Δ values of 133 and 188 cm^{-1}, in agreement with the result of single crystal analysis. The IR spectrum of **3** shows characteristic bands of carboxyl at 1518 cm^{-1} for the antisymmetric and 1369 cm^{-1} for symmetric stretch with Δ of 149 cm^{-1}, indicating bridging paz.

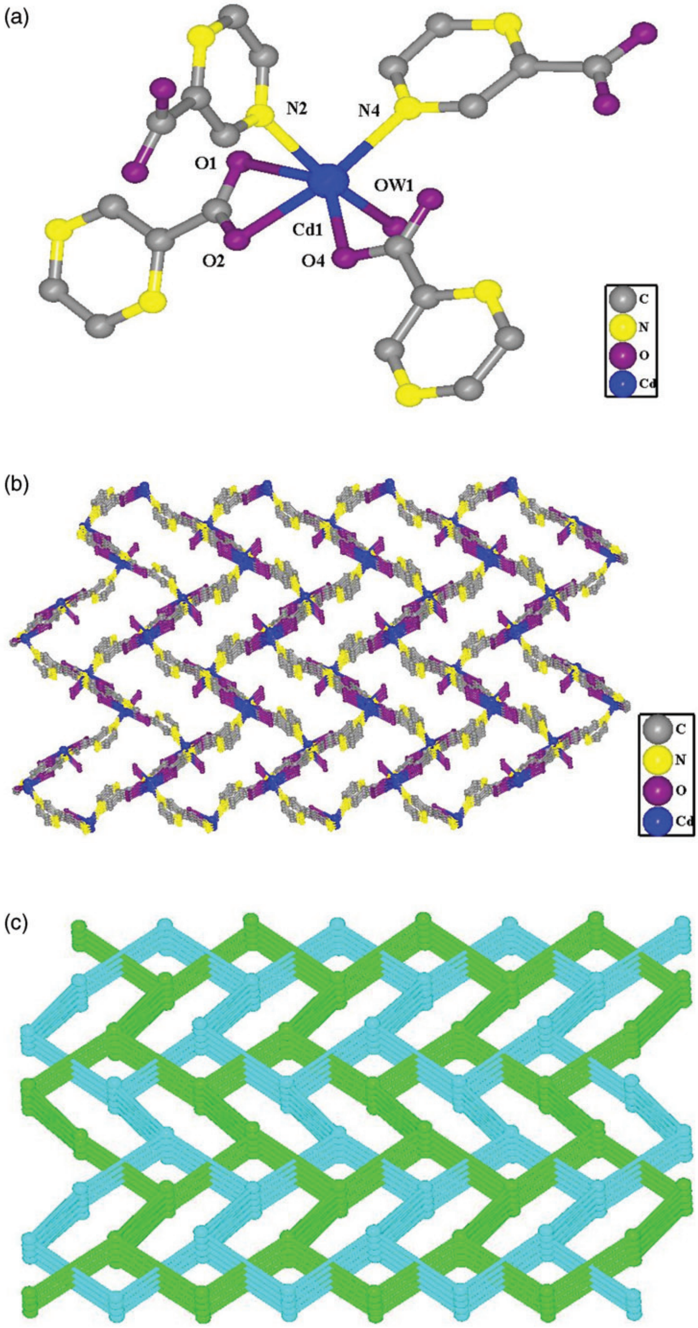

Figure 2. (a) The fundamental unit of **2**. (b) The 3-D network of **2**. (c) The schematic representation of two-fold interpenetration network of **2**.

