Cd(II) complexes based on a tricarboxylate: synthesis, structural characterization and properties

Hai-Wei Kuai [a], Xiao-Chun Cheng [a] & Xiao-Hong Zhu [a]

[a] Faculty of Life Science and Chemical Engineering, Huaiyin
Institute of Technology, Huaian, China
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Cd(II) complexes based on a tricarboxylate: synthesis, structural characterization and properties

HAI-WEI KUAI*, XIAO-CHUN CHENG and XIAO-HONG ZHU

Faculty of Life Science and Chemical Engineering, Huaiyin Institute of Technology, Huaian, China

Reactions of cadmium(II) with 5-(4-carboxybenzylamino)isophthalic acid (H_3L) in the presence of 2-(pyridin-2-yl)-1H-benzo[d]imidazole (pybim) and 2,2′-bipyridine (bpy) by hydrothermal method lead to two complexes, $[Cd(HL)(pybim)]\cdot H_2O$ (**1**) and $[Cd_2(L)(HCOO)(bpy)_2(H_2O)]\cdot H_2O$ (**2**). Complexes **1** and **2** have been characterized by single-crystal and powder X-ray diffraction, Infrared spectra, and elemental and thermogravimetric analyses. **1** has a double-chain structure while **2** consists of uninodal 3-connected 2-D **hcb** networks with (6^3) topology. Luminescence and sorption properties of **1** and **2** were also investigated.

Keywords: Cd(II) complexes; Structural characterization; Fluorescence; Adsorption

1. Introduction

Synthesis of metal-organic frameworks (MOFs) has attracted attention for esthetic architectures and potential applications in many fields [1]. Many MOFs have been reported and are a main aim of crystal engineering [2]. Properties of complexes are largely dependent on the nature of the metal centers, bridging ligands, and architectures. For example, complexes with porous frameworks may show sorption properties [3]; metal ions possessing unpaired electrons, such as Cu(II), could be bridged by ligands to form polynuclear subunits which may mediate magnetic interactions [4]; complexes containing metal centers with d^{10} electron configuration such as Cd(II) may exhibit luminescence [5]. Therefore, it is significant to pursue structural diversity using different experimental conditions for diverse properties of multifunctional materials [6]. The organic ligands play a decisive role in formation of complexes, providing impetus to select versatile ligands for MOFs [7].

In the previous research, rigid carboxylates, such as isophthalate, terephthalate, and 1,3,5-benzenetricarboxylate, have been studied in synthesis of complexes owing to coordination and connectivities [8]. Ligands that contain both rigid and flexible carboxylates deserve further study because of the variable and abundant coordination modes [9]. Recently, we have focused on coordination of metal salts with a tricarboxylate ligand, 5-(4-carboxybenzylamino)isophthalic acid (H_3L), to assemble complexes with fascinating

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*Corresponding author. Email: kuaihaiwei@hyit.edu.cn

structures and interesting properties. H_3L has an advantage over other carboxylates since it possesses both rigid and flexible coordinative groups. As a carboxylate-containing ligand, H_3L is of particular interest because of potential variable coordination modes such as terminal monodentate, chelating, bridging bidentate, and bridging tridentate, and also because of its ability to act as hydrogen bonding acceptors or donors to assemble supramolecular frameworks [10]. H_3L could be partially or completely deprotonated by alkaline reagents to L^{3-}, HL^{2-}, or H_2L^-, which further enrich the coordination patterns. H_3L contains a flexible carboxylate, which could axially rotate to meet coordinating requirements [11]. We report herein synthesis and characterization of two coordination polymers, $[Cd(HL)(pybim)] \cdot H_2O$ (**1**) and $[Cd_2(L)(HCOO)(bpy)_2(H_2O)] \cdot H_2O$ (**2**). Additionally, **1** and **2** were characterized by single crystal and powder X-ray diffraction (PXRD), infrared spectra (IR), and elemental and thermogravimetric analyses (TGA), and luminescence and sorption properties were investigated.

