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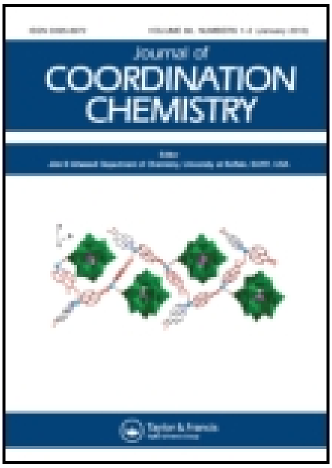

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Syntheses, structures, and properties of two 2-D Cd(II) complexes based on 2-(1H-imidazol-1-methyl)-1H-benzimidazole and polycarboxylate ligands

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Syntheses, structures, and properties of two 2-D Cd(II) complexes based on 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole and polycarboxylate ligands

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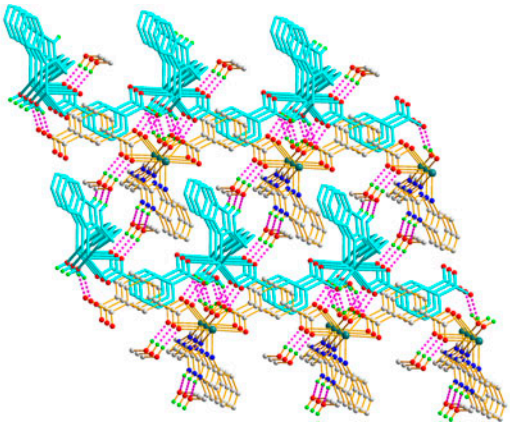

Two new 2-D Cd(II) complexes $\{[Cd(imb)(bdc)(H_2O)]\cdot CH_3OH\}_n$ (**1**) and $\{[Cd(imb)(Hbtc)(CH_3OH)]\cdot 2H_2O\cdot CH_3OH\}_n$ (**2**) have been synthesized and characterized by single crystal X-ray diffraction. Their IR, TG and fluorescent properties have also been investigated.

Two 2-D Cd(II) complexes, $\{[Cd(imb)(bdc)(H_2O)]\cdot CH_3OH\}_n$ (**1**) and $\{[Cd(imb)(Hbtc)(CH_3OH)]\cdot 2H_2O\cdot CH_3OH\}_n$ (**2**), have been synthesized by reactions of $CdCl_2\cdot 2.5H_2O$ with 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole (imb) and 1,3-benzenedicarboxylic acid (H_2bdc) or 1,3,5-benzenetricarboxylic acid (H_3btc). Single-crystal X-ray diffraction shows that **1** possesses an infinite 2-D layered structure in which all the carboxylates chelate Cd(II) and imb bridge Cd(II) ions. Complex **2** also features an infinite 2-D layered structure and imb ligands also bridge Cd(II) ions, but two carboxylates of each 1,3,5-benzenetricarboxylate coordinate to Cd(II) in monodentate or chelating mode, leaving the third one, which is not deprotonated, uncoordinated. IR spectra, fluorescent properties, and thermogravimetric analyses of both complexes have been investigated.

Keywords: Cadmium complex; Crystal structure; Fluorescence; Thermogravimetric analysis

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1. Introduction

It is a long-term challenge to construct complexes with desired structures and properties since many factors contribute to formation of products, such as metal ion and coordination possibilities [1–3], structural characterization of the organic ligand [4], counter ion, reaction temperature, and solvent [5–7]. Selection of the organic ligand plays an important role in construction of complexes. Multidentate *N*-heterocyclic flexible ligands have been widely employed to construct complexes because they have abundant coordination sites and flexible backbones like alkyl spacers that can form variable coordination modes and allow for greater structural diversity [8–10]; aromatic polycarboxylates have various coordination modes to form diverse structures and can act as hydrogen bonding acceptors and donors in the assembly of supramolecular structures [11]. Aromatic polycarboxylates such as 1,2-benzenedicarboxylate, 1,3-benzenedicarboxylate, 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 1,2,4,5-benzenetetracarboxylate have been used in preparation of metal–organic complexes with multidimensional networks and interesting properties [12–14]. Cd(II) ions coordinate to both oxygen-containing and nitrogen-containing ligands easily and the final products can exhibit promising luminescent properties [15].

Employment of *N*-heterocyclic ligands and aromatic polycarboxylates is an effective approach for construction of MOFs and numerous complexes based on these ligands have been reported [16–22]. In this article, we select *N*-heterocycle flexible 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole (imb) and 1,3-benzenedicarboxylic acid (H_2bdc) or 1,3,5-benzenetricarboxylic acid (H_3btc) as ligands with $CdCl_2{\cdot}2.5H_2O$ and obtain two 2-D complexes, $\{[Cd(imb)(bdc)(H_2O)]{\cdot}CH_3OH\}_n$ (**1**) and $\{[Cd(imb)(Hbtc)(CH_3OH)]{\cdot}2H_2O{\cdot}CH_3OH\}_n$ (**2**). The structures are characterized by single-crystal X-ray diffraction and luminescent properties and thermogravimetric features are also investigated.