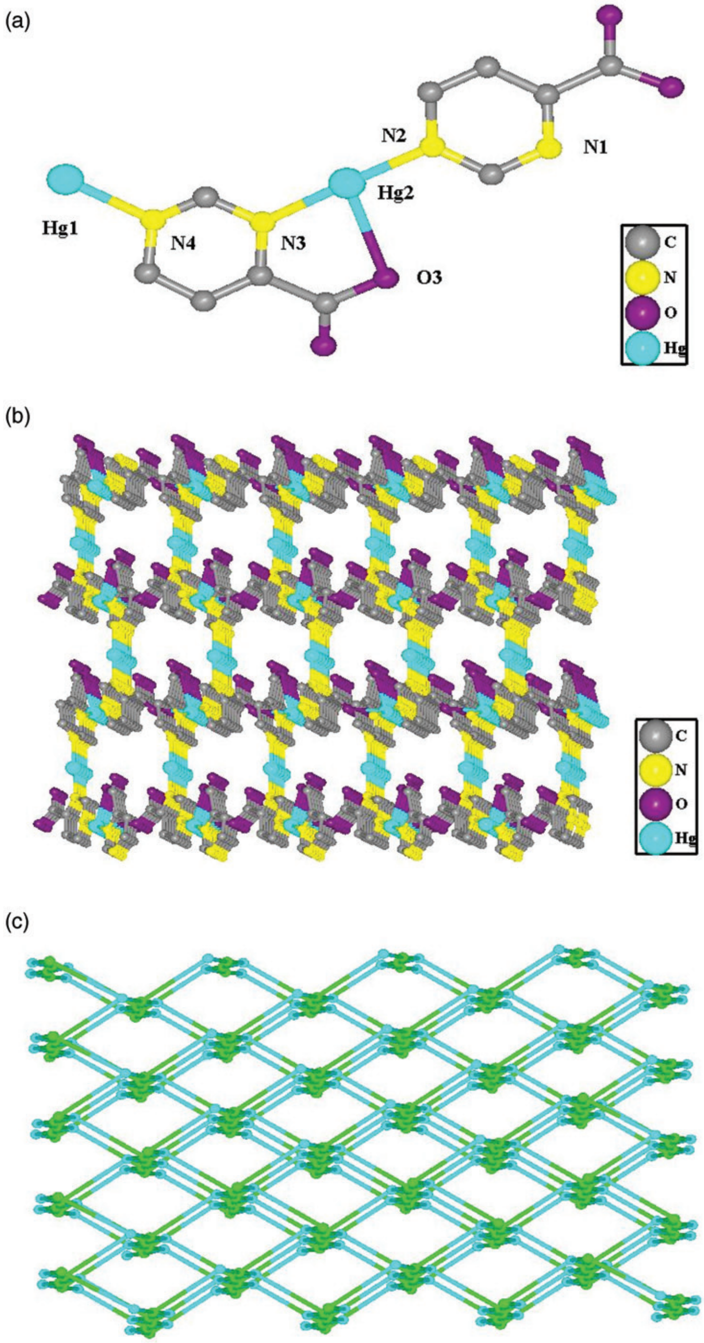

Figure 3. (a) The fundamental unit of **3**. (b) The 3-D network of **3**. (c) The schematic representations of the topologies of **3**.

3.3. *Thermal stability property*

In order to examine the stabilities of **1–3**, TGA were carried out in nitrogen from 30°C to 800°C as shown in figure S1(a), 1(b), and (c). For **1**, the thermal gravimetric curve shows one-step weight loss of 54.21% at 335–447°C corresponding to decomposition of organic ligands (Calcd 54.09%). For **2**, the thermal gravimetric curve shows weight loss of 4.81% at 144–179°C due to loss of water (Calcd 4.78%). Over the range 316–428°C, weight loss of 65.29% corresponds to the decomposition of organic ligands (Calcd 65.37%). Complex **3** also displays one-step weight loss (37.95%) from 311°C to 406°C, attributed to the loss of organic molecules (Calcd 38.03%).

3.4. *Photoluminescence property*

Photoluminescence properties of **1** and **2** in the solid state at room temperature are shown in figure 4. Complexes **1** and **2** exhibit photoluminescence with emission maxima at *ca* 432 and 419 nm upon excitation at 325 and 305 nm, respectively. According to previous reports, these emission bands could be assigned to ligand-to-metal charge transfer [40].

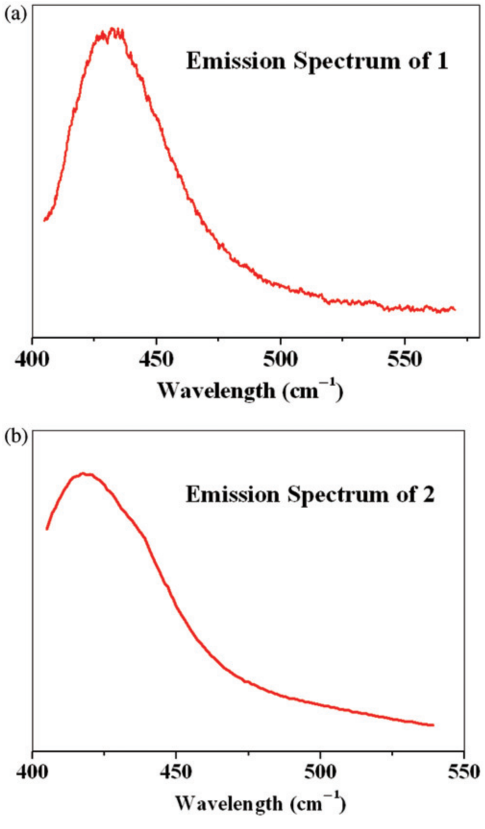

Figure 4. (a) The photoluminescence of **1**. (b) The photoluminescence of **2**.

4. Conclusions

Three new coordination polymers constructed from asymmetrical carboxylates had been synthesized under hydrothermal conditions and structurally characterized. These coordination polymers all show 3-D networks. Complexes **1** and **2** both exhibit photoluminescence at room temperature.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 763186 (**1**), 772192 (**2**), and 763187 (**3**).

Acknowledgments

We gratefully acknowledge financial support from the Fundamental Research Funds for the Central Universities (N09035002), Open Project of State Key Laboratory for Supramolecular Structure and Materials, China (SKLSSM 201002), and the Postdoctoral station Foundation of Northeast Normal University.

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