2. Experimental

2.1. *Materials and methods*

All commercially available chemicals are of reagent grade and used as received. A slightly revised experimental procedure [12] was used to synthesize H_3L. Elemental analyses of C, H, and N were taken on a Perkin–Elmer 240C elemental analyzer. IR were recorded on a Bruker Vector22 FT-IR spectrophotometer with KBr pellets. TGA was performed on a simultaneous SDT 2960 thermal analyzer under nitrogen with a heating rate of $10\,^{\circ}C\,min^{-1}$. PXRD patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα ($\lambda = 1.5418\,\text{Å}$) radiation at room temperature. Luminescence spectra for 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. Sorption experiments were carried out on a Belsorp-max volumetric gas sorption instrument. The bulk samples for sorption experiments were obtained by heating complexes for $10\,h$ at $150\,^{\circ}C$ for **1** and **2**.

2.2. *Preparation of [Cd(HL)(pybim)]·H₂O (1)*

A reaction mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (92.4 mg, 0.3 mM), H_3L (31.5 mg, 0.1 mM), and pybim (19.5 mg, 0.1 mM) in H_2O/DMF (5 mL : 5 mL) was sealed in a 16 mL Teflon-lined stainless steel container and heated at $100\,^{\circ}C$ for 72 h and cooled at $10\,^{\circ}Ch^{-1}$. After cooling to room temperature, colorless plates of **1** were obtained with an approximate yield of 20% based on H_3L. Calcd for $C_{28}H_{22}N_4O_7Cd$ (%): C, 52.64; H, 3.47; N, 8.77. Found (%): C, 52.90; H, 3.68; N, 9.02. IR (KBr pellet, cm^{-1}): 3372 (m), 1682 (s), 1607 (m), 1546 (s), 1425 (s), 1377 (s), 1317 (s), 1287 (m), 1244 (s), 1190 (w), 1142 (m), 1118 (w), 1105 (m), 1002 (w), 936 (w), 869 (m), 845 (s), 821 (m), 772 (s), 736 (s), 700 (m), 634 (w), 579 (w), 518 (w).

2.3. *Preparation of [Cd₂(L)(HCOO)(bpy)₂(H₂O)]·H₂O (2)*

Complex **2** was obtained under the same reaction conditions as for the preparation of **1** except that bpy (15.6 mg, 0.1 mM) was used instead of pybim. Colorless slender crystals

of **2** were obtained with an approximate yield of 15% based on H$_3$L. Calcd for C$_{37}$H$_{31}$N$_5$O$_{10}$Cd$_2$ (%): C, 47.76; H, 3.36; N, 7.53. Found (%): C, 47.55; H, 3.16; N, 7.75. IR (KBr pellet, cm^{-1}): 3462 (m), 1627 (s), 1579 (s), 1471 (m), 1443 (s), 1404 (s), 1357 (s), 1247 (m), 1149 (m), 1102 (m), 1056 (m), 1024 (m), 891 (m), 786 (s), 766 (s), 735 (m), 715 (m), 653 (m), 629 (m).

2.4. *X-ray crystallography*

The crystallographic data collections for **1** and **2** were carried out on a Bruker Smart ApexII CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The diffraction data were integrated using SAINT [13], which was also used for intensity corrections for Lorentz and polarization effects. Semi-empirical absorption correction was applied using *SADABS* [14]. The structures of **1** and **2** were solved by direct methods and all non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares using *SHELXL-97* package [15]. For **1** and **2**, all hydrogens attached to C were generated geometrically using the riding model, while hydrogens on oxygen and nitrogen 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; selected bond lengths and angles are listed in table S1.

3. Results and discussion

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

Complex **1** was obtained by the hydrothermal reaction of Cd(NO$_3$)$_2$·4H$_2$O, H$_3$L, and pybim in H$_2$O/DMF (1 : 1, V/V) in a Teflon-lined reactor at 100 °C. Single crystal X-ray

Table 1. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	C$_{28}$H$_{22}$N$_4$O$_7$Cd	C$_{37}$H$_{31}$N$_5$O$_{10}$Cd$_2$
Formula weight	638.90	930.47
Temperature/K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	*P2$_1$/c*
a/Å	10.2306(11)	14.4065(11)
b/Å	10.3931(11)	17.7616(13)
c/Å	14.593(2)	14.0776(10)
α/°	106.914(2)	90.00
β/°	95.523(2)	97.6380(10)
γ/°	114.188(2)	90.00
V(Å^3)	1312.3(3)	3570.3(5)
Z, D_{Calcd}/(Mg/m^3)	2	4
F (0 0 0)	644	1856
θ range/°	1.51–28.38	1.43–28.29
Reflections collected	9492	25,556
Independent reflections	6469	8850
Goodness-of-fit on F^2	0.996	1.024
R_1 [$I > 2\sigma(I)$][a]	0.0386	0.0356
wR_2 [$I > 2\sigma(I)$][b]	0.0948	0.0780

