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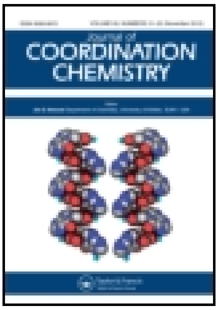

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Construction of two new photoluminescent coordination polymers via 5-position substituted 1,3-benzenedicarboxylate

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Construction of two new photoluminescent coordination polymers *via* 5-position substituted 1,3-benzenedicarboxylate

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Two coordination polymers, $[Cd(L1)(bib)]_n$ (**1**) and $[Cd(L2)(bib)_{0.5}]_n$ (**2**) [$H_2L1 = $ 5-hydroxyisophthalic acid, $H_2L2 = $ 5-methylisophthalic acid and bib = 1,4-bis(2-methyl-imidazol-1-yl)butane], have been synthesized and characterized by IR, elemental analysis, and X-ray diffraction. Compound **1** shows a 2-D layer structure and **2** is a two-fold interpenetrated 3-D pcu topology. The results suggest that the 5-position group affects the structure of coordination polymers. Luminescence properties of **1** and **2** are investigated.

Keywords: Coordination polymer; Crystal structure; Photoluminescence

1. Introduction

Metal–organic frameworks (MOFs) are currently of interest due to diverse structures and potential applications in gas storage, magnetism, catalysis, and luminescence [1–17]. Although rapid progress in MOFs has been made, it remains a challenge to control the structures and composition of target products in crystal engineering. Construction of MOFs is influenced by both structural and experimental factors, such as ligands, pH, temperature, and solvents [16–19]. The most effective and facile method to construct MOFs is choice of well-designed ligands containing modifiable backbones. Combination of carboxylates with N-donor auxiliary ligands is a good choice for the construction of new coordination polymers because of the varieties in coordination modes of carboxylate [20–23]. Different non-coordinating groups in the 5-position of 1,3-benzenedicarboxylate can generate different polymers [24]. Bis(imidazole) with $–CH_2–$ spacers are good N-donor bridging ligands. The flexible nature of $–CH_2–$ spacers allows the ligands to bend and rotate freely when coordinating to metal centers to conform to the coordination geometries of metal ions [25–27].

Our work is devoted to the construction of MOFs through tuning the 5-position of 1,3-benzenedicarboxylate to study the effect on the MOFs. In this article, we use 5-hydroxyisophthalic acid, 5-methylisophthalic acid, and bib [1,4-bis(2-methyl-imidazol-1-yl) butane] as N-donor to synthesize two Cd(II) complexes. The results reveal that

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5-position group affects the structure of coordination polymers, changing from 2-D layer structure to 3-D pcu network.

2. Experimental

2.1. *Materials and physical measurements*

All reagents and solvents were commercially available and used as received. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a KBr pellet from 400 to 4000 cm^{-1}. Solid-state fluorescence spectra were recorded on a Hitachi F-4600 equipped with a xenon lamp and a quartz carrier at room temperature. X-ray powder diffraction (XRPD) measurements were performed on a Bruker D8 diffractometer operated at 40 kV and 40 mA using Cu-Kα radiation ($\lambda = 0.15418$ nm).

2.2. *Syntheses*

2.2.1. [Cd(L1)(bib)]$_n$ (1). A mixture of $Cd(OAc)_2 \cdot 4H_2O$ (0.308 g, 1 mmol), H_2L_1 (0.182 g, 1 mmol), bib (0.218 g, 1 mmol), NaOH (0.08 g, 2 mmol), and deionized water (18 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160°C for 96 h. After cooling to room temperature, colorless block crystals were obtained and washed with alcohol several times (yield: 42% based on Cd). Elemental Anal. Calcd for $C_{20}H_{22}CdN_4O_5$ (%): C, 47.02; H, 4.34; N, 10.97. Found (%): C, 47.24; H, 4.28; N, 11.30. IR: 1605 s, 1487 s, 1428 m, 1351 m, 1237 m, 1157 m, 924 m, 857 m, 742 m.

2.2.2. [Cd(L2)(bib)$_{0.5}$]$_n$ (2). Compound **2** was obtained by hydrothermal procedure as for preparation of **1** only using 5-methylisophthalic acid (0.180 g, 0.1 mmol) instead of 5-hydroxyisophthalic acid. Colorless block crystals of **2** were collected in 40% yield based on Cd after washing by ethanol several times. Elemental Anal. Calcd for $C_{15}H_{15}CdN_2O_4$ (%): C, 45.07; H, 3.78; N, 7.01. Found (%): C, 45.24; H, 3.75; N, 7.04. IR: 1655 s, 1524 s, 1462 s, 1307 m, 1278 w, 10 971m, 904 m, 841 w, 754 m.

2.3. *X-ray crystallography*

Diffraction intensity data of the single crystals of **1** and **2** were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using a ω-scan mode. Empirical absorption correction was applied using SADABS [28]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHEXL 97 [29]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located geometrically and their positions and thermal parameters were fixed during structure refinement. Crystallographic data are summarized in table 1 with relevant bond lengths and angles listed in table 2.

