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Structure modulation of metal–organic frameworks via reaction pH: Self-assembly of a new carboxylate containing ligand *N*-(3-carboxyphenyl)iminodiacetic acid with cadmium(II) and cobalt(II) salts

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Abstract

Self-assembly of a new carboxylate containing ligand, *N*-(3-carboxyphenyl)iminodiacetic acid (H_3L), with Cd(II) and Co(II) salts under different reaction pH results in the formation of four new coordination polymers, namely $[Cd(HL)(H_2O)]$ (**1**), $[Co(HL)(H_2O)]$ (**2**), $[Cd(HL)(H_2O)_4]$ (**3**) and $[Cd_3(L)_2(H_2O)_9] \cdot 7H_2O$ (**4**). Single crystal X-ray diffraction analysis indicates that **1** and **2** are isomorphous and isostructural with a 2D wave-like network structure, while **3** has a 1D zigzag chain structure. The complexes **1**–**3** were obtained at low pH (<7) which makes the ligands only partly deprotonated. However, complex **4**, obtained at pH 7 with all the carboxylate groups deprotonated, exhibits a 2D network structure. The results suggest that the reaction pH is one of the key factors in the formation of the coordination architectures. In addition, the photoluminescence properties of the free ligand (H_3L) and complexes **1**, **3** and **4** were studied in the solid state at room temperature. Moreover, the magnetic property of complex **2** was investigated.

Keywords: Coordination polymer; Carboxylate ligand; Cadmium(II); Cobalt(II); Photoluminescence property

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1. Introduction

In recent years, much attention has been focused on metal–organic frameworks (MOFs) due to their fascinating structures such as zero-dimensional (0D) cages, one-dimensional (1D) helical chains, two-dimensional (2D) grids and three-dimensional (3D) frameworks [1], as well as their attractive properties which can be further utilized in the fields of magnetism, catalysis, absorption, optics, etc. [2]. Among them, MOFs with carboxylate containing ligands are especially of great interest in recent years because the carboxylate groups can adopt varied coordination modes such as monodentate, bis-monodentate, chelating, and as a result diverse structures can be obtained [3]. However, it is still a labyrinth because not all of the structures could be generated as predicted, which might be attributed to the factors that influence the formation of the architectures [4]. Particularly, the pH value of the reaction solution and crystallization conditions are crucial parameters, for example, Stock and co-workers have demonstrated the role of the acid/base ratio, temperature, etc., in determining the structure of the complexes [5].

Taking in account of the factors mentioned above, we have focused our attention on the reactions of various metal salts with multi-carboxylate ligands and the influence of reaction pH on the structure of the resultant complexes was investigated. Recently, a new carboxylate containing

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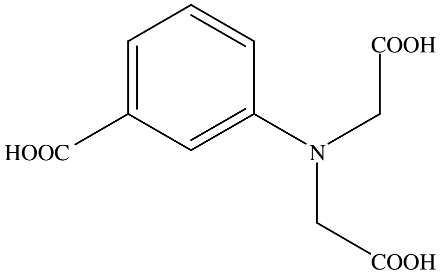


Scheme 1. Schematic drawing structure of the H_3L ligand.

ligand, *N*-(3-carboxyphenyl)iminodiacetic acid (H_3L) (Scheme 1), was obtained, which has remarkable features as follows: (a) it contains three carboxylate groups, therefore quite a lot of bridging modes could be adopted in the formation of MOFs; (b) the three carboxylate groups would be partially or completely deprotonated by tuning the reaction pH; (c) it is a semi-rigid ligand with a carboxyphenyl group fixed and an iminodiacetic moiety which is somewhat flexible, whereby different conformations of the ligand could be achieved which would further generate various architectures; (d) the introduced aromatic and the carboxylate groups could offer additional π–π and hydrogen bonding interactions, respectively, to further consolidate the structure [6].

Herein, we report the synthesis, crystal structure and properties of four new coordination polymers, namely $[Cd(HL)(H_2O)]$ (**1**), $[Co(HL)(H_2O)]$ (**2**), $[Cd(HL)(H_2O)_4]$ (**3**) and $[Cd_3(L)_2(H_2O)_9] \cdot 7H_2O$ (**4**), obtained by the reactions of H_3L with $Cd(NO_3)_2 \cdot 4H_2O$ or $CoCl_2 \cdot 4H_2O$ under different reaction pH.

2. Experimental

2.1. Materials and methods

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C Elemental Analyzer at the Analysis Center of Nanjing University. FT-IR spectra were recorded in the range 400–4000 cm^{-1} on a Bruker Vector22 FT-IR spectrophotometer as KBr pellets. ^1H NMR spectra were measured on a Bruker DRX 500 MHz NMR spectrometer at room temperature. Magnetic measurements for complex **2** in the range 1.8–300 K were performed on a MPMS-SQUID magnetometer at a field of 2 kOe on crystalline samples in the temperature settle mode. The diamagnetic contributions of the samples were corrected by using Pascal's constants. 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 was 5.0 nm. All the measurements were carried out under the same experimental conditions.

2.2. Synthesis of the ligand N-(3-carboxyphenyl)iminodiacetic acid (H_3L)

A solution of KOH (33.6 g, 0.6 mol) in water (100 ml) was added dropwise to a solution of monochloroacetic acid (28.4 g, 0.3 mol) in water (100 ml). To the resulting alkaline solution, 3-aminobenzoic acid (13.7 g, 0.1 mol) was added and the mixture was refluxed for 30 h. Then the reaction mixture was cooled to room temperature and a pale brown precipitate appeared, which was collected by filtration, washed by water and recrystallized from water (yield: 52% based on 3-aminobenzoic acid). ^1H NMR (500 MHz, in K_2CO_3, D_2O): δ 7.18 (t, 1H), 7.03 (d, 1H), 6.89 (s, 1H), 6.55 (d, 1H), 3.83 (s, 4H). IR (KBr pellet, cm^{-1}): 3446 (w), 2926 (w), 2552 (w), 1723 (m), 1682 (s), 1603 (m), 1580 (m), 1494 (w), 1465 (m), 1423 (w), 1376 (m), 1361 (m), 1299 (m), 1230 (w), 1183 (w), 1130 (w), 992 (w), 975 (w), 864 (w), 757 (m), 679 (w), 661 (w), 608 (w).