[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 $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

structural analysis revealed that **1** crystallizes in the triclinic space group *P-1* exhibiting a double-chain structure. H_3L was deprotonated to HL^{2-}. The asymmetric unit of **1** consists of one Cd(II), one HL^{2-}, one pybim, and one lattice water. As shown in figure 1(a), Cd1 is seven-coordinate with a distorted pentagonal bipyramidal geometry by N1 and N2 from coordinated pybim with Cd–N bond distances of 2.398(3) and 2.280(3) Å (table S1); five carboxylate oxygens from three different HL^{2-} with Cd–O bond lengths of 2.254(2)–2.715(2) Å. The Cd–O and Cd–N bond distances are comparable to previously reported values [16]. The coordinating bond angles around Cd(II) vary from 51.43(7) to 164.57 (7)°. In **1**, each HL^{2-} adopts coordination mode **A**, as shown in scheme 1, as a μ_3-bridge to link three Cd(II), and each carboxylate in HL^{2-} links one Cd(II). Each Cd(II) is surrounded by three different HL^{2-}. This interconnection repeats infinitely to give a double-chain structure along the [1 0 0] direction (figure 1(b)). Because of the flexibility of HL^{2-}, the double-chain stretches in a spiral way. If some organic moieties are ignored, a pair of right- and left-handed helical chains can be isolated from the neutral double-stranded chain (figure 1(c)). Weak interactions are available in **1** (figure S1a, table S2). Adjacent chains can be further linked to form the 2-D supramolecular network (figure 1 (d)) by hydrogen bonding interactions O6–H6A···O3#2 [#2: *x*, *y*, 1+*z*]. Lattice waters bridge different layers through H bonds [O1W–H1WA···O2(#1) and O1W–H1WB···O2 (#2), #1: 1−*x*, −*y*, 1−*z*; #2: *x*, *y*, 1+*z*] to finally build the 3-D supramolecular framework (figure S1b).

3.2. *Crystal structure description of [Cd$_2$(L)(HCOO)(bpy)$_2$(H$_2$O)]·H$_2$O (2)*