2. Experimental

2.1. *General information and materials*

All chemicals were purchased of AR grade and used without purification. 2-(1*H*-imidazole-1-yl-methyl)-1*H*-benzimidazole (imb) was synthesized according to the literature [23, 24]. The IR spectra were obtained on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses (C, H, and N) were performed on a FLASH EA 1112 elemental analyzer. PXRD pattern was recorded using Cu-Kα radiation on a PANalytical X'Pert PRO diffractometer. Solid-state luminescence spectra were recorded with a Fluoro Max-P fluorescence spectrophotometer. TG measurement was performed by heating the sample from 30 to 650 °C (or 590 °C for **2**) at 10 °C min^{-1} in air on a NETZSCH STA 409 PC/PG differential thermal analyzer.

2.2. *Synthesis of $\{[Cd(imb)(bdc)(H_2O)]{\cdot}CH_3OH\}_n$ (1)*

A methanol solution (6 mL) of imb (0.1 mM) and H_2bdc (0.1 mM) was added dropwise into 2 mL water solution of $CdCl_2{\cdot}2.5H_2O$ (0.1 mM) to give a clear solution. The reaction mixture was left to stand at room temperature for five weeks and a number of clear crystals were obtained. Anal. Calcd for $C_{20}H_{20}CdN_4O_6$ (%): C, 45.77; H, 3.84; N, 10.68. Found (%): C, 45.63; H, 3.81; N, 10.92. IR (KBr, cm^{-1}): 3408(m), 3109(m), 1624(s), 1612(s), 1562(s), 1533(w), 1469(m), 1449(m), 1377(s), 1345(s), 1288(m), 1237(s), 1100(s), 952(s), 834(s), 766(s), 739(s), 654(s), 447(s).

2.3. *Synthesis of {[Cd(imb)(Hbtc)(CH$_3$OH)]·2H$_2$O·CH$_3$OH}$_n$ (2)*

The synthesis procedure of **2** was the same as for **1**, except H$_3$btc (0.1 mM) was used instead of H$_2$bdc. Colorless crystals were obtained five weeks later at room temperature. Anal. Calcd for $C_{22}H_{26}CdN_4O_{10}$ (%): C, 42.70; H, 4.23; N, 9.05. Found (%): C, 42.61; H, 4.42; N, 9.16. IR (KBr, cm^{-1}): 3445(m), 3130(m), 1750(m), 1622(m), 1596(w), 1535(m), 1520(s), 1444(m), 1417(s), 1376(s), 1319(s), 1287(m), 1131(s), 1012(s), 985(w), 879(m), 848(w), 771(s), 707(m), 666(s), 439(m).

2.4. *Single-crystal structure determination*

The crystals were carefully selected and attached to a thin glass fiber. Crystal structure determinations by X-ray diffraction were performed on a Rigaku Saturn 724 CCD area detector with graphite monochromator for the X-ray source (Mo K$_\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The data were collected by a ω scan mode at 293(2) K; the crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by Direct Methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2, using the SHELXS-97 program package [25]. Hydrogens bound to carbon and nitrogen were placed in calculated positions. The hydrogens of water and hydroxyl of methanol in **1**

Table 1. Crystal data and structural refinement of **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{20}H_{20}CdN_4O_6$	$C_{22}H_{26}CdN_4O_{10}$
Formula weight	524.80	618.87
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*P2(1)/c*
a (Å)	8.3724(17)	10.359(2)
b (Å)	10.105(2)	14.594(3)
c (Å)	13.069(3)	17.516(4)
α (°)	105.82(3)	90
β (°)	99.06(3)	99.51(3)
γ (°)	99.77(3)	90
Volume (Å^3)	1023.9(4)	2611.6(9)
Z	2	4
Calculated density (Mg m^{-3})	1.702	1.574
Absorption coefficient (mm^{-1})	1.113	0.896
F(0 0 0)	528	1256
Crystal sizes (mm)	0.26 × 0.18 × 0.16	0.21 × 0.19 × 0.16
R (int)	0.0297	0.0444
Data/restraints/parameters	3918/1/284	4860/0/335
Goodness-of-fit on F^2	1.041	1.180
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0263$	$R_1 = 0.0507$
	$wR_2 = 0.0555$	$wR_2 = 0.1082$
Final wR_2 indices (all data)	$R_1 = 0.0310$	$R_1 = 0.0572$
	$wR_2 = 0.0582$	$wR_2 = 0.1117$
$\Delta\rho_{\text{fin}}$ (max/min), e.Å^{-3}	0.684/−0.349	0.768/−0.544

and **2** and deprotonated carboxylic acid of Hbtc^{-} in **2** were found at reasonable positions in the differential Fourier map and located there. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogens. Crystallographic parameters and structure refinement data are summarized in table 1. Selected bond lengths and angles are listed in table 2. Hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *IR spectroscopy of 1 and 2*

