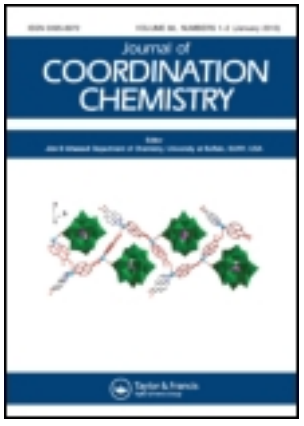


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Cd(II) complexes from imidazole substitute isophthalate ligand: syntheses, structural characterization, and fluorescence property

Hai-Wei Kuai[a], Xing-You Xu[a], Xiao-Chun Cheng[a], Liang-Dong Feng[a] & Xiao-Hong Zhu[a]

[a] Faculty of Life Science and Chemical Engineering, Jiangsu Provincial Engineering Laboratory for Advanced Materials of Salt Chemical Industry, Huaiyin Institute of Technology, Huaian, China

Published online: 10 Dec 2013.

To cite this article: Hai-Wei Kuai, Xing-You Xu, Xiao-Chun Cheng, Liang-Dong Feng & Xiao-Hong Zhu (2013) Cd(II) complexes from imidazole substitute isophthalate ligand: syntheses, structural characterization, and fluorescence property, Journal of Coordination Chemistry, 66:24, 4304-4315, DOI: 10.1080/00958972.2013.867025

To link to this article: http://dx.doi.org/10.1080/00958972.2013.867025

Journal of Coordination Chemistry, 2013
Vol. 66, No. 24, 4304–4315, http://dx.doi.org/10.1080/00958972.2013.867025

Cd(II) complexes from imidazole substitute isophthalate ligand: syntheses, structural characterization, and fluorescence property

HAI-WEI KUAI, XING-YOU XU, XIAO-CHUN CHENG*, LIANG-DONG FENG and XIAO-HONG ZHU

Faculty of Life Science and Chemical Engineering, Jiangsu Provincial Engineering Laboratory for Advanced Materials of Salt Chemical Industry, Huaiyin Institute of Technology, Huaian, China

(*Received 1 June 2013; accepted 14 November 2013*)

The hydrothermal reaction of Cd(II) salt with 5-[(2-methyl-1H-imidazol-1-yl)methyl]isophthalic acid (H_2L) leads to the formation of a new complex [Cd(L)(H_2O)] (**1**). While in the presence of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) as auxiliary ligands, complexes [Cd(L)(bpy)]·H_2O (**2**) and [Cd(L)(phen)]·2H_2O (**3**) were obtained. Complexes **1–3** have been characterized by single crystal and powder X-ray diffractions, IR, and elemental and thermogravimetric analyzes. As a result, complex **1** exhibits twofold interpenetrated 3-D (10,3)-a architecture, **2** displays chain structure, and **3** shows uninodal 3-connected **hcb** network with (6^3) topology. The impact of auxiliary ligands on the structures of resultant complexes is discussed. Moreover, luminescence property of **1–3** was investigated.

Keywords: Cd(II) complex; Structural characterization; Fluorescence

1. Introduction

Metal-organic frameworks (MOFs) have been increasingly focused on, which is justified not only due to their fascinating structures and topologies, but also for their potential applications in many fields [1]. Consequently, a great number of MOFs have been deliberately prepared and discussed in some comprehensive reviews [2]. It is known that one of the effective strategies for construction of MOFs is to select suitable organic ligands as building blocks to bridge metal centers into infinite frameworks [3]. Among the well employed organic ligands, N- and/or O-multidentate donors ligands are often regarded as excellent building blocks for desirable frameworks. Meanwhile, many influential factors can impact on self-assembly process, including the nature of metal ions and ligands, acidic or basic media, and other experimental conditions such as solvent, reaction temperature, and ratio of metal-to-ligand [4]. Therefore, it still seems a great challenge to achieve controllable assembly of a target structure driven by the global energy minimization of one system under specific condition.

*Corresponding author. Email: hxldh@126.com

Recently, we have been focusing our attention on the utilization of a new methylimidazol-1-yl and carboxylate-containing ligand: 5-[(2-methyl-1H-imidazol-1-yl)methyl]isophthalic acid (H_2L) as a building block for construction of MOFs with different structures. One main goal is to investigate the impact of synthetic conditions on the structures and properties of resultant complexes. The arene-cored ligand H_2L exhibits a advantage over other N- or O-donor ligands since it contains two coordination groups, namely rigid carboxylate and flexible methylimidazole. Given the relative orientation of these two carboxylate groups and their variable coordination patterns such as μ_1-$\eta^1:\eta^0$-monodentate and μ_1-$\eta^1:\eta^1$-chelating modes, the H_2L ligand can act as a multi-connector in formation of complexes [5]. Furthermore, the flexible coordination group in H_2L has more spatial freedom to adopt different orientations, which is originated from its freely axial rotation on the demand of coordinating requirements [6]. The potential variable coordination modes of H_2L provide the feasibility to assemble complexes with various structures by adjusting synthetic conditions, which may be helpful to further comprehend the correlation between experimental conditions and the structure of resultant complexes and would lay a solid groundwork for finally achieving the goal of controllable self-assembly.

We report herein syntheses and structural characterization of three new coordination polymers [Cd(L)(H_2O)] (**1**), [Cd(L)(bpy)]·H_2O (**2**), and [Cd(L)(phen)]·$2H_2O$ (**3**). These complexes exhibited structural diversity dependent on the presence and alteration of auxiliary ligands. In addition, fluorescence properties of complexes **1–3** have been examined.

2. Experimental

2.1. *Materials and methods*

All commercially available chemicals are of reagent grade and were used as received without further purification. Elemental analysis of C, H, and N were taken on a Perkin–Elmer 240C elemental analyzer. Infrared spectra (IR) were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα (λ = 1.5418 Å) radiation at room temperature. The luminescence spectra for the powdered solid samples were measured 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 nm, and all the measurements were carried out under the same experimental conditions.