When 2,2′-bipyridine (bpy) was introduced into the hydrothermal reaction instead of pybim, **2** was obtained, which is composed of uninodal 3-connected 2-D **hcb** (6^3) networks in monoclinic *P2$_1$*/c space group. H_3L was completely deprotonated to L^{3-}, which could be confirmed by IR spectrum for the absence of vibration bands at 1680–1760 cm^{-1}. The asymmetric unit of **2** contains two Cd(II), one L^{3-}, one *in situ* generated formate, two 2,2′-bipyridines, one coordinated water, and one lattice water. As shown in figure 2(a), Cd1 and Cd2 are six-coordinate and display distorted octahedral geometries, supplied by two nitrogens of bpy and four oxygens. The coordinating bond angles vary from 54.73(7) to 165.62(8)° for Cd1 and from 53.61(8) to 165.00(9)° for Cd2; the average bond lengths around Cd1 and Cd2 are 2.365 and 2.328 Å, respectively. Two Cd(II) are bridged by one *in situ* formate resulting in a dinuclear secondary building unit (SBU) [Cd$_2$(COO)(bpy)$_2$] with Cd···Cd distance of 4.29 Å, which is shorter than the sum of the van der Waals radii (4.60 Å) [17]. Existing π–π stacking interactions between almost parallel planes of 2,2′-bipyridines further consolidate the SBU. The centroid–centroid distance between two pairs of pyridine rings are 3.92 and 3.81 Å, respectively (figure 2(b)). The two 2,2′-bipy molecules are practically planar with dihedral angles between the mean pyridyl planes of 3.36 and 1.60°, respectively]. The coordination of L^{3-} in **2** is shown in scheme 1(B); each L^{3-} links three SBUs and every SBU is also surrounded by three L^{3-}, which repeat infinitely to exhibit a 2-D network structure (figure 2(c)). Both SBUs and L^{3-} could be regarded as 3-connector nodes in **2**. Its structure could be simplified as a uninodal 3-connected 2-D **hcb** network with (6^3) topology (figure 2(d)) [18]. Hydrogen bonds exist in **2** (figure S2a), which further superpose 2-D layers to construct the 3-D supramolecular network (figure S2b).
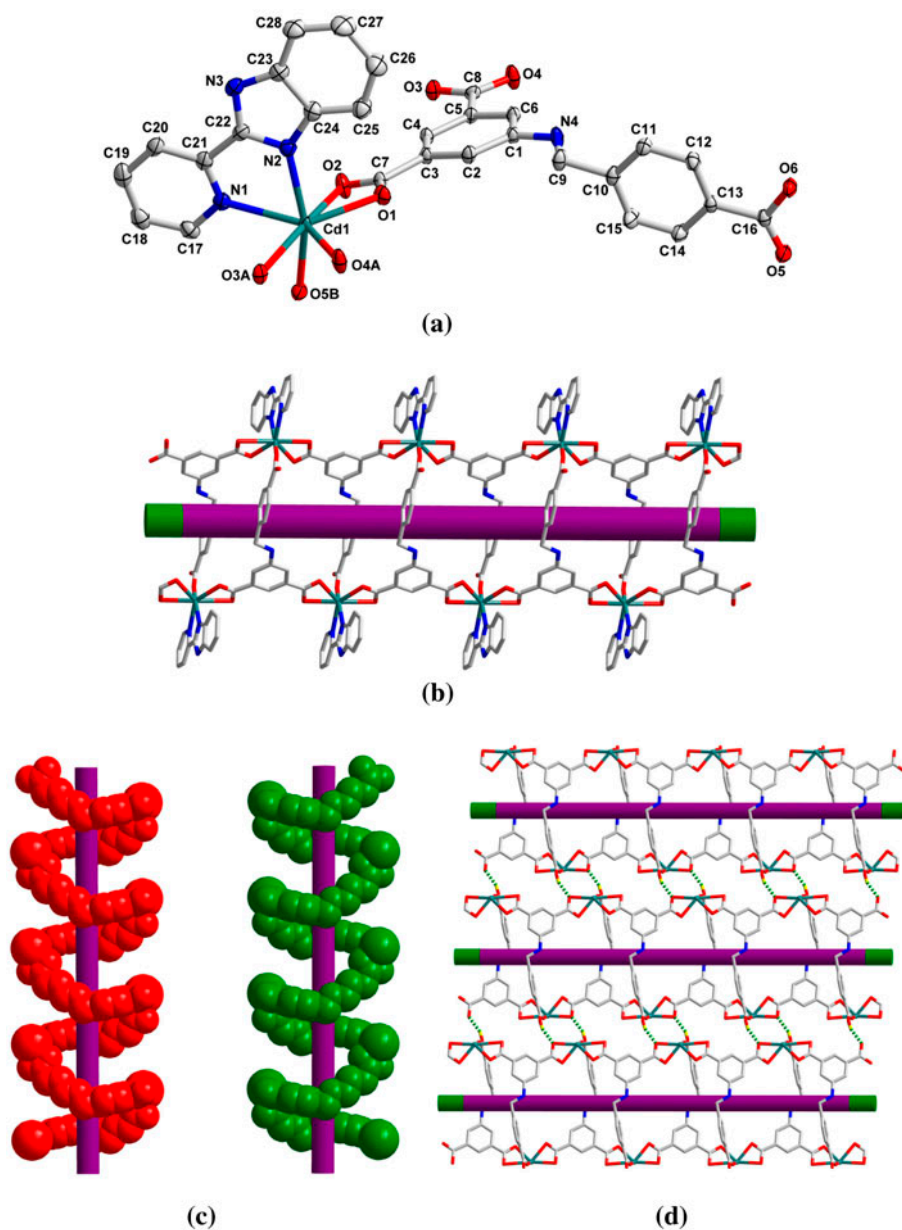
(a)

(b)

(c)

(d)

Figure 1. (a) The coordination environment of Cd(II) in **1** with ellipsoids drawn at the 30% probability level. Hydrogens and lattice water are omitted for clarity. Symmetry transformations: #A, $-1+x$, y, z; #B, $1-x$, $-y$, $1-z$. (b) The neutral double-stranded chain of **1**. (c) Schematic view of the right- and left-handed helical chains in **1**. (d) The 2-D network of **1** extended by hydrogen bonding interactions.