IR spectra of **1** and **2** show absorptions at 3408 cm^{-1} for **1** and 3445 cm^{-1} for **2** attributed to the O–H stretch. Absorptions at 3109 cm^{-1} for **1** and 3130 cm^{-1} for **2** originate from Ar–H stretches. The C=O absorption in the free carboxylic acid occurs at *ca.* 1760–1680 cm^{-1}. Upon complexation, v(C=O) disappears and two new bands relating to the asymmetric v(O–C–O)$_\mathrm{a}$ and symmetric v(O–C–O)$_\mathrm{s}$ stretches appear at 1650–1507 and 1469–1366 cm^{-1}, respectively; the separations (Δ) between v(O–C–O)$_\mathrm{a}$ and v(O–C–O)$_\mathrm{s}$ are different for uncoordinated, unidentate, and chelating carboxylates [26]. In **1**, the separation (Δ) between v(O–C–O)$_\mathrm{a}$ and v(O–C–O)$_\mathrm{s}$ is 64 cm^{-1} (1533 cm^{-1} and 1469 cm^{-1}). This Δ value is comparable to those of chelating complexes so that carboxylates in **1** can be assigned to chelating coordination. Different from **1**, coordination of **2** are mixed. The chelating carboxylates

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

Complex **1**			
Cd(1)–N(3)#1	2.320(2)	Cd(1)–N(1)	2.321(2)
Cd(1)–O(2)	2.332(2)	Cd(1)–O(5)	2.3686(19)
Cd(1)–O(4)#2	2.3798(19)	Cd(1)–O(1)	2.503(2)
Cd(1)–O(3)#2	2.5831(18)		
N(3)#1–Cd(1)–N(1)	88.95(8)	N(3)#1–Cd(1)–O(2)	145.55(7)
N(1)–Cd(1)–O(2)	91.30(8)	N(3)#1–Cd(1)–O(5)	84.87(7)
N(1)–Cd(1)–O(5)	172.87(7)	O(2)–Cd(1)–O(5)	95.81(7)
N(3)#1–Cd(1)–O(4)#2	134.53(7)	N(1)–Cd(1)–O(4)#2	93.77(8)
O(2)–Cd(1)–O(4)#2	79.83(7)	O(5)–Cd(1)–O(4)#2	88.06(7)
N(3)#1–Cd(1)–O(1)	92.45(7)	N(1)–Cd(1)–O(1)	100.47(8)
O(2)–Cd(1)–O(1)	53.68(6)	O(5)–Cd(1)–O(1)	83.38(8)
O(4)#2–Cd(1)–O(1)	131.23(7)	N(3)#1–Cd(1)–O(3)#2	83.73(7)
N(1)–Cd(1)–O(3)#2	82.48(7)	O(2)–Cd(1)–O(3)#2	130.42(6)
O(5)–Cd(1)–O(3)#2	93.29(7)	O(4)#2–Cd(1)–O(3)#2	51.88(6)
O(1)–Cd(1)–O(3)#2	175.16(6)		
Complex **2**			
Cd(1)–N(4)#1	2.241(4)	Cd(1)–O(3)#2	2.265(3)
Cd(1)–O(1)	2.334(3)	Cd(1)–N(1)	2.355(4)
Cd(1)–O(7)	2.414(3)	Cd(1)–O(2)	2.570(3)
N(4)#1–Cd(1)–O(3)#2	125.26(13)	N(4)#1–Cd(1)–O(1)	139.90(13)
O(3)#2–Cd(1)–O(1)	89.43(12)	N(4)#1–Cd(1)–N(1)	105.30(13)
O(3)#2–Cd(1)–N(1)	88.38(13)	O(1)–Cd(1)–N(1)	93.94(12)
N(4)#1–Cd(1)–O(7)	84.27(13)	O(3)#2–Cd(1)–O(7)	83.88(12)
O(1)–Cd(1)–O(7)	79.85(12)	N(1)–Cd(1)–O(7)	170.09(12)
N(4)#1–Cd(1)–O(2)	88.77(13)	O(3)#2–Cd(1)–O(2)	141.76(11)
O(1)–Cd(1)–O(2)	52.96(11)	N(1)–Cd(1)–O(2)	99.69(13)
O(7)–Cd(1)–O(2)	82.81(12)		

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

Table 3. Hydrogen bonds of **1** and **2**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	(D–H···A) (°)
Complex **1**				
O(5)–H(1 W)···O(4)#5	0.85	1.95	2.725(3)	150.5
O(5)–H(2 W)···O(2)#6	0.85	1.88	2.698(3)	159.8
N(4)–H(4)···O(6)#7	0.86	1.91	2.748(3)	163.1
O(6)–H(6)···O(3)#8	0.82	1.84	2.656(3)	172.3
Complex **2**				
O(8)–H(8)···O(5)	0.82	1.80	2.601(6)	166.0
O(9)–H(9B)···O(2)	0.85	2.22	2.871(7)	133.7
O(10)–H(10A)···O(9)	0.85	1.90	2.683(12)	153.1
O(10)–H(10B)···O(4)	0.85	1.99	2.829(10)	168.0
O(4)–H(4)···N(1)#4	0.82	2.55	3.304(6)	152.9
N(2)–H(2)···O(6)#5	0.86	2.00	2.855(5)	173.5
O(7)–H(7A)···O(1)#6	0.82	2.03	2.803(5)	157.3
O(9)–H(9A)···O(8)#7	0.85	1.92	2.706(9)	153.3