2.2. *Preparation of ligand*

The H_2L was synthesized via similar experimental procedure to that reported for preparation of other imidazole substitute isophthalate ligands [7]. Potassium hydroxide (0.56 g, 10 mM) was added to a solution of 2-methyl-1H-imidazole (0.82 g, 10 mM) in 10 mL DMF. The mixture was then stirred for 10 h at room temperature, following which dimethyl 5-(bromomethyl)isophthalate (1.44 g, 5 mM) was added and the solution was stirred further at room temperature for 24 h. Then, 200 mL water and potassium hydroxide (1.12 g, 20 mM) were added into the resulting mixture. The reaction mixture was refluxed for 10 h, and then poured into ice water, acidified with acetic acid to pH 5–6. After filtration,

the product was dried at 100 °C under vacuum and obtained as a pale yellow solid (1.06 g, 82%). ^{1}H NMR (500 MHz, DMSO-d_6, 25 °C): δ = 8.40 (s, 1H); 7.92 (s, 2H); 7.26 (s, 1H); 6.92 (s, 1H); 5.36 (s, 2H); 2.27 (s, 3 H). Calcd for $C_{13}H_{12}N_2O_4$ (%): C, 60.00; H, 4.65; N, 10.76. Found (%): C, 60.26; H, 4.38; N, 10.98.

2.3. *Preparation of [Cd(L)(H$_2$O)] (1)*

Reaction mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (61.8 mg, 0.2 mM), H_2L (26.0 mg, 0.1 mM), and KOH (11.2 mg, 0.2 mM) in 10 mL H_2O was sealed in a 16 mL Teflon-lined stainless steel container and heated at 180 °C for 72 h. After cooling to the room temperature, colorless needle crystals of **1** were collected by filtration and washed by water and ethanol for several times with the yield of 30% (11.6 mg) based on the H_2L. Calcd for $C_{13}H_{12}N_2O_5Cd$ (%): C, 40.17; H, 3.11; N, 7.21. Found (%): C, 39.90; H, 3.38; N, 6.98. IR (KBr pellet, cm^{-1}): 3213 (m), 1609 (s), 1548 (s), 1458 (s), 1422 (s), 1373 (s), 1284 (s), 1255 (m), 1227 (m), 1159 (m), 1146 (m), 1130 (m), 1106 (m), 1008 (m), 801 (m), 769 (s), 733 (s), 688 (m), 664 (m), 640 (m).

2.4. *Preparation of [Cd(L)(bpy)]·H$_2$O (2)*

Complex **2** was obtained under the same reaction condition as that for preparation of **1** except that bpy (15.6 mg, 0.1 mM) was introduced into the synthetic system as auxiliary ligand. Colorless plate-shaped crystals of **2** were obtained with the yield of 25% (13.6 mg) based on the H_2L. Calcd for $C_{23}H_{20}N_4O_5Cd$ (%): C, 50.70; H, 3.70; N, 10.28. Found (%): C, 50.40; H, 3.45; N, 10.55. IR (KBr pellet, cm^{-1}): 3416 (m), 1620 (s), 1600 (s), 1567 (s), 1498 (m), 1474 (m), 1441 (s), 1409 (m), 1360 (s), 1316 (m), 1284 (m), 1158 (m), 1016 (m), 814 (m), 785 (m), 761 (s), 724 (s), 700 (m), 663 (m), 635 (m).

2.5. *Preparation of [Cd(L)(phen)]·2H$_2$O (3)*

Complex **3** was obtained under the same reaction condition as that for preparation of **1** except that phen (18.0 mg, 0.1 mM), instead of bpy, was used as auxiliary ligand. Colorless block crystals of **3** were obtained with the yield of 32% (18.7 mg) based on the H_2L. Calcd for $C_{25}H_{22}N_4O_6Cd$ (%): C, 51.16; H, 3.78; N, 9.55. Found (%): C, 51.40; H, 3.50; N, 9.66. IR (KBr pellet, cm^{-1}): 3449 (m), 1617 (s), 1565 (s), 1512 (s), 1475 (m), 1452 (m), 1423 (s), 1366 (s), 1309 (m), 1281 (m), 1236 (m), 1131 (m), 1102 (m), 998 (m), 847 (s), 807 (m), 778 (m), 758 (m), 730 (s), 669 (m), 636 (m).

2.6. *X-ray crystallography*

The crystallographic data collections for complexes **1–3** were carried out on a Bruker Smart ApexII CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The diffraction data were integrated using the SAINT program [8], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [9]. The structure of **1–3** was solved by direct methods 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]. For complexes **1–3**, all hydrogen

atoms attached to C were generated geometrically using the riding model. The hydrogen atoms of lattice water in **2** were excluded from the refinement, as the directions of H atoms towards O acceptors and the O–H bond distances are outside normal ranges, and deliberately artificial restraints always make the structural refinement unstable and arouse many crystallographic errors. Besides, other hydrogen atoms of water molecules in **1** and **3** were found at reasonable positions in the difference fourier maps and located there. The details of crystal parameters, data collection, and refinements for the complexes are summarized in table 1; the selected bond lengths and angles are listed in table S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.867025).