3.3. *PXRD and TGA*

The phase purity of **1** and **2** could be proved by PXRD analyses. As shown in figure S3, each pattern of the bulk sample was in agreement with the simulated pattern from the corresponding single crystal data.
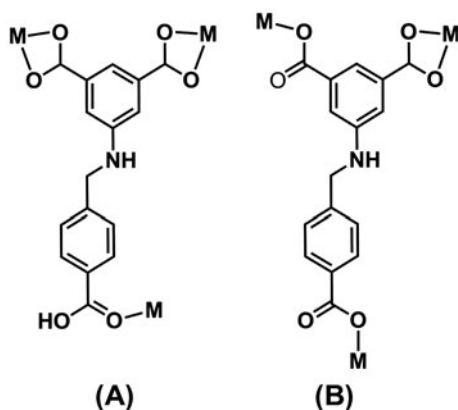
Scheme 1. Coordination modes of HL^{2-}/L^{3-} in the complexes: A in **1**; B in **2**.

To estimate the thermal stabilities of **1** and **2**, TGA were carried out under N_2 with a heating rate of 10 °C/min; TGA curves of **1** and **2** were recorded from 30 to 800 °C (figure S4). Complex **1** shows a weight loss (2.53%) from 100 to 132 °C corresponding to loss of lattice water (Calcd 2.82%) and the residue is stable up to 263 °C. For **2**, there is continuous weight loss of 3.99% starting at 55 °C assigned to liberation of water (Calcd 3.87%); decomposition of the framework occurs at 252 °C.

3.4. *Luminescence*

Luminescent properties of Cd(II) are of interest for their potential applications as photoactive materials [19]. Therefore, the luminescences of **1** and **2**, as well as free H_3L, were investigated in the solid state at room temperature. As shown in figure 3, intense bands were observed at 436 nm ($\lambda_{ex} = 365$ nm) for **1**, 536 nm ($\lambda_{ex} = 373$ nm) for **2**, and 451 nm ($\lambda_{ex} = 336$ nm) for H_3L. The fluorescence may be assigned to intra-ligand transition of HL^{2-}/L^{3-}, since Cd(II) is difficult to be oxidized or reduced and a similar emission can be observed for free H_3L [20]. The observed red shift for **2** and blue shift for **1** of the emission maximum for complexes *versus* H_3L may originate from coordination interactions [21]. Luminescent intensities are very difficult to analyze quantitatively, because they relate not only to structures of complexes but also to amounts of samples used in the measurements.