Symmetry transformations used to generate equivalent atoms: for **1**: #5 $-x+2$, $-y+1$, $-z+1$; #6 $-x+2$, $-y$, $-z+1$; #7 x, $y-1$, $z-1$; #8 $-x+1$, $-y+1$, $-z+1$. For **2**: #4 $x-1$, y, z; #5 $-x+1$, $y-1/2$, $-z+5/2$; #6 $-x+1$, $-y+2$, $-z+2$; #7 $-x$, $-y+2$, $-z+2$.

exhibit $\nu(O–C–O)_a$ and $\nu(O–C–O)_s$ at 1520 cm^{-1} and 1444 cm^{-1} ($\Delta = 76\ cm^{-1}$), whereas unidentate carboxylates exhibit the $\nu(O–C–O)_a$ and $\nu(O–C–O)_s$ at 1622 cm^{-1} and 1376 cm^{-1} ($\Delta = 246\ cm^{-1}$). The carboxyl frequencies for the aforementioned stretches appear to be shifted to lower values compared with those of free aromatic acid, indicating changes in the vibrational status upon coordination [27–30]. The absorption observed at 1750 cm^{-1} in **2** can be attributed to the presence of COOH. The stretching frequencies of the benzene rings overlap those of the carboxylates. The absorptions at 1288 cm^{-1} for **1** and 1287 cm^{-1} for **2** are due to the C–N stretches. The absorptions at 739 cm^{-1} for **1** and 771 cm^{-1} for **2** are bending of the external plane of 1,2-disubstituted phenyl. The absorption at 766 cm^{-1} for **1** corresponds to bending of the external plane of 1,3-disubstituted phenyl. Absorptions at 707 and 848 cm^{-1} for **2** correspond to bending of the external plane of 1,3,5-disubstituted phenyl. The above analyses are confirmed by X-ray diffraction.

3.2. *Crystal structure of {[Cd(imb)(bdc)(H_2O)]·CH_3OH}$_n$ (1)*

Single-crystal X-ray diffraction reveals that **1** crystallizes in the triclinic system with space group *P*$\bar{1}$, with the asymmetric unit consisting of one Cd(II), one imb, one 1,3-benzenedicarboxylate, one coordinated water, and one uncoordinated methanol. As illustrated in figure 1(a), each Cd(II) is seven-coordinate by four oxygens belonging to two chelating carboxylates of two symmetry-related 1,3-benzenedicarboxylates, two nitrogens from two symmetry-related imb ligands, and one coordinated water. O1, O2, O3#2, O4#2, N3#1, and Cd1 which are nearly coplanar (the mean deviation from plane is 0.1216 Å) complete the equatorial plane, while the apical positions are occupied by N1 and O5 with the N1–Cd1–O5 bond angle of 172.87(7)°. Therefore, the local environment around Cd1 can be described as a distorted pentagonal bipyramid. Cd–N bond lengths range from 2.320(2) to 2.321(2) Å and the Cd–O bond lengths range from 2.332(2) to 2.5831(18) Å. These Cd–N and Cd–O bond lengths are close to those in [Cd(bimt)(Hbtc)]$_n$, {[Cd(bimt)(bdc)(H_2O)]·2H_2O}$_n$, and {[Cd(Hbtc)(bmt)]·0.5DMF·0.5H_2O}$_n$ (bimt = 2-((benzoimidazol-yl)methyl)-1*H*-tetrazole, H_3btc = 1,3,5-benzenetricarboxylic acid, H_2bdc = 1,3-benzenedicarboxylic acid, bmt = 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole) [31, 32].

As shown in figure 1(b), 1,3-benzenedicarboxylic acid is fully deprotonated and the dihedral angles between the mean plane defined by the benzene ring and the planes of the carboxylates are *ca*. 11.5° and 0.4°, respectively. Each bdc^{2-} bridges two Cd(II) ions to form a 1-D chain via Cd–O bonds; carboxylates chelate Cd(II). The 1-D chains extend along the *b*-direction with intrachain Cd···Cd distances separated by bdc^{2-} group being *ca*. 10.1 Å. Along the crystallographic *a*-direction, the 1-D chains are further connected through bridging imb ligands to form a 2-D layered structure along the *ab* plane and Cd···Cd distance separated by imb is *ca*. 8.4 Å. As shown in figure 1(c), there are two kinds of $\mathrm{O_{water}{-}H\cdots O_{carboxylate}}$ hydrogen bonds between coordination water and carboxylate, one kind of $\mathrm{O_{methanol}{-}H\cdots O_{carboxylate}}$ hydrogen bond between methanol and carboxylate, and one kind of $\mathrm{N_{benzimidazole}{-}H\cdots O_{methanol}}$ hydrogen bond between benzimidazole and methanol. As depicted in figure 1(d), layers A and B are a group. In the same group, two layers are linked through two kinds of $\mathrm{O_{water}{-}H\cdots O_{carboxylate}}$ hydrogen bonds. Adjacent groups