3. Results and discussion

3.1. *Crystal structure description of [Cd(L)(H$_2$O)] (1)*

X-ray structural analysis showed that complex **1** is composed of 3-D frameworks in orthorhombic crystal system with *Pbca* space group (table 1). As shown in figure 1(a), the asymmetric unit of **1** contains one Cd(II), one L^{2-} ligand, and one coordinated water molecule. Each Cd(II) is six-coordinated by one nitrogen atom from methylimidazolyl of L^{2-}, four carboxylate oxygen atoms from two different L^{2-} ligands, and one oxygen atom from the coordinated water molecule to show a greatly distorted octahedral coordination geometry. Both carboxylate groups of the L^{2-} in **1** adopt μ_1-$\eta^1:\eta^1$-chelating coordination mode (scheme 1). Thus in complex **1** each L^{2-} ligand bridges three different Cd(II) atoms and each Cd(II) is also coordinated by three different L^{2-} ligands. This kind of interconnection repeats infinitely to construct a neutral 3-D architecture (figure 1(b)), where 2-D layer structure can be isolated (figure 1(b) and (c)). Within this 2-D structure five L^{2-} ligands and five metal atoms are connected together via coordination bonds to form a 48-membered

Table 1. Crystallographic data and structure refinement details for complexes **1–3**.

	1	**2**	**3**
Empirical formula	$C_{13}H_{12}N_2O_5Cd$	$C_{23}H_{20}N_4O_5Cd$	$C_{25}H_{22}N_4O_6Cd$
Formula weight	388.65	544.83	586.87
Temperature/K	293(2)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	*P-1*
a/Å	10.637(5)	10.3236(5)	8.791(2)
b/Å	13.702(5)	14.3355(8)	10.174(3)
c/Å	18.612(5)	15.3792(8)	15.061(4)
α/°	90.000(5)	90.00	89.355(4)
β/°	90.000(5)	95.3350(10)	83.637(4)
γ/°	90.000(5)	90.00	67.995(4)
V (Å^3)	2712.7(18)	2266.2(2)	1240.5(6)
Z, D_{Calcd}/(Mg m^{-3})	8	4	2
F (000)	1536	1096	592
θ Range/°	2.19–27.50	1.95–28.35	1.36–28.00
Reflections collected	15,439	16,254	8669
Independent reflections	3069	5660	5896
Goodness-of-fit on F^2	1.080	1.033	1.068
R_1 [$I > 2\sigma(I)$][a]	0.0300	0.0360	0.0335
wR_2 [$I > 2\sigma(I)$][b]	0.0831	0.1124	0.0952

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

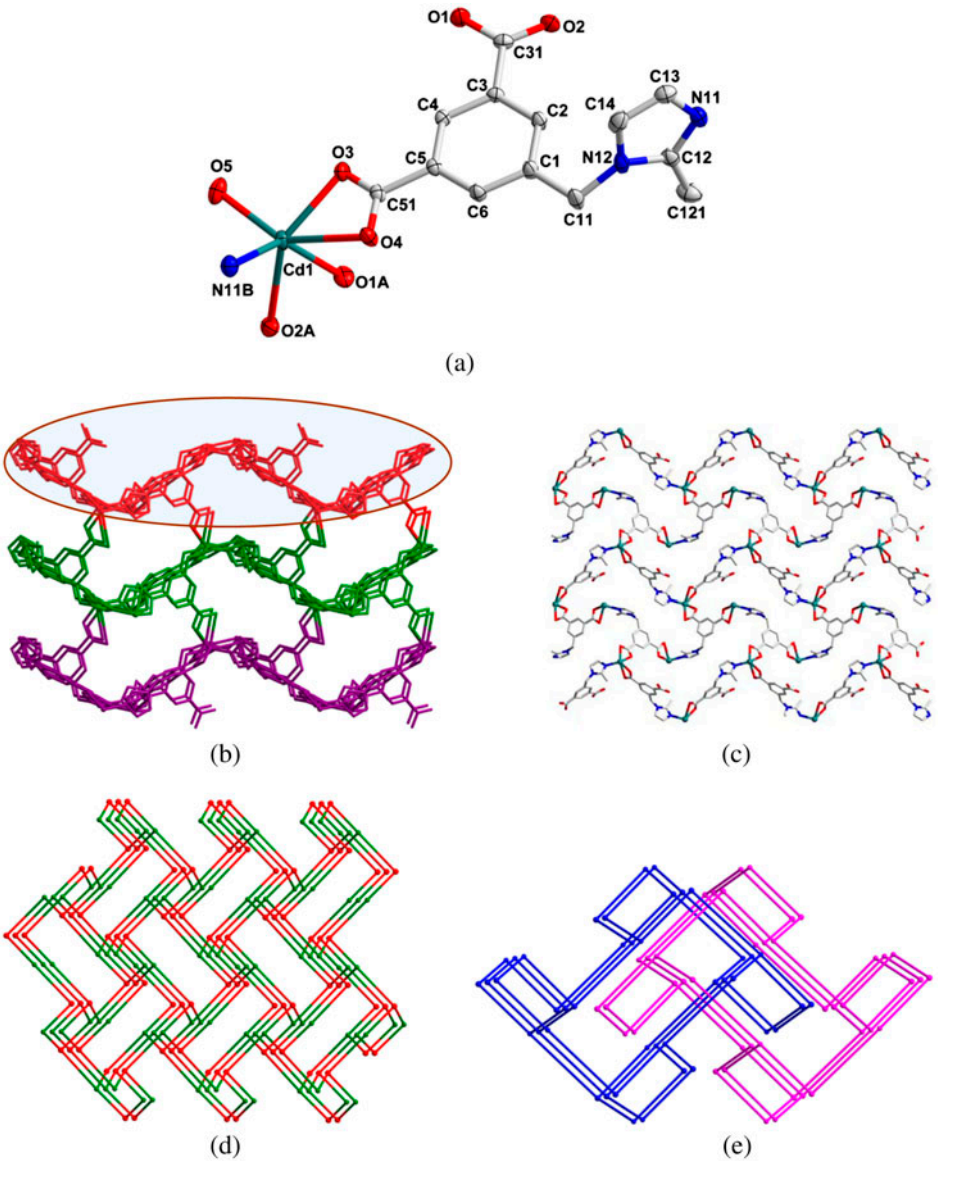
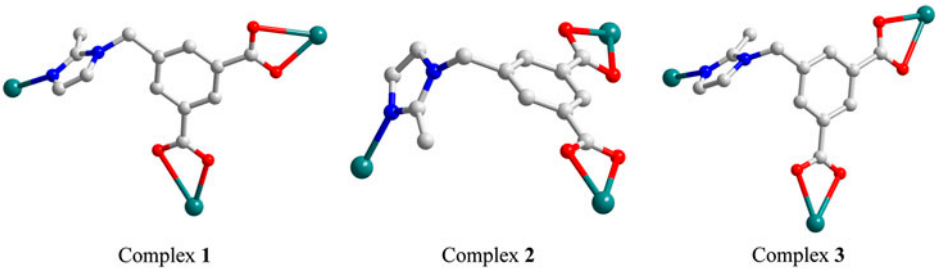