2.3. Synthesis of the complexes

2.3.1. Synthesis of $[Cd(HL)(H_2O)]$ (1)

A mixture containing $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), H_3L (25.3 mg, 0.1 mmol), KOH (2.8 mg, 0.05 mmol), 6 ml H_2O and 3 ml CH_3OH was sealed in a 16 ml Teflon lined stainless steel container and heated at 140 °C for 3 days. After cooling to room temperature for 12 h, colorless block crystals of **1** suitable for X-ray diffraction analysis were obtained in 68% yield. *Anal.* Calc. for $C_{11}H_{11}CdNO_7$: C, 34.62; H, 2.90; N, 3.67. Found: C, 34.65; H, 2.90; N, 3.70%. IR (KBr pellet, cm^{-1}): 3493 (m), 2917 (w), 1699 (m), 1583 (s), 1439 (m), 1416 (m), 1341 (w), 1313 (m), 1294 (m), 1197 (w), 1135 (w), 992 (w), 971 (w), 931 (w), 878 (w), 809 (w), 774 (w), 756 (w), 720 (w), 690 (w), 664 (w), 620 (w).

2.3.2. Synthesis of $[Co(HL)(H_2O)]$ (2)

The preparation of **2** is similar to that of **1** except that $CoCl_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol) was used and that the Teflon container was heated at 120 °C for 3 days. After cooling to room temperature for 12 h, purple block crystals of **2** were collected in 63% yield. *Anal.* Calc. for $C_{11}H_{11}CoNO_7$: C, 40.26; H, 3.38; N, 4.27. Found: C, 40.16; H, 3.27; N, 4.38%. IR (KBr pellet, cm^{-1}): 3474 (m), 2921 (w), 1698 (m), 1586 (s), 1492 (w), 1445 (m), 1419 (m), 1340 (w), 1315 (m), 1295 (m), 1248 (w), 1193 (w), 1175 (w), 1123 (w), 1048 (w), 990 (w), 968 (w), 936 (w), 925 (w), 907 (w), 879 (w), 808 (w), 777 (w), 756 (w), 729 (w), 690 (w), 666 (w), 632 (w).

2.3.3. Synthesis of $[Cd(HL)(H_2O)_4]$ (3)

Complex **3** was prepared by a layering method. An aqueous solution (5 ml) of H_3L (25.3 mg, 0.1 mmol) was carefully adjusted to pH 6 by tetrabutylammonium hydroxide (10%) solution and placed at the bottom of a test tube. Then a buffer layer of a solution (5 ml) of methanol/H_2O 1:1 was layered over it, and afterward, a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol) in methanol (5 ml) was layered over the buffer layer. Colorless block crystals of **3** were collected in 61% yield after several days. *Anal.* Calc. for $C_{11}H_{17}CdNO_{10}$: C, 30.32; H, 3.93; N, 3.22. Found: C, 30.21; H, 3.91; N, 3.29%. IR (KBr pellet, cm^{-1}): 3408 (m), 2930 (w), 1720 (m), 1572 (s), 1535 (s), 1455 (m), 1434 (m), 1413 (m), 1374 (m), 1357 (m), 1317 (m), 1295 (m), 1268 (w), 1234 (w), 1183 (w), 994 (w), 979 (w), 800 (w), 762 (w), 679 (w).

2.3.4. Synthesis of $[Cd_3(L)_2(H_2O)_9] \cdot 7H_2O$ (4)

The preparation of **4** was similar to that described for **3** except that the pH of the bottom solution of H_3L was adjusted to 7 rather than 6. Yield: 53%. *Anal.* Calc. for $C_{22}H_{48}Cd_3N_2O_{28}$: C, 23.47; H, 4.30; N, 2.49. Found: C, 23.59; H, 4.12; N, 2.45%. IR (KBr pellet, cm^{-1}): 3474 (m), 2908 (w), 1597 (s), 1574 (s), 1452 (w), 1402 (s), 1379 (m), 1329 (w), 1297 (m), 1215 (w), 1180 (w), 1135 (w), 987 (w), 933 (w), 891 (w), 800 (w), 762 (w), 681 (w).

2.4. X-ray crystallography

The crystallographic data collections for complexes **1**–**3** were carried out on a Bruker Smart Apex CCD with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) at 293(2) K using the ω-scan technique. The data were integrated by using the SAINT program [7], which also used for intensity corrections for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [8]. The structures were solved by direct methods using the program SHELXS-97 [9] and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [10]. The hydrogen atoms H2, H3, H5, H6, H7, H7A and H7B in **1**, H7A, H7B and H16 in **2** and all of the hydrogen atoms in **3** were located from difference Fourier maps, and the other hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97crystallographic software package. The X-ray diffraction measurement for **4** was carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). A symmetry-related absorption correction using the program ABSCOR [11] was applied and the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [11] and expanded using Fourier techniques [12]. The non-hydrogen atoms were refined anisotropically. All calculations for **4** were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation [13]. Atoms Cd2 and Cd3 in complex **4** are disordered Cd(II) with an occupancy of 0.5, and atoms O3, O4, O10, C13 and C14 in **4** have two positions with site occupancy factors of 0.53(2) and 0.47(2). Atom O17 in **4** is also