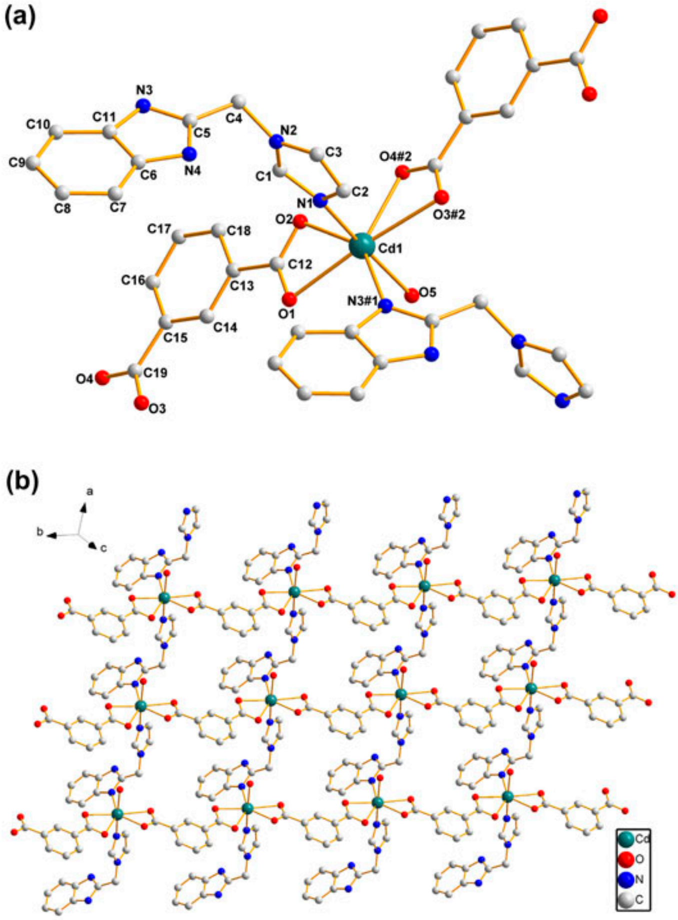

Figure 1. (a) Coordination environment of Cd(II) in **1** with the atom numbering scheme; hydrogens and uncoordinated methanols are omitted for clarity (#1 $x+1, y, z$; #2 $x, y-1, z$); (b) view of the 2-D network structure of **1**; (c) view of hydrogen bonds in **1**; and (d) 3-D structure of **1** linked through hydrogen bonds indicated by dashed lines.

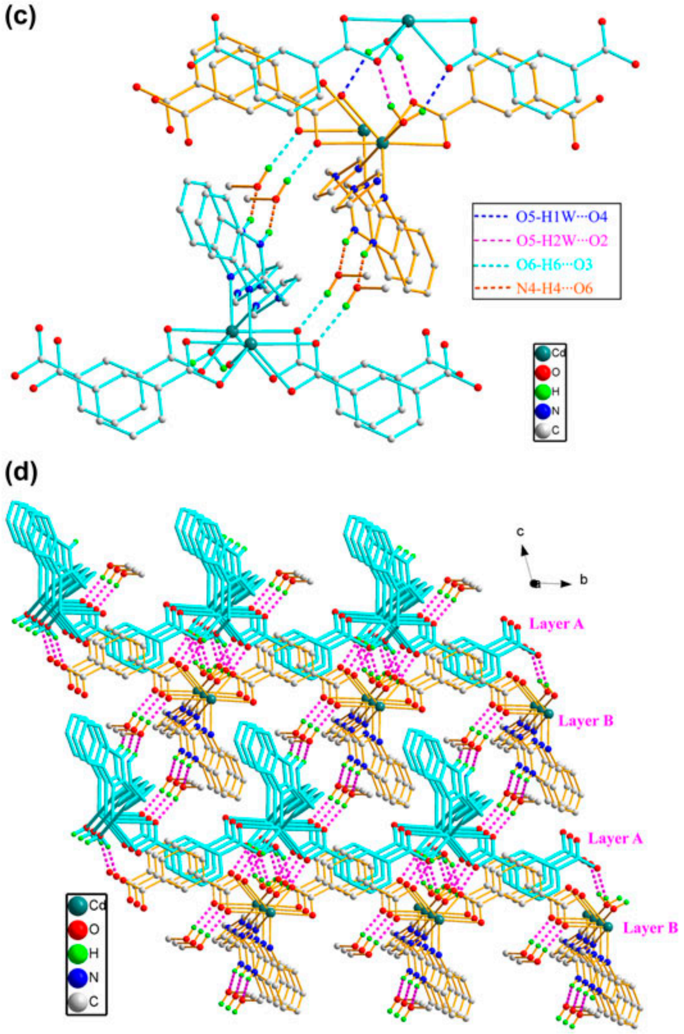

Figure 1. (*Continued*)

are further connected by $O_{methanol}–H\cdots O_{carboxylate}$ and $N_{benzimidazole}–H\cdots O_{methanol}$ hydrogen bonds leading to the 3-D packing structure.