Figure 1. (a) The coordination environment of Cd(II) ions in complex **1** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, (b) view of 3-D architecture of **1**. The red circle highlights 2-D network in **1**, (c) view of 2-D network in **1**, (d) schematic illustrating the uninodal 3-connected architecture of **1** with (10,3)-a topology; the bigger balls (red): metal centers; the smaller balls (green): the L^{2-} ligands, and (e) topological representation of twofold interpenetrating framework of **1** (see http://dx.doi.org/10.1080/00958972.2013.867025 for color version).

macrocyclic ring. In **1**, both L^{2-} ligand and metal atom act as 3-connected nodes, then the 3-D framework can be simplified as uninodal 3-connected (10,3) a net which is intrinsically chiral [11] (figure 1(d)). But the twofold interpenetrating networks are of the opposite hands and form an enantiomeric pair of racemate (figure 1(e)).



Scheme 1. The coordination modes of the L^{2-} appearing in complexes **1–3**.

3.2. *Crystal structure description of [Cd(L)(bpy)]·H_2O (2)*

Complex **2** exhibits double-stranded chain structure in the monoclinic system with $P2_1/c$ space group (table 1). There are one Cd(II), one L^{2-} ligand, one coordinated bpy, and one lattice water molecules in the asymmetric unit of **2**. As shown in figure 2(a), each Cd(II) is seven-coordinated by one methylimidazole N atom, two N atoms from coordinated bpy, and four carboxylate O atoms from two different L^{2-} ligands to furnish a distorted pentagonal bipyramidal geometry. Two apexes are occupied by methylimidazole and bpy N atoms and the equatorial plane can be well defined by four carboxylate O atoms and the other bpy N atom. Both carboxylate groups in the L^{2-} ligand exhibit μ_1-$\eta^1:\eta^1$-chelating coordination modes (scheme 1). As depicted in figure 2(b), each L^{2-} ligand bridges three Cd(II) centers to construct a double-stranded chain structure with the nearest intrachain Cd···Cd distance of 10.101 Å. Because of the flexibility of the L^{2-} ligand, the double chain extends along the *a*-axis direction in a spiral way. If some organic moieties are ignored, a pair of right- and left-handed helical chains could be distinguished in the neutral double-stranded chain (figure 2(c)).

3.3. *Crystal structure description of [Cd(L)(phen)]·2H_2O (3)*

When phen was introduced into hydrothermal reaction system as auxiliary ligand instead of bpy, complex **3** was obtained, which consists of 2-D networks based on Cd(II), L^{2-}, and phen in triclinic *P-1* space group (table 1). The asymmetric unit of **3** contains one Cd(II), one L^{2-}, one coordinated phen molecule, and two lattice water molecules. Each Cd(II) is seven-coordinated (figure 3(a)), with a distorted pentagonal bipyramidal geometry, by four carboxylate O atoms and three N atom from methylimidazole and phen. Just as in **2**, both carboxylate groups in the L^{2-} ligand exhibit μ_1-$\eta^1:\eta^1$-chelating coordination modes, respectively, and thus the L^{2-} can be described as a μ_3-bridge. Each metal ion is also surrounded by three L^{2-} ligands. The interconnection of Cd(II) and L^{2-} infinitely extends to form a 2-D network (figure 3(b)). Both of L^{2-} ligand and metal center can be treated as a 3-connected node. Thus the structure of **3** can be simplified as a uninodal 3-connected 2-D **hcb** network with (6^3) topology (figure 3(c)).

3.4. *Coordination modes of H_2L ligand and structural comparison of 1–3 with previously reported Cd(II) complexes*

All carboxylate groups of the L^{2-} in the three complexes are found to be completely deprotonated and involved in coordination showing the same μ_1-$\eta^1:\eta^1$-chelating coordination modes (scheme 1) and the flexible coordination groups coordinate to a single metal atom,