Table 1
Crystallographic data for complexes **1**–**4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{11}H_{11}CdNO_7$	$C_{11}H_{11}CoNO_7$	$C_{11}H_{17}CdNO_{10}$	$C_{22}H_{48}Cd_3N_2O_{28}$
Formula weight	381.61	328.14	435.66	1125.82
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/c	*C*2/c	*P*2_1/n	*C*2/m
a (Å)	30.192(4)	30.299(7)	5.4335(6)	20.837(3)
b (Å)	9.6582(13)	9.513(2)	25.563(3)	23.271(4)
c (Å)	8.4591(11)	8.3489(18)	10.4650(11)	8.3863(13)
β (°)	93.916(2)	95.395(4)	91.133(2)	97.352(3)
T (K)	293(2)	293(2)	293(2)	200
V ($Å^3$)	2460.9(6)	2395.8(9)	1453.3(3)	4033.0(11)
Z	8	8	4	4
D_c (g cm^{-3})	2.060	1.820	1.991	1.854
μ (mm^{-1})	1.808	1.466	1.558	1.663
F(000)	1504	1336	872	2248
$2\theta_{max}$ (°)	52.00	50.98	52.00	50.00
Data collected	6436	6099	7750	14335
Independent data	2421	2226	2852	3638
R_{int}	0.0346	0.0528	0.0489	0.0892
Parameters refined	209	193	276	316
Goodness-of-fit	1.011	0.936	1.001	1.075
R_1 [$I > 2\sigma(I)$]	0.0365	0.0426	0.0259	0.0787
wR_2 [$I > 2\sigma(I)$]	0.0884[a]	0.0658[b]	0.0542[c]	0.2046[d]
R_1 (all data)	0.0424	0.0635	0.0318	0.1018
wR_2 (all data)	0.0919	0.0708	0.0562	0.2294

[a] $w = 1/[\sum^2(F_o)^2 + (0.0560P)^2 + 1.7000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

[b] $w = 1/[\sum^2(F_o)^2 + (0.0156P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

[c] $w = 1/[\sum^2(F_o)^2 + (0.0208P)^2 + 0.0651P]$, where $P = (F_o^2 + 2F_c^2)/3$.

[d] $w = 1/[\sum^2(F_o)^2 + (0.1006P)^2 + 51.4441P]$, where $P = (F_o^2 + 2F_c^2)/3$.

disordered into two positions with site occupancy factors of 0.63(5) and 0.37(5). The hydrogen atoms of the uncoordinated water molecules O14, O15 and O16 could not be found from the difference Fourier maps. The details of the crystal parameters, data collection and refinements for the complexes are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

3. Results and discussion

3.1. Crystal structure of complexes **1–4**

3.1.1. [Cd(HL)(H_2O)] (**1**) and [Co(HL)(H_2O)] (**2**)

The result of X-ray crystallographic analysis revealed that complexes **1** and **2** crystallize in the same monoclinic *C*2/*c* space group with similar cell parameters (Table 1), which indicate that they are isomorphous and isostructural. Thus, as a typical example, only the structure of **1** is described here in detail. The asymmetric unit of **1** consists of one Cd(II) atom, one HL^{2-} ligand and one coordinated water molecule. Each Cd(II) atom is six-coordinated with a distorted octahedral geometry, by one nitrogen atom (N1) from the HL^{2-} ligand and five oxygen atoms from one coordinated H_2O molecule (O7) and three different HL^{2-} ligands (O3 and O5, O4A and O6B), as shown in Fig. 1a. The coordination bond lengths and angles around the Cd(II) centre are in the range 2.234(3)–2.556(3) Å and 68.59(10)–159.67(11)°, respectively as listed in Table 2. On the other hand, each HL^{2-} ligand adopts a μ_3 bridging mode to connect three Cd(II) atoms using its iminodiacetate moiety, in which each carboxylate group links two Cd(II) atoms in a *syn–anti* fashion and the central Cd(II) atom is coordinated by two oxygen atoms from two carboxylate groups and the central nitrogen atom (Scheme 2a). In addition, it is noteworthy that the carboxyphenyl group of the ligand, without deprotonation, is free of coordination. The non-deprotonation of the H_3L ligand in **1** and **2** was further confirmed by IR spectral measurements. The IR spectra of complexes **1** and **2** indicate the incomplete deprotonation of the H_3L ligand since vibration bands at 1699 cm^{-1} for **1** and 1698 cm^{-1} for **2** were