3.3. *Crystal structure of {[Cd(imb)(Hbtc)(CH_3OH)]·$2H_2O$·CH_3OH}$_n$ (2)*

When H_3btc, instead of the H_2bdic, is used in the reaction with other experimental conditions unchanged, **2** was obtained. It can be seen from figure 2(a) that the coordination number of Cd(II) is six, different from that in **1**. In **2**, each Cd(II) is coordinated by four oxygens from one chelating and one monodentate carboxylate of two 1,3,5-benzenetricarboxylates, one coordinated methanol, and two nitrogens from two imb, featuring an irregular CdO_4N_2 coordination geometry. As shown in table 2, most of the bond angles around Cd(II)

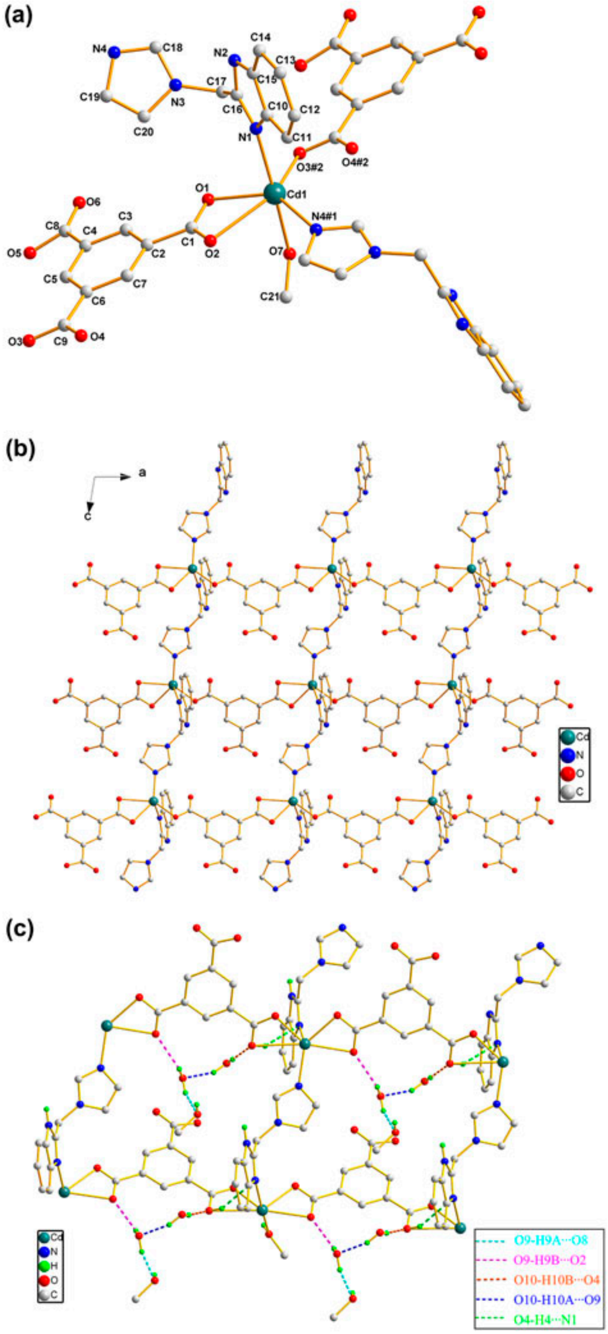

Figure 2. (a) Coordination environment of Cd(II) in **2** with the atom numbering scheme; hydrogens, uncoordinated methanols, and uncoordinated waters are omitted for clarity (#1 x, $-y+3/2$, $z-1/2$; #2 $x+1$, y, z); (b) view of the 2-D network structure of **2** with coordinated methanols omitted for clarity; (c) view of intralaminar hydrogen bonds in **2**; (d) view of hydrogen bonds between the adjacent layers in **2**; part of the benzene rings are omitted for clarity; and (e) 3-D structure of **2** linked through hydrogen bonds indicated by dashed lines.