3.5. *Dynamic nature of the complexes and sorption properties*

According to TGA data of **1** and **2**, the frameworks are stable to 250 °C and the stability of the frameworks upon dehydration and rehydration can be evaluated via PXRD measurements (figures S3 and S4). Water can be completely removed from the frameworks through heating in high vacuum at 150 °C for **1** and **2**. The dehydrated samples of **1** are still crystalline while **2** lost most of its crystallinity. The difference between the PXRD patterns of the as-synthesized sample and the dehydrated one indicates the transformation of the framework upon the desolvation. To further investigate dynamic nature of the
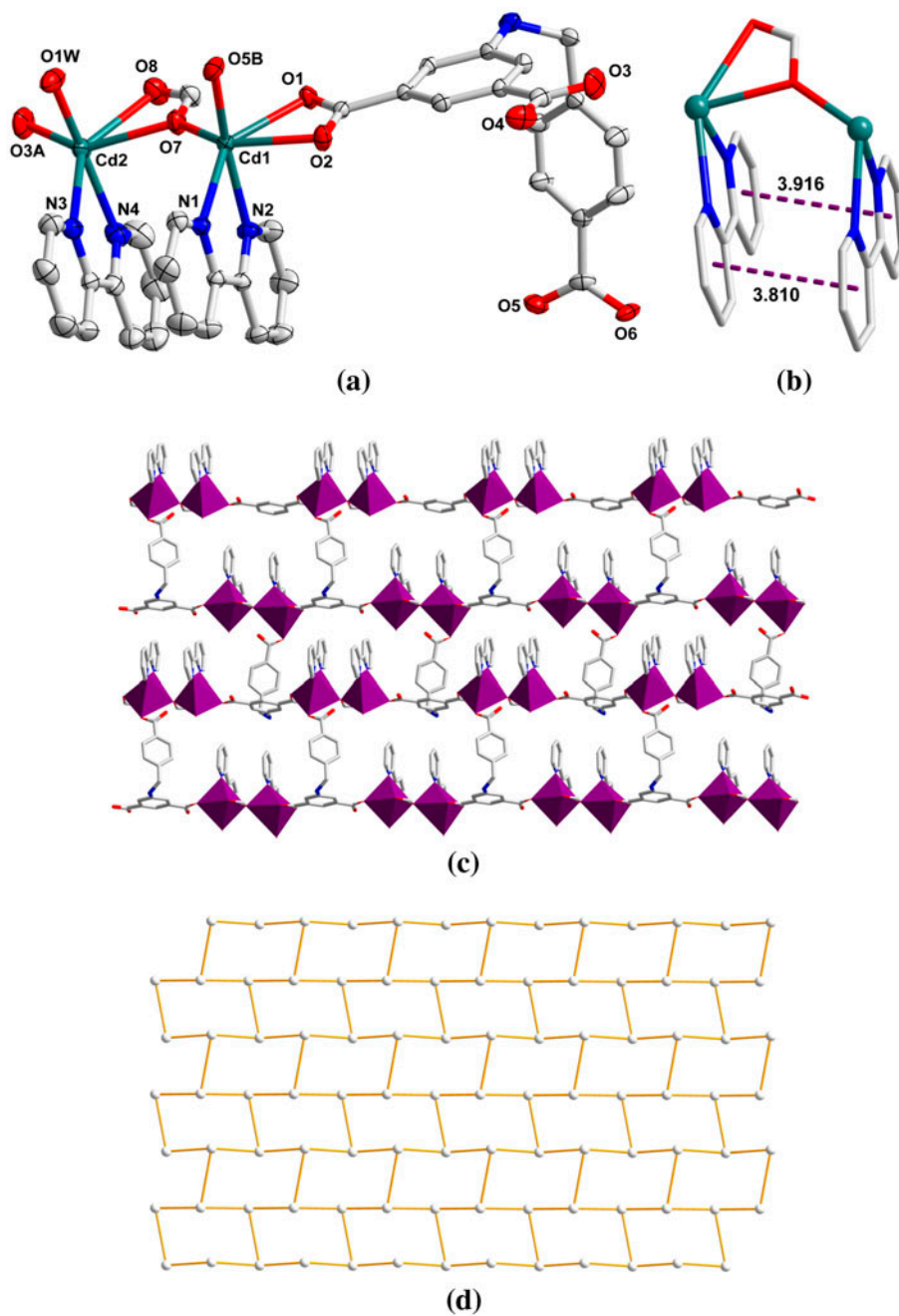
Figure 2.   (a) The coordination environment of Cd(II) in **2** with ellipsoids drawn at the 30% probability level. Hydrogens and lattice water are omitted for clarity. Symmetry transformations: #A, $-1+x$, y, z; #2, $2-x$, $1/2+y$, $1/2-z$. (b) View of SBU $[Cd_2(COO)(bpy)_2]$ in **2**. (c) View of the 2-D network of **2**. (d) Topological view of the 2-D **hcb** (6^3) network of **2**.
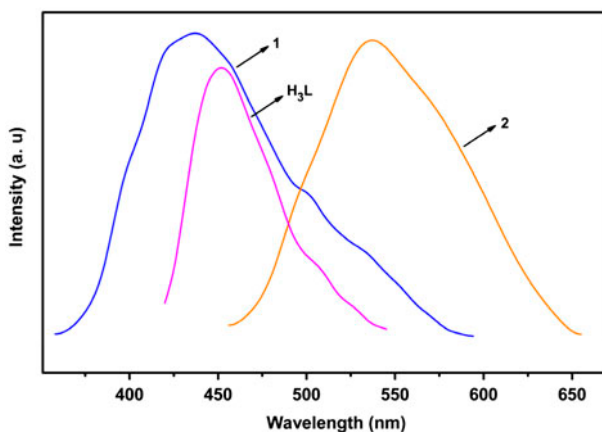
Figure 3.   Emission spectra of **1** and **2** and H₃L in the solid state at room temperature.