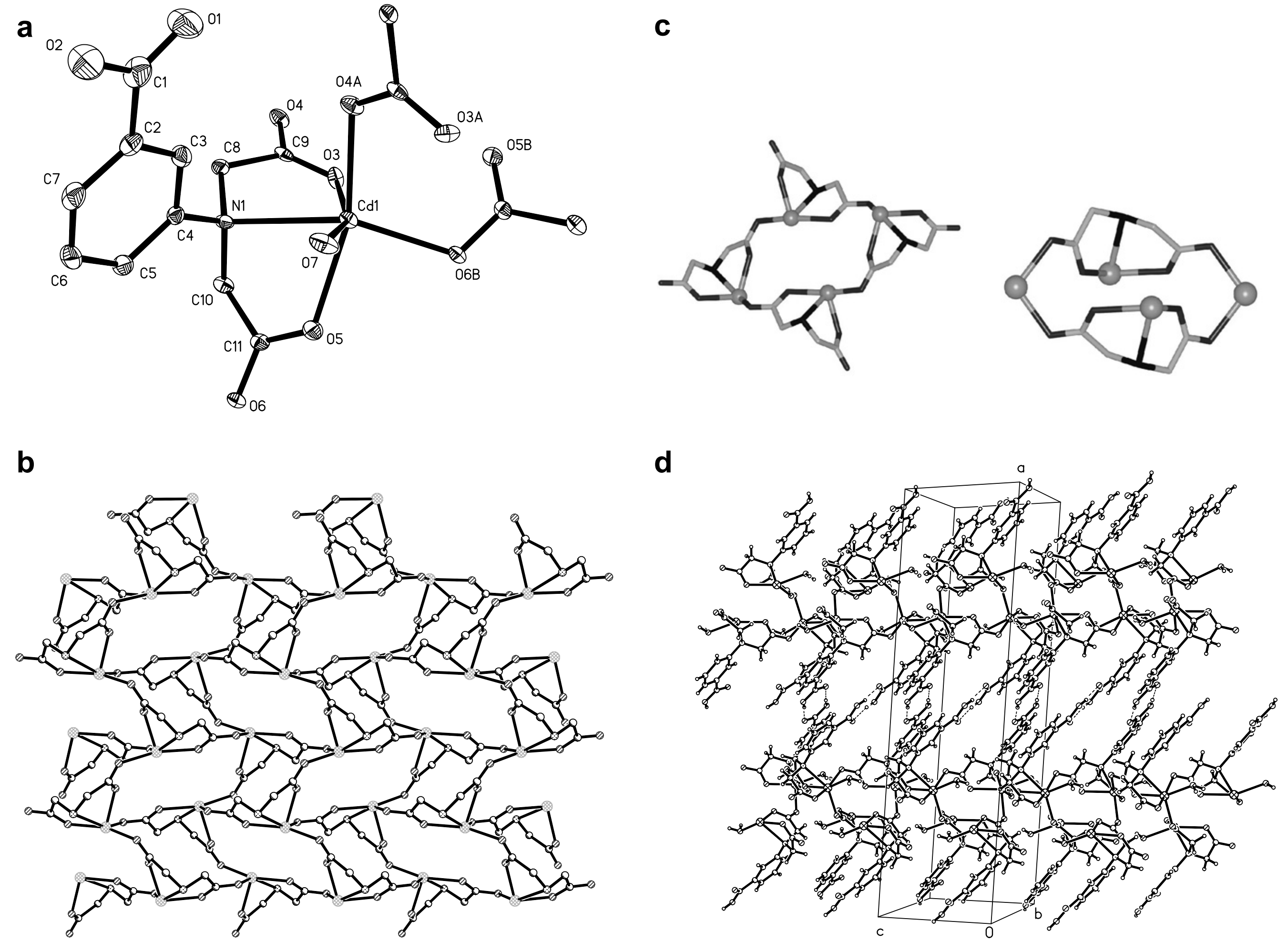
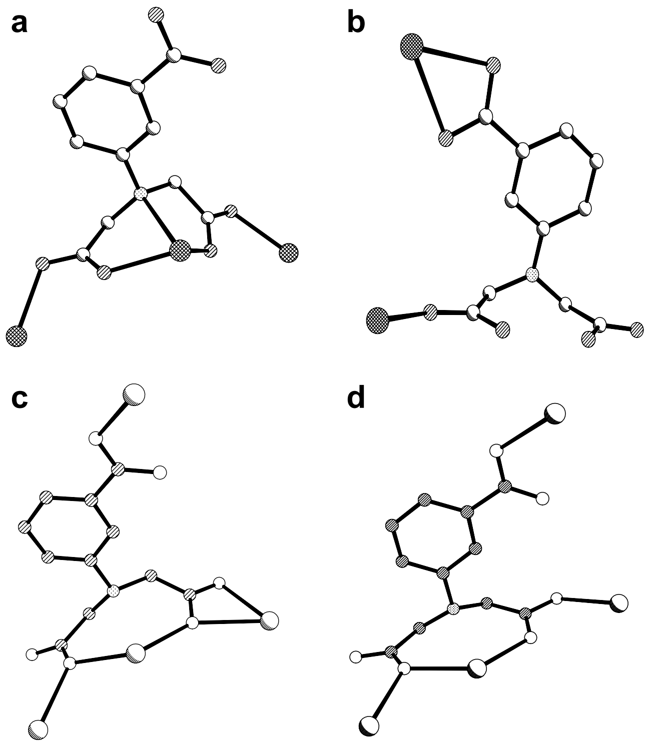


Fig. 1. (a) Coordination environment of the Cd(II) atom in complex **1** with the ellipsoids drawn at the 30% probability level, hydrogen atoms are omitted for clarity. (b) 2D network structure of **1**. (c) Views of the M_4L_4 (left) and M_4L_2 (right) units linked by four and two ligands with the carboxylphenyl groups omitted for clarity. (d) 3D structure of **1** with hydrogen bonds indicated by dashed lines.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