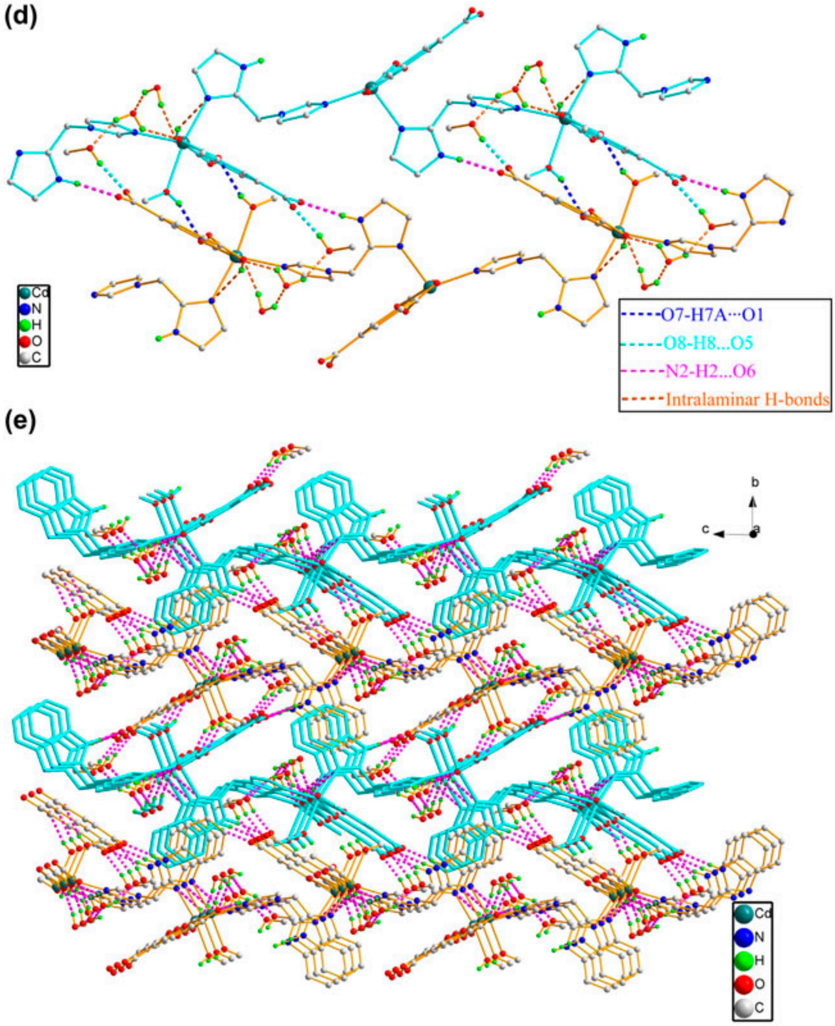

Figure 2. (*Continued*)

deviate dramatically from the ideal 90° or 180° expected for octahedral geometry, as exemplified by the angles of O1–Cd1–O2, N4#1–Cd1–O3#2, N4#1–Cd1–O1 and O3#2–Cd1–O2 (52.96(11)°, 125.26(13)°, 139.90(13)°, and 141.76(11)°, respectively). The Cd–O bond lengths of 2.265(3)–2.570(3) Å and Cd–N bond lengths of 2.241(4)–2.355(4) Å are close to those observed in **1**.

Although there are three carboxyl groups in each 1,3,5-benzenetricarboxylate, not all carboxyl groups are involved in coordination. Two carboxyl groups of each 1,3,5-benzenetricarboxylate coordinate to Cd(II) in [Cd(bimt)(Hbtc)]$_n$, {[Cd(Hbtc)(bmt)]·0.5DMF·0.5H_2O}$_n$, and {$Na_2[Cd_2(Htma)_2(ox)(H_2O)_2]$}$_n$ (bimt = 2-((benzoimidazol-yl)methyl)-1*H*-tetrazole, bmt = 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole, ox = oxalate, Htma = 1,3,5-benzenetricarboxylate) [31–33]; only one carboxyl group of each 1,3,5-benzenetricarboxylate coordinates to Cd(II) ions in $[Cd(C_9H_5O_6)_2(C_{12}H_8N_2)]$ and $[Cd(C_2O_4)(C_{12}H_8N_2)$

$(C_9H_6O_6)]\cdot C_6H_5N_3\cdot H_2O$ ($C_9H_6O_6$ = 1,3,5-benzenetricarboxylate, $C_{12}H_8N_2$ = 1,10-phenanthroline, C_2O_4 = oxalate, $C_6H_5N_3$ = benzotriazole) [34, 35] and none of the carboxyl groups coordinate to Cd(II) in $\{[Cd(btrp)_2(H_2O)_2]\cdot H_2O\cdot 2H_2btc\}_n$ (btrp = 1,3-bis(1,2,4-triazol-1-yl) propane) [36]. In **2**, two of the carboxyl groups of each 1,3,5-benzenetricarboxylate coordinate monodentate or chelating to the Cd(II) and the third, which is not deprotonated, remains uncoordinated. This kind of coordination of 1,3,5-benzenetricarboxylate is in agreement with those previously reported in other benzenetricarboxylate-containing Cd(II) complexes [31–33]. The values of the dihedral angle between the mean plane defined by the benzene ring and the chelating, monodentate, and uncoordinated carboxyl groups are *ca*. 6.3°, 0.3°, and 8.5°, respectively.

As depicted in figure 2(b), each $Hbtc^{2-}$ coordinates to two Cd(II) ions to form an infinite 1-D chain along the *a*-direction and the intrachain Cd···Cd distance separated by $Hbtc^{2-}$ group is *ca*. 10.4 Å. Along the *c*-direction, Cd(II) ions are connected by imb ligands generating another linear chain with the intrachain Cd···Cd distance of *ca*. 9.0 Å. Linear chains along the two directions are interconnected to complete the 2-D layered framework. As shown in figure 2(c), four kinds of intralaminar O–H···O hydrogen bonds between solvent water and solvent methanol, between solvent water and carboxylate groups, between solvent water/water molecules, and one kind of intralaminar O–H···N hydrogen bond between carboxyl and benzimidazole groups stabilize the molecular configuration. As depicted in figure 2(d), adjacent layers are linked through two kinds of O–H···O hydrogen bonds between coordination methanol and carboxylate, between solvent methanol and carboxylate, and one kind of N–H···O hydrogen bond between benzimidazole and carboxylate leading to the 3-D structure in the solid state [figure 2(e)].