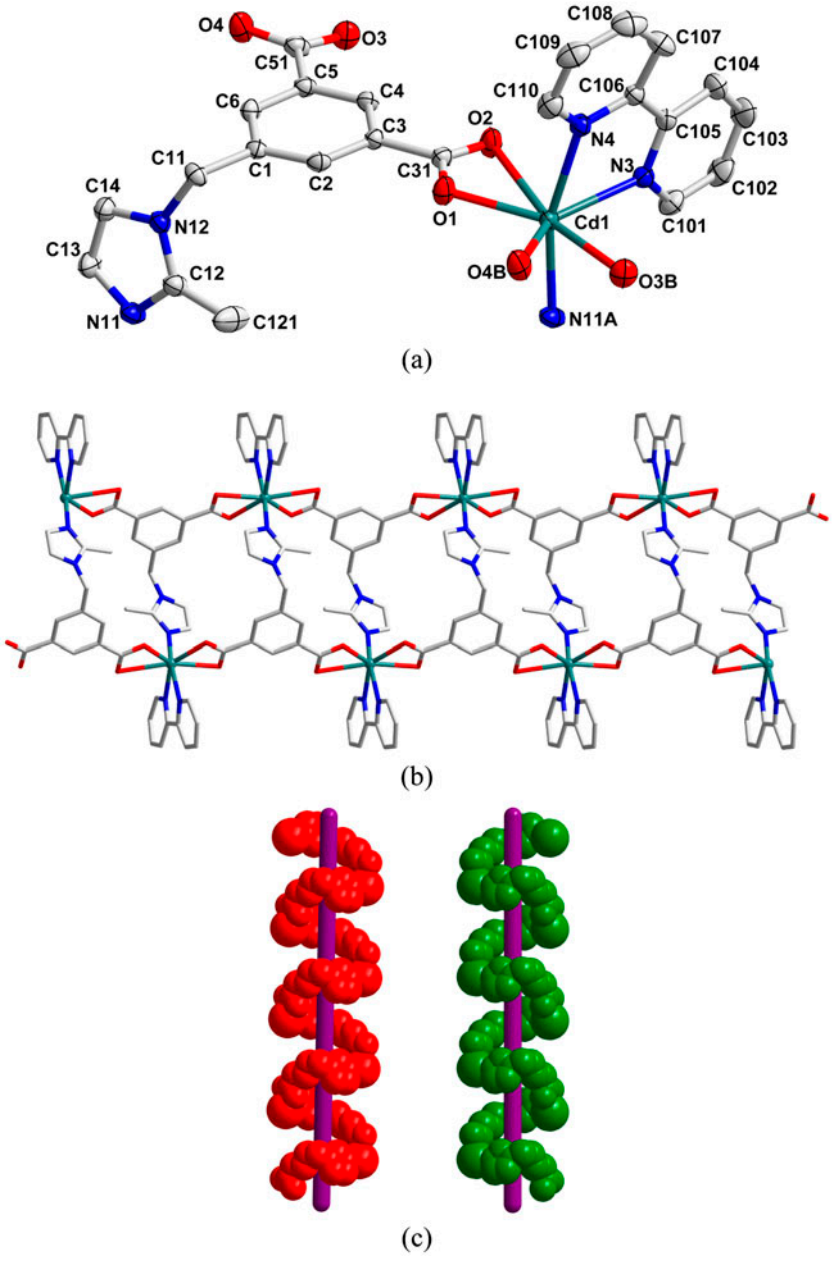


Figure 2. (a) The coordination environment of Cd(II) in complex **2** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms and lattice water are omitted for clarity, (b) view of the 1-D chain structure of **2** along *a*-axis, and (c) view of the right- and left-handed helical chains in **2**.

and thus, the L^{2-} ligands act as μ_3-linkers in **1–3**. Given the flexibility of the μ_3-linkers, the dihedral angles between the phenyl and imidazole rings are 81.32°, 75.89°, and 83.98° for complexes **1–3**. The metal coordination numbers are six for **1** and seven for **2** and **3**. The difference of the dihedral angles and coordination numbers may subtly impact on the