*[Cd(HL)(H$_2$O)] (**1**)*			
Cd(1)–N(1)	2.556(3)	Cd(1)–O(3)	2.283(3)
Cd(1)–O(4)#1	2.250(3)	Cd(1)–O(5)	2.263(3)
Cd(1)–O(6)#2	2.234(3)	Cd(1)–O(7)	2.306(3)
*[Co(HL)(H$_2$O)] (**2**)*			
Co(1)–N(1)	2.346(3)	Co(1)–O(3)	2.053(2)
Co(1)–O(4)#3	2.086(2)	Co(1)–O(5)	2.067(2)
Co(1)–O(6)#4	2.093(2)	Co(1)–O(7)	2.097(3)
*[Cd(HL)(H$_2$O)$_4$] (**3**)*			
Cd(1)–O(1)	2.435(2)	Cd(1)–O(2)	2.417(2)
Cd(1)–O(3)#5	2.282(2)	Cd(1)–O(7)	2.237(2)
Cd(1)–O(8)	2.383(2)	Cd(1)–O(9)	2.301(2)
Cd(1)–O(10)	2.339(2)		
*[Cd$_3$(L)$_2$(H$_2$O)$_9$] · 7H$_2$O (**4**)*			
Cd(1)–O(6)#6	2.261(7)	Cd(1)–O(2)	2.333(7)
Cd(1)–O(3)	2.339(17)	Cd(1)–O(7)	2.344(8)
Cd(1)–O(8)	2.380(7)	Cd(1)–O(2)#7	2.446(6)
Cd(2)–O(9)	2.15(2)	Cd(2)–O(10)	2.25(2)
Cd(2)–O(4)	2.339(14)	Cd(2)–O(3)	2.517(15)
Cd(3)–O(10B)	2.30(3)	Cd(3)–O(4B)	2.302(16)
Cd(3)–O(13)	2.335(18)	Cd(3)–O(11)	2.36(2)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+1, z-1/2$; #2 $-x+1/2, y+1/2, -z+3/2$; #3 $x, -y, z+1/2$; #4 $-x+1/2, y-1/2, -z+1/2$; #5 $x-1/2, -y+1/2, z-1/2$; #6 $x+1/2, -y+1/2, z+1$; #7 $-x, y, -z+1$.



Scheme 2. Coordination modes of the ligand in complexes **1**–**4**.

observed. Such coordination mode makes a 2D network structure of **1**, as illustrated in Fig. 1b in which the carboxyphenyl groups and coordinated water molecules are omitted for clarity.

It can be seen clearly from Fig. 1b that there are two different macrocyclic rings in the 2D sheet of **1**, namely M$_4$L$_4$ and M$_4$L$_2$ (Fig. 1c), respectively. In the M$_4$L$_4$ ring, each iminodiacetate group of the HL^{2-} ligand coordinates with two Cd(II) atoms using three of its four oxygen atoms and this affords one oxygen atom to link to another Cd(II) atom from a neighbouring ring. While in the case of the M$_4$L$_2$ ring, four Cd(II) centers are linked by two HL^{2-} ligands and in turn each HL^{2-} ligand connects three Cd(II) atoms using its four oxygen atoms. These two kinds of macrocyclic rings are arranged alternately to generate a 2D wave-like network. Furthermore, as shown in Fig. 1b, the M$_4$L$_4$ and M$_4$L$_2$ rings adopt entirely different motifs, i.e. the iminodiacetate moiety of the ligand occupies the space of the M$_4$L$_2$ ring whilst there is relatively large cavity in the M$_4$L$_4$ ring which is filled by the coordinated water molecules (Fig. S1).

The non-deprotonated carboxyphenyl groups point out of the 2D sheet, up and down alternately, and further connect the 2D network to give a 3D framework through the formation of O–H···O hydrogen bonds between the uncoordinated O atoms of the carboxyphenyl groups from two adjacent layers, with an O···O distance of 2.607(6) Å (Fig. 1d). The hydrogen bonding data are summarized in Table S1. There are other O–H···O and C–H···O hydrogen bonds within the 2D network, which further consolidate the structure [14].

3.1.2. *[Cd(HL)(H$_2$O)$_4$] (**3**)*

When the reaction of ligand H$_3$L with Cd(NO$_3$)$_2$ · 4H$_2$O was carried out by the layering method instead of a hydrothermal reaction as used for the preparation of **1** and **2**, the new complex **3** was obtained. The crystallographic data showed that complex **3** crystallizes the in monoclinic $P2_1/n$ space group and the Cd(II) atom has a pentagonal bipyramid coordination geometry with an O$_7$ donor set, as illustrated in Fig. 2a. Two oxygen atoms (O1 and O2) from the carboxyphenyl group of the ligand and three other oxygen atoms (O8, O9 and O10) from coordinated water molecules occupy planar positions with Cd–O bond lengths ranging from 2.301(2) to 2.435(2) Å (Table 2). The axial positions are occupied by one oxygen atom (O3A) from the iminodiacetate group of another ligand and O7 from another coordinated water molecule, with Cd–O bond lengths of 2.282(2) and 2.237(2) Å (Table 2), respectively. As illustrated in Scheme 2b, each HL^{2-} ligand links two Cd(II) atoms in **3**, in which the carboxyphenyl group is in a μ_1–η^1:η^1 chelating mode, and one carboxylate of the iminodiacetate group takes a μ_1–η^1:η^0 monodentate fashion and the other one does not take part in the coordination. It is noteworthy that the coordination mode of the ligand in **3** is quite different from that in **1** and **2**, as discussed above. Firstly, one carboxylate unit from the iminodiacetate group of the ligand remains protonated and is free of coordination in **3**, which was confirmed by the observation of a vibration band at 1720 cm^{-1} in the IR spectrum, however, the one in **1** and **2** non-deprotonated and free of