3.4. *XRD patterns*

To confirm the phase purity of each complex, powder X-ray diffraction patterns (Supplementary material [see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.879574]) were recorded for **1** and **2**. The patterns were comparable to corresponding simulated patterns calculated from single-crystal diffraction data, indicating a pure phase of each bulk sample.

3.5. *Luminescent properties*

Complexes involving Cd(II) ion exhibit interesting luminescence as luminescent materials [37]. Therefore, the solid-state photoluminescence spectra of **1** and **2** were investigated at room temperature. As shown in figure 3, the main emission peaks are observed at 336 nm for **1** (λ_{ex} = 300 nm) and 323 nm for **2** (λ_{ex} = 283 nm). Photoluminescent spectra of free imb, H_2bdc, and H_3btc were also measured in the solid state to understand the nature of the emission bands. The free imb displays an emission band at 305 nm (λ_{ex} = 285 nm), probably attributable to the $\pi \rightarrow \pi^*$ transitions [38]. While H_2bdc and H_3btc give emission bands at 375 nm (λ_{ex} = 315 nm) and 390 nm (λ_{ex} = 347 nm), respectively, which are probably attributable to the $n \rightarrow \pi^*$ transitions [39, 40]. Since Cd(II) ions are difficult to oxidize or reduce due to d^{10} configuration, the emissions of **1** and **2** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) [41, 42]. So we can presume that both the

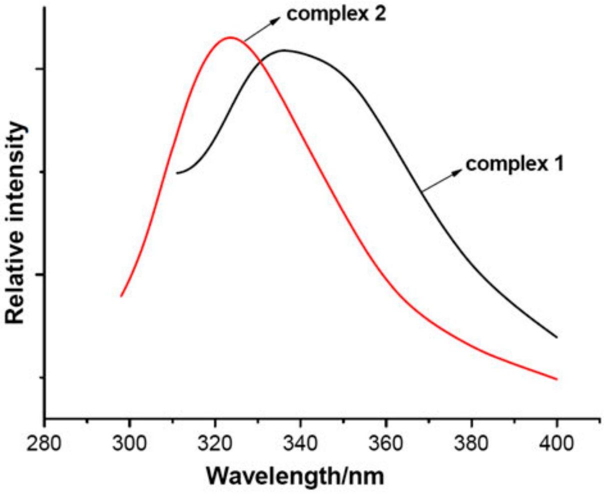

Figure 3. Solid-state emission spectra of **1** and **2** at room temperature.

imb and aromatic polycarboxylate ligands make contribution to the fluorescence emissions of the two complexes [31].

3.6. *Thermogravimetric analysis*

Thermogravimetric analyses of **1** and **2** were performed by heating the complexes from 30 to 650 °C (or 590 °C for **2**) in air. As shown in Supplementary material, the TG curve of **1** exhibits that first mass loss of 9.36% between 77 and 171 °C corresponds to release of solvent methanol and coordination water (Calcd 9.54%). Then the solid continues to lose mass from 313 to 604 °C, corresponding to decomposition of imb and 1,3-benzenedicarboxylates. Finally, a plateau occurs from 604 to 650 °C. The residue equals 24.92%, which is attributed to CdO (Calcd 24.47%). The TG curve of **2** reveals a weight loss of 15.95% from 56 to 179 °C, which can be assigned to release solvent methanol and water, as well as coordination methanol (Calcd 16.18%). Continuous weight loss from 241 to 523 °C corresponds to decomposition of imb and 1,3,5-benzenetricarboxylates. A plateau is observed from 523 to 590 °C. The residues of 20.57% should be CdO (Calcd 20.75%). All these results are in agreement with the aforementioned crystal structure.

4. Conclusion

Through reactions of imb with $CdCl_2 \cdot 2.5H_2O$, we have synthesized two 1-D complexes, $\{[Cd(Himb)(\mu_2\text{-}Cl)Cl] \cdot CH_3OH\}_n$ and $\{[Cd(Himb)(\mu_2\text{-}Cl)_2] \cdot DMF\}_n$, in which Cd(II) ions are bridged by chloride and imb ligands [43]. In this article, we added H_2bdc or H_3btc to the above reaction system and obtained two new 2-D complexes, $\{[Cd(imb)(bdc)(H_2O)] \cdot CH_3OH\}_n$ (**1**) and $\{[Cd(imb)(Hbtc)(CH_3OH)] \cdot 2H_2O \cdot CH_3OH\}_n$ (**2**), in which the coordination environments of Cd(II) have been changed compared with those in the former two complexes. The results suggest that the combination of *N*-heterocyclic ligands and aromatic polycarboxylates with metal centers might be a promising strategy for construction of MOFs with a specific structure and topology. Change of aromatic polycarboxylates can influence the coordination number of the central Cd(II), and thus influence the detailed architectures of the complexes, and finally lead to the different properties of them.

Supplementary material

Crystallographic data reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. CCDC numbers are 860561 and 860562. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1 223 336 033).

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