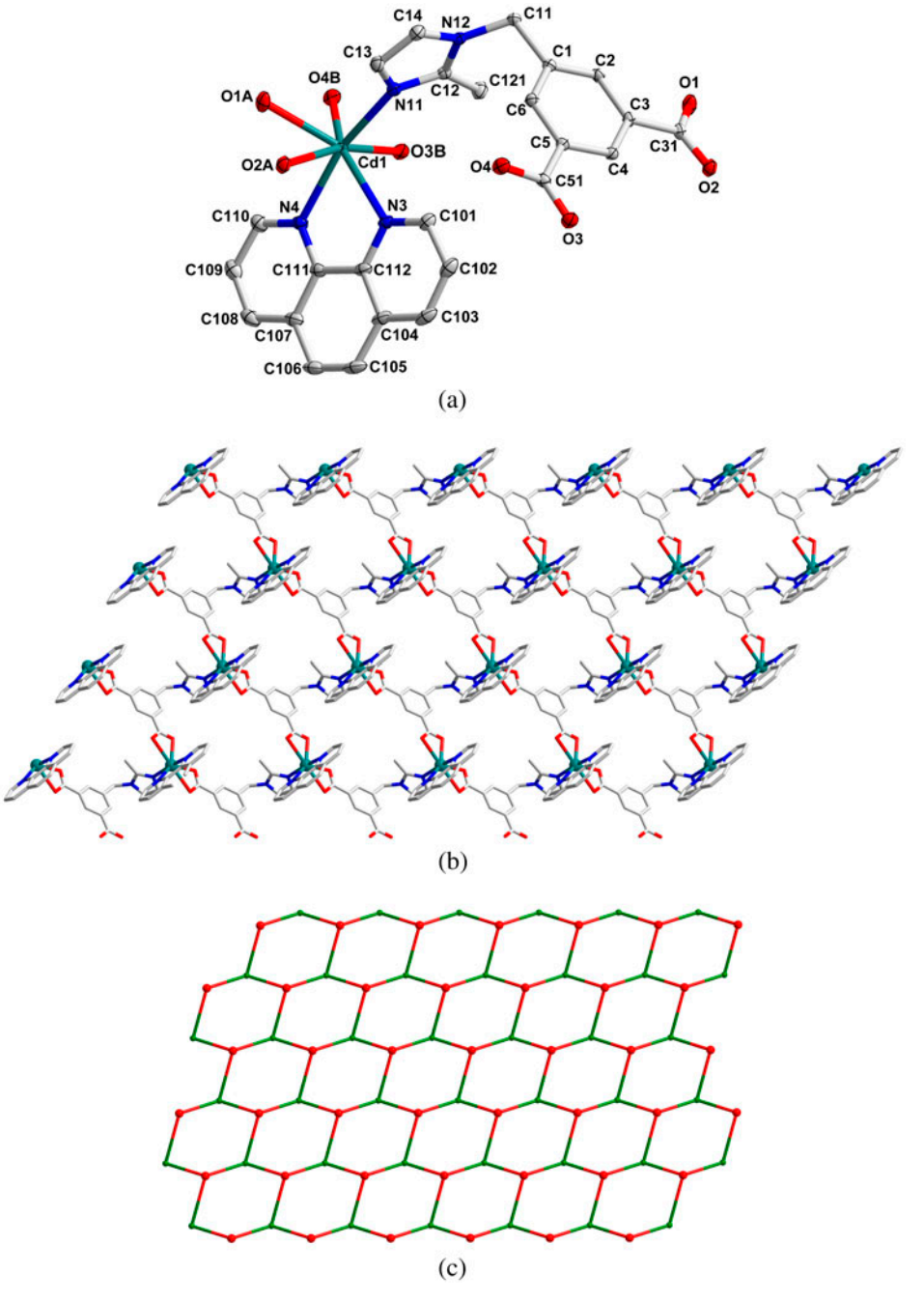


Figure 3. (a) The coordination environment of Cd(II) in complex **3** with the ellipsoids drawn at the 30% probability level. Hydrogen atoms and lattice water are omitted for clarity, (b) view of the 2-D network of **3**, and (c) topological view of the 2-D network of **3**; the bigger balls (red): metal centers; the smaller balls (green): the L^{2-} ligands (see http://dx.doi.org/10.1080/00958972.2013.867025 for color version).

diversity of structures: **1** shows 3-D framework architecture; **2** is 1-D structure; **3** displays 2-D network structure. All carboxylate in complexes **1–3** show chelating coordination modes, but they are asymmetrically chelating ones, reflected by dramatically different Cd–O bond distances within each chelating moiety, such as in complex **1**, Cd1–O1 = 2.173 Å, Cd1–O2 = 2.673 Å, Cd1–O3 = 2.237 Å and Cd1–O4 = 2.706 Å (table S1). Despite the existence of the longer Cd–O distances, they are still much shorter than the sum of van der Waals radii of Cd and O atoms (3.70 Å). Therefore, these longer Cd–O interactions are regarded as coordination bonds here. The Cd–N distances in **1** are 2.176(3) Å, and the average ones are 2.962 and 2.949 Å for **2** and **3**, which are much shorter than the sum of van der Waals radii of Cd and N atoms (3.71 Å). Because the coordination geometries of **1–3** are greatly distorted, bond angles around Cd(II) are also dramatically different (table S1).

To further comprehend the coordintion chemisty of Cd(II) Complexes with imidazole and carboxylate-containing ligands, we would here like to carry out a structural comparison of **1–3** with the Cd(II) complexes previously reported by Sun *et al.* [12–14]:

(1) Three Cd(II) complexes $[Cd(L^1)(DMF)(H_2O)]\cdot H_2O$ (**R1**), $[Cd(L^1)(H_2O)_2]_2\cdot 5H_2O$ (**R2**), and $[Cd_2(L^1)_2(H_2O)_2]_2\cdot H_2O$ (**R3**) show 1-D, 2-D (6^3) network and 3-D $(4.6^2)_2(4^2.6^{10}.8^3)$ framework structure, respectively (H_2L^1 = 5-(imidazol-1-ylmethyl)isophthalic acid) [12]. In complex **R1**, both carboxylate groups show μ_1-$\eta^1:\eta^1$-chelating coordination modes. The bond distances are in the range of 2.283(3)–2.588(3) Å and the average bond distance is 2.379 Å. In complex **R2**, the coordination mode of carboxylate is also chelating one. The longest bond distance is 2.636(3) Å; the shortest is 2.241(3) Å; the average one is 2.392 Å. In complex **R3**, carboxylate groups exhibit μ_1-$\eta^1:\eta^1$-chelating and μ_2-$\eta^1:\eta^1$-bridging coordination modes. The bond distances differ from 2.235(5) to 2.537(3) Å which can be averaged to 2.322 Å. The Cd–N distances in complexes **R1–R3** are 2.292(3), 2.241(3) and 2.263(4), and 2.235(5) Å, respectivley.

(2) Two homochiral Cd(II) complexes were obtained from a one-pot reaction L-$[Cd(tib)(BDC)]\cdot 2H_2O$ (**R4**) and R-$[Cd(tib)(BDC)]\cdot 2H_2O$ (**R5**) (tib = 1,3,5-tris(1-imidazolyl)benzene and BDC^{2-} = 1,4-benzenedicarboxylate) [13]. Complexes **R4** and **R5** display the 3-D $(8^3)_2(8^6)$ framework structures and contain the left- and right-handed helical chains. The ranges of bond distance for **R4** and **R5** are 2.272(5)–2.612(5) Å and 2.280(4) Å–2.621(4) Å. The average Cd–O and Cd–N distances are 2.468 and 2.330 Å for **R4**, which are almost identical to **R5** (2.468 and 2.333 Å).

(3) Two 3-D Cd(II) complexes D-$[Cd6(L^2)_4(D\text{-}Cam)_4(H_2O)_4]\cdot 2H_2O$ (**R6**) and L-$[Cd_6(L^2)_4(L\text{-}Cam)_4(H_2O)_4]\cdot 2H_2O$ (**R7**) with chiral chains constructed by Cd(II) cations and camphorate anions, which are a pair of enantiomers [HL = 3,5-di(imidazol-1-yl)benzoic acid, D-H_2Cam = D-camphoric acid, L-H_2Cam = L-camphoric acid]. The Cd–O distances differ from 2.312(2) to 2.641(5) for **R6** and 2.320(3) to 2.648(4) **R7**. The average Cd–O and Cd–N distances are 2.476 and 2.327 Å for **R6** and 2.479 and 2.363 Å for **R7**.