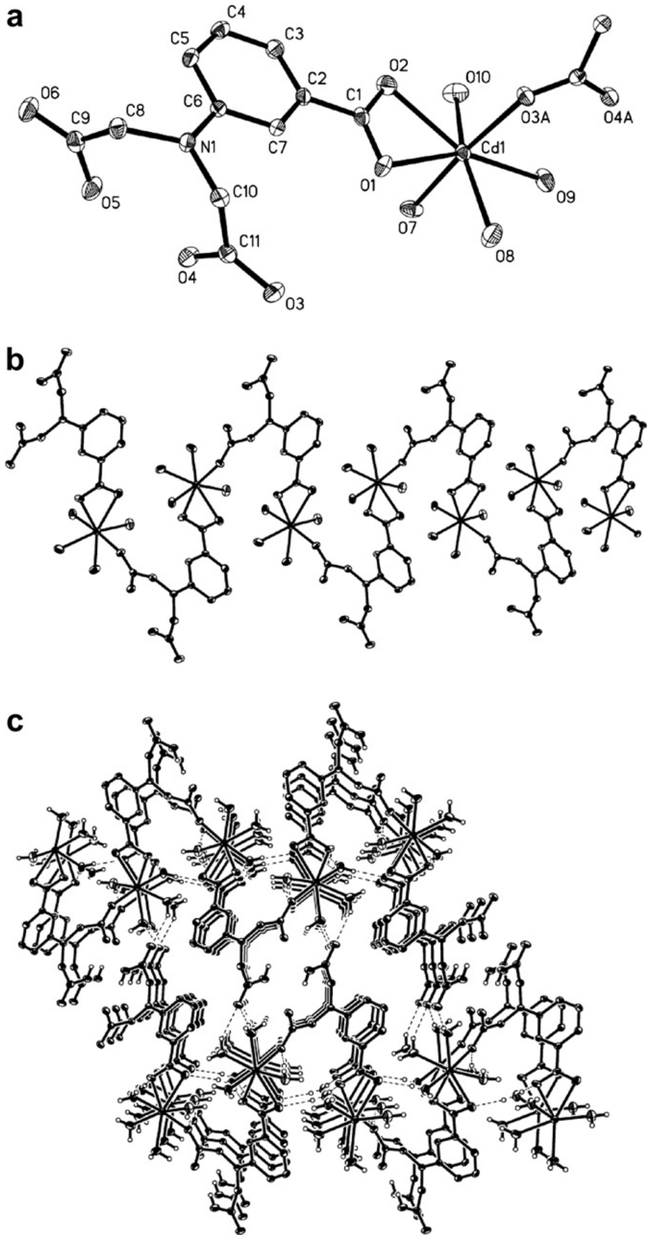


Fig. 2. (a) Coordination environment of the Cd(II) atom in **3** with the ellipsoids drawn at the 30% probability level, hydrogen atoms are omitted for clarity. (b) 1D zigzag chain structure of **3** with hydrogen atoms omitted for clarity. (c) 3D packing structure of **3** with hydrogen bonds indicated by dashed lines.

coordination is the carboxyphenyl group. Moreover, the nitrogen atom of the ligand also does not take part in coordination, and four water molecules participate in coordination to satisfy the coordination need of the Cd(II) atom in **3**. As a result of such differences, a 1D chain-like structure for complex **3** is generated, in which the ligand, utilizing its carboxyphenyl group and one of the iminodiacetate groups, acts as bridge to link the Cd(II) atoms into a zigzag chain structure (Fig. 2b).

In the packing structure of **3**, as shown in Fig. 3c, the 1D chains are firstly linked into a 2D layer by O–H···O hydrogen bonds between the oxygen atoms of the coordinated water molecules (O7 and O10) and carboxyphenyl group from adjacent chains, with O···O distances ranging from 2.707(3) to 3.192(4) Å (Table S1). Then the 2D layers are further connected through O–H···O hydrogen bonds between the oxygen atoms of the coordinated water molecules (O8 and O9) and the free arm of iminodiacetate group from an adjacent layer with O···O distances of 2.814(3) and 2.946(3) Å (Table S1).

3.1.3. *$[Cd_3(L)_2(H_2O)_9]\cdot 7H_2O$ (**4**)*

In order to further investigate the pH influence on the formation and structure of the complex, the pH value of the ligand solution was carefully adjusted to 7.0, while the other experiment conditions remained the same as those used for the preparation of **3**. As a result, complex **4**, with an entirely different structure, was obtained and the result of crystallographic analysis confirmed that all the carboxylate groups of the ligand are deprotonated and coordinated with the metal atoms in **4**. The complete deprotonation of all three carboxylate groups in **4** was also confirmed by IR spectroscopy since no vibration band around 1700 cm^{-1} for a protonated carboxylate group was observed in the IR spectrum of **4**. The complex crystallizes in the monoclinic *C*2/*m* space group, and in the repeat unit there are two Cd(II) atoms (Cd2 and Cd3) sitting on a symmetry plane with a separation of 2.44 Å and one disordered carboxylate group of the iminodiacetate of the L^{3-} ligand was found near these two Cd(II) atoms. Thus Cd2 and Cd3 are disordered Cd(II) with an occupancy of 0.5. As shown in Fig. 3a, Cd1 is six coordinated by four oxygen atoms (O2, O3, O2A and O6A) from three different L^{3-} ligands, and two oxygen atoms (O7, O8) from two coordinated water molecules, with Cd–O bond lengths ranging from 2.261(7) to 2.446(6) Å (Table 2). While Cd2 and Cd3 are also six coordinated, it is with four oxygen atoms (O3, O4, O3A and O4A) from two L^{3-} ligands and two oxygen atoms (O9, O10) from two coordinated water molecules for Cd2, and two oxygen atoms (O4B and O4BA) from two L^{3-} ligands, and four oxygen atoms (O10B, O11, O13 and O13A) from four coordinated water molecules for Cd3. In addition, two Cd1 atoms (e.g. Cd1 and Cd1A in Fig. 3a) are bridged by two carboxylate oxygen atoms (O2 and O2A) to form a Cd_2O_2 rhombic ring. Therefore, each L^{3-} ligand connects four Cd(II) atoms in two different forms (Scheme 2c and d) in **4** using its three carboxylate groups, and the central nitrogen atom (N1) does not take part in the coordination since the Cd1–N1 distance is 2.70 Å.