frameworks, dehydrated samples of **1** and **2** were exposed to water vapor at 298 K for 10 h. As a result, the PXRD patterns of the rehydrated samples of **1** and **2** matches with the as-synthesized ones, indicating the frameworks of **1** and **2** are recoverable, exhibiting their dynamic natures.

A further study was undertaken to quantitatively investigate water (kinetic diameter, 2.65 Å) and methanol (3.80 Å) vapor adsorption of dehydrated samples of **1** and **2**. At 298 K and 1 atm, the water vapor adsorption amount of $40.22 \, cm^3 \, g^{-1}$ ($32.32 \, mg \, g^{-1}$) and $56.27 \, cm^3 \, g^{-1}$ ($45.22 \, mg \, g^{-1}$) correspond to 1.1 and 2.2 waters per formula unit for **1** and **2**, respectively (figure 4), approximately equal to the corresponding amount of 1.0 and 2.0 waters determined by crystallographic analysis; the final methanol vapor adsorption amount is much less than water vapor: $19.79 \, cm^3 \, g^{-1}$ ($28.30 \, mg \, g^{-1}$) and $26.26 \, cm^3 \, g^{-1}$ ($37.56 \, mg \, g^{-1}$) corresponding to 0.55 and 0.52 methanols per formula unit for **1** and **2** (figure 4). The large hysteresis and stepwise process of H_2O and MeOH adsorption profiles of **1** and **2** are characteristic of the dynamic nature of flexible frameworks [22]. The affinity of **1** and **2** to water is ascribed to the restoration of coordinated and lattice waters into the frameworks [23]. The adsorption of dehydrated samples for
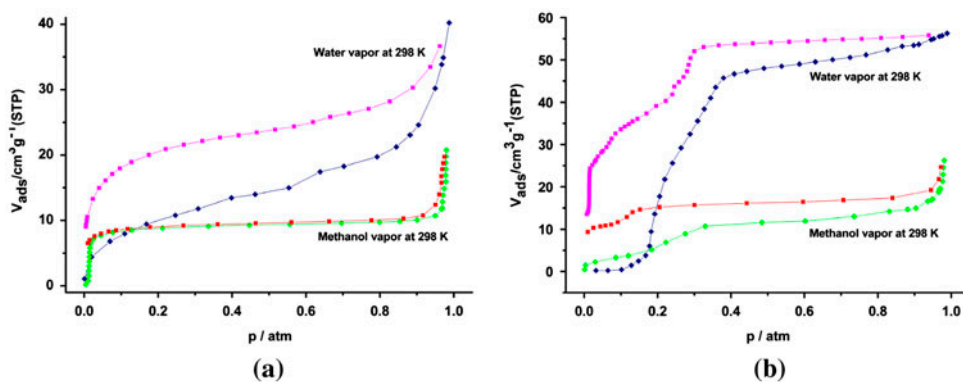

Figure 4.   Sorption isotherms of water and methanol vapor for **1** (a) and **2** (b).

methanol vapor is ascribed to high polarity of the pore surfaces since methanol is polar and can interact effectively through the O–H···O/N–H···O hydrogen bonding interactions with the host frameworks [24].

4. Conclusion

Two new Cd(II) complexes based on H_3L have been synthesized under hydrothermal conditions. In spite of very similar synthetic strategies, the *in situ* reaction takes places for **2**, but not for **1**, showing that auxiliary ligands can subtly influence the formation of complexes. Complexes **1** and **2** emit intense photoluminescence. Moreover, **1** and **2** show dynamic water and methanol vapor sorption.

Supplementary material

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication [CCDC 917698 and 917699 for **1** and **2**]. 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).

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