In summary, the bond distances of the complexes **1–3** are comparable to the reported Cd(II) complexes including Cd–O and Cd–N distances. Just as those reported instances, the structures of **1–3** vary from chain structure to 3-D twofold interpenetrating framework architecture under different synthetic conditions.

3.5. *PXRD and TGA*

PXRD patterns of complexes **1–3** consist with the simulated ones based on the single-crystal X-ray diffraction analysis, as shown in figure S1. The diffraction peaks correspond well in positions, indicating the phase purity of the as-synthesized samples.

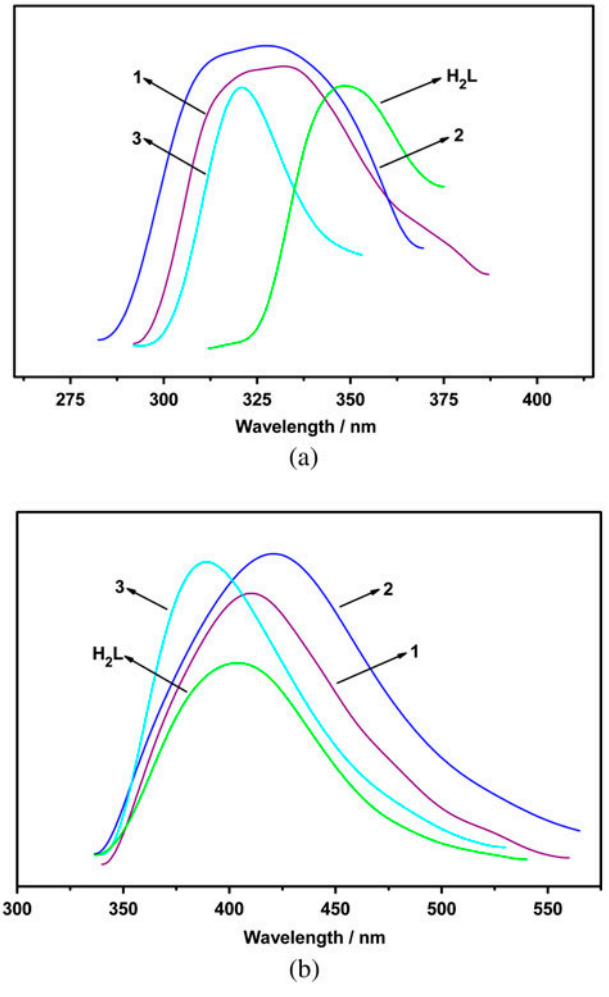


Figure 4. Fluorescence of **1–3** and H_2L in the solid state at room temperature: (a) excitation spectra, and (b) emission spectra.

To estimate the thermal stability of **1–3**, TGA were carried out under N_2 atmosphere with a heating rate of 10 °C min^{-1} and the TGA curves of **1–3** were recorded from 30 to 800 °C (figure S2). Complex **1** shows a weight loss (4.36%) in the temperature range of 180–267 °C, corresponding to the loss of coordinated water (Calcd 4.63%), and the residue is stable up to about 360 °C. For complex **2**, there is a weight loss (3.10%) from 80 to 117 °C, attributed to the release of lattice water (Calcd 3.30%), and the decomposition of the residue can be observed at 360 °C nearby. The TGA curve of **3** displays an initial weight loss of 5.85% from 72 to 123 °C, suggesting the loss of lattice water (Calcd 6.13%) and the framework can be stable up to 350 °C. When temperature approaches at 800 °C, the total weight losses for **1–3** are 63.10, 75.63, and 73.76%. However, the continuous decomposition of **1–3** does not terminate at 800 °C, so the final residuals of them are not characterized.

3.6. *Luminescent property*

Previous studies have shown that coordination compounds containing d^{10} metal centers such as Cd(II) may exhibit excellent luminescent properties and have potential applications as photoactive materials [15]. In the present work, luminescence of complexes **1–3** and the H_2L has been investigated in the solid state at room temperature. As shown in figure 4, intensive fluorescent emission can be observed with emission bands at 410 nm (λ_{ex} = 327 nm) for **1**, 421 nm (λ_{ex} = 323 nm) for **2**, 388 nm (λ_{ex} = 320 nm) for **3**, and 403 nm (λ_{ex} = 348 nm) for H_2L ligand, respectively. Moreover, the emission spectra of bpy and phen have also been recorded with emission bands at 526 nm (λ_{ex} = 337 nm) and 521 nm (λ_{ex} = 369 nm) (figure S3). The fluorescent emission of **1–3** may be tentatively assigned to intra-ligand transition of coordinated L^{2-} ligands, since similar emission was observed for free H_2L [15]. Meanwhile, the emission of the L^{2-} ligands in **1–3** may be affected by their incorporation into the Cd(II)-containing polymeric compounds, as evidenced by the red- or blue-shift compared with free H_2L ligand. The observation of red- (**1** and **2**) or blue- (**3**) shifts of the emission maximum in **1–3** may originate from the coordination of the ligands to the metal centers [16]. Accordingly, complexes **1–3** could be potentially used as luminescent materials due to their good thermal stabilities and strong photoluminescence.

4. Conclusion

In summary, three new Cd(II) coordination polymers have been synthesized under the hydrothermal synthetic conditions. The structures of complexes **1–3** varied from chain structure to 3-D twofold interpenetrating framework architecture with different topologies. The structural diversity of resultant complexes is achieved by the presence and alteration of auxiliary ligands. The results imply that auxiliary ligands can subtly impact on formation of complexes.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication [CCDC 942463-942465 for **1–3**]. 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).

Funding

This work was supported by the Huaian Administration of Science and Technology of Jiangsu Province of China [HAG201222] and [HC201216].