The most striking feature of complex **4** is that the Cd(II) centers are connected by the L^{3-} ligand to furnish a 2D network with two different types of cavities filled with water molecules. Firstly, as illustrated in Fig. 3b, six Cd(II) atoms are linked by four L^{3-} ligands to generate a near rectangular ring, and four Cd1 atoms are located at the four corners. Then further connection of the rectangular rings through the Cd_2O_2 rhombic rings results in the formation of an infinite 2D network as

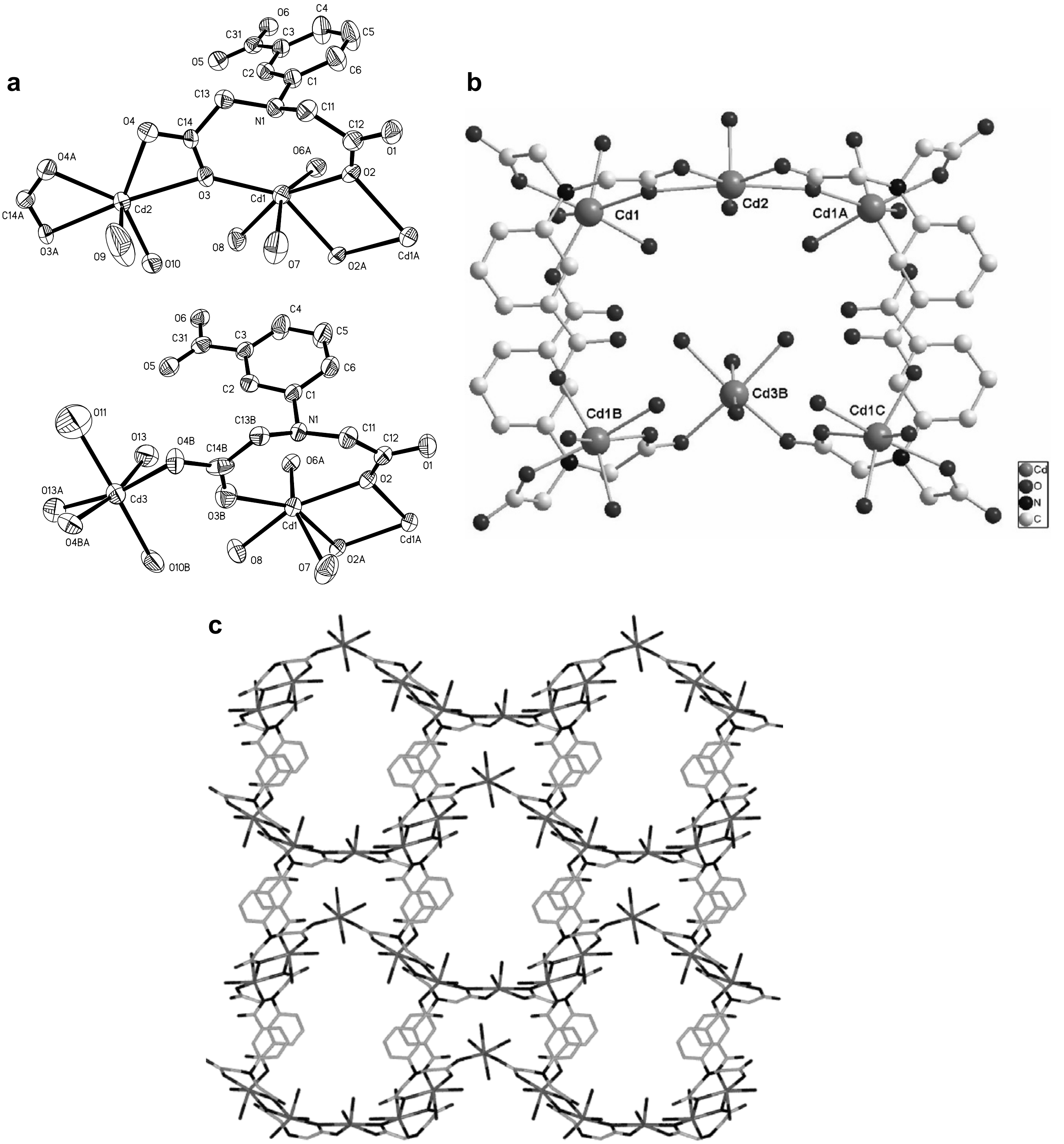


Fig. 3. (a) Coordination environments of the Cd(II) atoms in **4** with the ellipsoids drawn at the 30% probability level, hydrogen atoms and uncoordinated water molecules are omitted for clarity. Top: disordered part with Cd2; bottom: disordered part with Cd3. (b) A near rectangular ring with six Cd(II) atoms linked by four L^{3-} ligands. (c) 2D network structure of **4**. The hydrogen atoms and uncoordinated water molecules are omitted for clarity.

depicted in Fig. 3c. In the crystal packing mode, the 2D sheets are further linked into a 3D structure by C–H···O hydrogen bonds between the C11 atom of an iminodiacetate group and the O1 atom from an adjacent layer, with a C···O distance of 3.552(13) Å, and C–H···O hydrogen bonds also exist in the crystal packing diagram, which further consolidate the structure (Fig. S2, Table S1).

3.2. Effect of synthetic conditions on the structure of the complexes

It has been reported that synthetic conditions, such as pH value, reaction temperature, solvent, etc., are the key factors in assembling MOFs [15,16]. As to the synthesis of **3** and **4**, all the reaction conditions are the same except for the difference of the reaction pH. As a result, complex

3, obtained at a relatively low pH value, is a 1D zigzag chain structure with each Cd(II) center bonded by four water molecules. However in **4**, obtained at a high pH, a more complicated 2D network was generated. Therefore, a rough conclusion could be made that an increase of the pH value in the synthetic process would generate higher dimensionality of the final structure, which is in agreement with the previous reports [17].

In addition, complex **1** was synthesized at a lower pH value and a 2D sheet was obtained rather than a 1D zigzag chain, as in **3**. It might be ascribed to the fact that complex **1** was formed at a high reaction temperature, namely 140 °C under a hydrothermal process, which is considered to be in favor of generating high dimensional structures [18].

From the points discussed above, it is suggested that the increase of reaction pH and temperature may result in a higher connectivity of the carboxylate ligand and further feature a more complicated high dimensional structure.

*3.3. Photoluminescence properties of complexes **1**, **3** and **4***

Inorganic–organic hybrid coordination compounds, especially with d^{10} metal centers, have been investigated for fluorescence properties owing to their potential applications as luminescent materials, such as light-emitting diodes (LEDs) [19]. Therefore, in the present study, the photoluminescence properties of **1**, **3** and **4** as well as the free H_3L ligand were investigated in the solid state at room temperature. As shown in Fig. 4, intense emission bands were observed at 407 nm ($\lambda_{ex} = 360$ nm) for the H_3L ligand, 422 nm ($\lambda_{ex} = 350$ nm) for **1**, 414 nm ($\lambda_{ex} = 360$ nm) for **3** and 392 nm ($\lambda_{ex} = 342$ nm) for **4**, respectively. These emissions cannot be attributed to either a metal-to-ligand charge transfer (MLCT) or a ligand-to-metal charge transfer (LMCT) because the Cd(II) ions are in a d^{10} configuration and are difficult to oxidize or to reduce. Therefore, they could be assigned to the π–π* intraligand fluorescence due to their resemblance to the emission of the H_3L ligand. The enhancement and slight shift of the emissions for **1**, **3** and **4** compared to that of the free ligand probably result from the fact that the coordination of Cd(II) ions increases the ligand conformational rigidity and thus reduces the loss of energy by thermal vibrational decay [20].

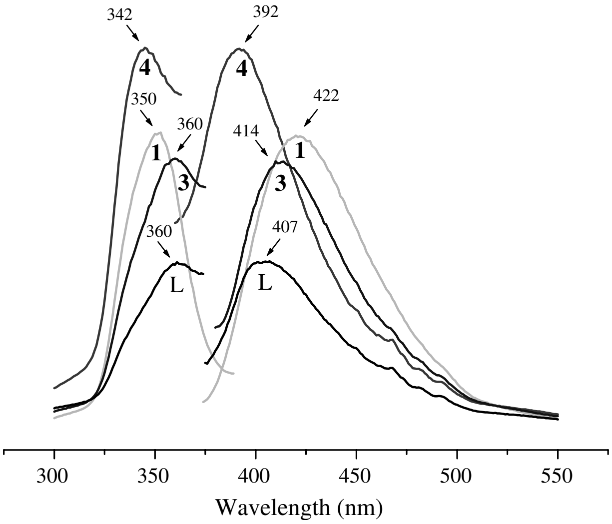


Fig. 4. Excitation and emission spectra of the H_3L ligand and **1**, **3** and **4** in the solid state at room temperature.

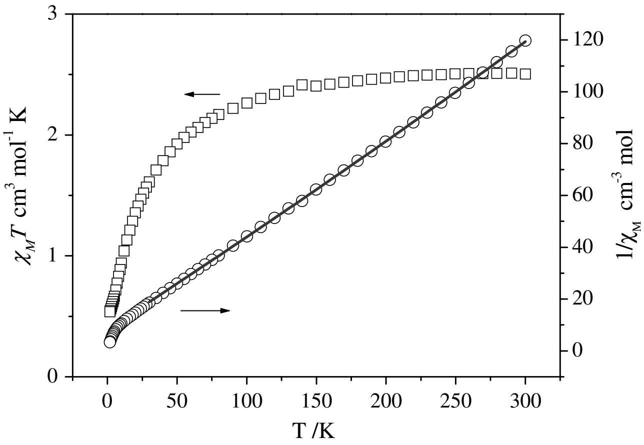


Fig. 5. Temperature dependence of $\chi_M T$ and $1/\chi_M$ for **2**. The solid line shows the Curie–Weiss fitting.

*3.4. Magnetic properties of complex **2***

The magnetic susceptibility of **2** versus temperature at a field of 2 kOe is shown in Fig. 5, where χ_M is the susceptibility per Co(II) ion. The $\chi_M T$ value is 2.50 cm^3 mol^{-1} K at 300 K, which is significantly larger than the spin-only value of 1.875 cm^3 mol^{-1} K and decreases upon cooling to 0.54 cm^3 mol^{-1} K at 2 K. The magnetic susceptibility above 30 K obeys the Curie–Weiss law with a Weiss constant, $\theta = -24.11$ K, and a Curie constant, $C = 2.88$ cm^3 mol^{-1} K. The high value of C (1.875 cm^3 mol^{-1} K for spin-only Co^{2+}) and negative θ value may be due to the spin–orbit coupling, which is remarkable for the $^4T_{1g}$ state of Co^{2+} in an octahedral ligand field [21].

4. Conclusion

In conclusion, we have successfully synthesized a new carboxylate containing ligand and four new coordination polymers were isolated accordingly under different pH conditions. The results revealed that the reaction pH plays an important role in modulating the architecture of coordination compounds. In addition, complexes **1**, **3** and **4** showed π–π* intraligand fluorescence in the solid state at room temperature, and the magnetic property of complex **2** was also investigated.

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Appendix A. Supplementary material

CCDC 645328, 645329, 645330 and 645331 contain the supplementary crystallographic data for complexes **1**, **2**, **3** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.11.029.

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