References

[1] (a) Z.M. Wang, K.L. Hu, S. Gao, H. Kobayashi. *Adv. Mater.*, **22**, 1526 (2010); (b) L.F. Ma, X.Q. Li, L.Y. Wang, H.W. Hou. *CrystEngComm.*, **13**, 4625 (2011); (c) H.W. Kuai, X.C. Cheng, X.H. Zhu. *Polyhedron*, **50**, 390 (2013); (d) H.W. Kuai, X.C. Cheng, X.H. Zhu. *Polyhedron*, **53**, 113 (2013); (e) Y. Liu, K. Li, S.C. Wei, M. Pan, C.Y. Su. *CrystEngComm.*, **13**, 4564 (2011).

[2] (a) D.J. Tranchemontagne, J.L. Mendoza-Cortés, M. O'Keeffe, O.M. Yaghi. *Chem. Soc. Rev.*, **38**, 1257 (2009); (b) J.R. Li, R.J. Kuppler, H.C. Zhou. *Chem. Soc. Rev.*, **38**, 1477 (2009); (c) C.A. Bauer, T.V. Timofeeva, T.B. Settersten, B.D. Patterson, V.H. Liu, B.A. Simmons, M.D. Allendorf. *J. Am. Chem. Soc.*, **129**, 7136 (2007); (d) B.L. Chen, S.C. Xiang, G.D. Qian. *Acc. Chem. Res.*, **43**, 1115 (2010).
[3] (a) X.J. Wang, Z.M. Cen, Q.L. Ni, X.F. Jiang, H.C. Lian, L.C. Gui, H.H. Zuo, Z.Y. Wang. *Cryst. Growth Des.*, **10**, 2960 (2010); (b) H.W. Kuai, X.C. Cheng, X.H. Zhu. *Inorg. Chem. Commun.*, **25**, 43 (2012); (c) Y. Qiu, Z. Liu, J. Mou, H. Deng, M. Zeller. *CrystEngComm.*, **12**, 277 (2010); (d) H.W. Kuai, X.C. Cheng, X.H. Zhu. *J. Coord. Chem.*, **66**, 1795 (2013); (e) H.W. Kuai, X.C. Cheng, X.H. Zhu. *J. Coord. Chem.*, **66**, 28 (2013).
[4] (a) H.N. Miras, I. Chakraborty, R.G. Raptis. *Chem. Commun.*, **46**, 2569 (2010); (b) S. Hu, Z.M. Zhang, Z.S. Meng, Z.J. Lin, M.L. Tong. *CrystEngComm.*, **12**, 4378 (2010); (c) H.B.T. Jeazet, K. Gloe, T. Doert, O.N. Kataeva, A. Jager, G. Geipel, G. Bernhard, B. Buchner, K. Gloe. *Chem. Commun.*, **46**, 2373 (2010).
[5] (a) H.W. Kuai, X.C. Cheng, L.D. Feng, X.H. Zhu. *Z. Anorg. Allg. Chem.*, **637**, 1560 (2011); (b) B. Zhao, L. Yi, Y. Dai, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem.*, **44**, 911 (2005); (c) H.W. Kuai, X.C. Cheng, X.H. Zhu. *J. Coord. Chem.*, **64**, 3323 (2011); (d) S. Mishra, E. Jeanneau, H. Chermette, S. Daniele, L.G. Hubert-Pfalzgraf. *Dalton Trans.*, 620 (2008).
[6] (a) H.W. Kuai, T.A. Okamura, W.Y. Sun. *J. Coord. Chem.*, **65**, 3147 (2012); (b) H.W. Kuai, C. Hou, W.Y. Sun. *Polyhedron*, **52**, 1268 (2013).
[7] (a) J. Fan, B.E. Hanson. *Inorg. Chem.*, **44**, 6998 (2005); (b) G.C. Xu, Q. Hua, T.A. Okamura, Z.S. Bai, Y.J. Ding, Y.Q. Huang, G.X. Liu, W.Y. Sun, N. Ueyama. *CrystEngComm.*, **11**, 261 (2009).
[8] Bruker. *SAINT. Program for Data Extraction and Reduction*, Bruker AXS Inc., Madison, Wiskonsin, USA (2002).
[9] G.M. Sheldrick. *SADABS, Program for Bruker Area Detector Absorption Correction*, University of Göttingen, Göttingen, Germany (1997).
[10] G.M. Sheldrick. *Acta Cryst. A*, **64**, 112 (2008).
[11] (a) V.A. Blatov. *IUCr CompComm Newsletter*, **7**, 4 (2006); (b) V.A. Blatov. *TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package*, Samara State University, Samara, Russia (2009).
[12] H.W. Kuai, J. Fan, Q. Liu, W.Y. Sun. *CrystEngComm.*, **14**, 3708 (2012).
[13] Z. Su, M.S. Chen, J. Fan, M. Chen, S.S. Chen, L. Luo, W.Y. Sun. *CrystEngComm.*, **12**, 2040 (2010).
[14] Z. Su, G.C. Lv, J. Fan, G.X. Liu, W.Y. Sun. *Inorg. Chem. Commun.*, **15**, 317 (2012).
[15] (a) G.H. Wei, J. Yang, J.F. Ma, Y.Y. Liu, S.L. Li, L.P. Zhang. *Dalton Trans.*, 3080 (2008); (b) W. Chen, J.Y. Wang, C. Chen, Q. Yue, H.M. Yuan, J.S. Chen, S.N. Wang. *Inorg. Chem.*, **42**, 944 (2003).
[16] (a) S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong. *Inorg. Chem.*, **43**, 830 (2004); (b) L. Zhang, Z.J. Li, Q.P. Lin, Y.Y. Qin, J. Zhang, P.X. Yin, J.K. Cheng, Y.G. Yao. *Inorg. Chem.*, **48**, 6517 (2009).