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

Empirical formula	$C_{20}H_{22}CdN_4O_5$	$C_{15}H_{15}CdN_2O_4$
Formula weight	510.82	366.69
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å, °)		
a	9.131(2)	9.345(4)
b	20.516(4)	12.133(5)
c	11.364(3)	13.349 (5)
β	104.588(3)	91.948 (5)
Volume (Å^3), Z	2060.5(15), 4	1512.7(11), 4
Calculated density (Mg m^{-3})	1.545	1.755
Independent reflections [$I > 2\sigma(I)$]	3286	3144
$F(000)$	1032	796
θ range for data collection	2.51–28.59	2.27–27.54
Limiting indices	$-10 \le h \le 10$; $-24 \le k \le 18$; $-24 \le l \le 18$	$-12 \le h \le 8$; $-15 \le k \le 15$; $-12 \le l \le 17$
Goodness-of-fit on F^2	1.083	1.016
R_1^a, wR_1^b [$I > 2\sigma$(I)]	$R_1 = 0.0219$ $wR_2 = 0.0502$	$R_1 = 0.0206$ $wR_2 = 0.0524$
R_1^a, wR_1^b (all data)	$R_1 = 0.0252$ $wR_2 = 0.0520$	$R_1 = 0.0236$ $wR_2 = 0.0543$
Largest difference peak and hole (e Å^{-3})	0.282 and −0.314	0.650 and −0.263

$^a R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^b wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)]^{1/2}$.

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

Compound **1**			
Cd (1)–N(1)	2.259(2)	Cd(1)–O(4)	2.323(2)
Cd(1)–N(3)	2.2596(19)	Cd(1)–O(5)	2.4044(17)
Cd(1)–O(1)^i	2.2941(19)	Cd(1)–O(2)^i	2.4915(18)
N(1)–Cd(1)–N(3)	92.70(7)	O(1)^i–Cd(1)–O(4)	88.87(6)
N(1)–Cd(1)–O(1)^i	140.50(7)	N(1)–Cd(1)–O(5)	94.08(7)
N(3)–Cd(1)–O(1)^i	109.94(8)	N(3)–Cd(1)–O(5)	141.33(7)
N(1)–Cd(1)–O(4)	124.24(8)	O(1)^i–Cd(1)–O(5)	87.91(7)
N(3)–Cd(1)–O(4)	89.75(6)	O(4)–Cd(1)–O(5)	55.52(6)
N(1)–Cd(1)–O(2)^i	87.53(7)	O(4)–Cd(1)–O(2)^i	141.05(6)
N(3)–Cd(1)–O(2)^i	112.71(7)	O(5)–Cd(1)–O(2)^i	105.59(7)
O(1)^i–Cd(1)–O(2)^i	54.28(6)		
Compound **2**			
Cd(1)–N(1)	2.2061(17)	Cd(1)–O(4)^{ii}	2.2745(15)
Cd(1)–O(3)^i	2.2652(15)	Cd(1)–O(1)^{iii}	2.3436(17)
N(1)–Cd(1)–O(3)^i	105.80(6)	O(4)^{ii}–Cd(1)–O(1)^{iii}	80.04(7)
N(1)–Cd(1)–O(4)^{ii}	94.12(6)	N(1)–Cd(1)–O(1A)	162.34(7)
O(3)^i–Cd(1)–O(4)^{ii}	152.53(6)	O(3)^i–Cd(1)–O(1A)	81.71 (6)
N(1)–Cd(1)–O(1)^{iii}	105.53(7)	O(4)^{ii}–Cd(1)–O(1A)	84.82(6)
O(3)^i–Cd(1)–O(1)^{iii}	76.55(7)	O(1)^{iii}–Cd(1)–O(1A)	91.68(5)
N(1)–Cd(1)–O(2)	109.28(7)	O(1)^{iii}–Cd(1)–O(2)	144.39(6)
O(3)^i–Cd(1)–O(2)	86.91(6)	O(1)–Cd(1)–O(2)	54.41(6)
O(4)^{ii}–Cd(1)–O(2)	104.43(7)		

Symmetry codes: for **1**: ^{i} $x - 1/2$, $-y + 1/2$, $z + 1/2$; for **2**: ^{i} $-x + 1/2$, $y - 1/2$, $-z + 1/2$; ^{ii} $x - 1/2$, $-y + 3/2$, $z + 1/2$; ^{iii} $-x$, $-y + 1$, $-z + 1$.

3. Results and discussion

3.1. *Description of crystal structures*

3.1.1. Cd(L_1)(bib)]$_n$ (1). X-ray diffraction analysis revealed that [Cd(L1)(bib)]$_n$ (**1**) consists of one Cd(II), one L_1, and one bib. Each Cd^{II} is six-coordinate by four oxygen atoms from L_1 [Cd(1)–O(1) = 2.294(19), Cd(1)–O(2) = 2.492(18), Cd(1)–O(4) = 2.323(2), and Cd(1)–O(5) = 2.404(14) Å] and two nitrogen atoms from two bib ligands [Cd(1)–N(1) = 2.259(2) and Cd(1)–N(3) = 2.260(19) Å], showing a distorted octahedral geometry (figure 1a). Each L_1 adopts a bis-chelating mode to link adjacent Cd's to form 1-D chains, which are further connected by bib to form a 2-D layer (figure 1b). The 2-D layers are further assembled by intermolecular hydrogen bonds with a H(21)···O(2) distance of 1.89 Å and the angle of 168° [O(3)–H(21)···O(2)], leading to formation of a 3-D framework (figure 1c).

Considering the hydrogen-bonding interaction, L_1 can be simplified as a three-connected node; Cd(II) can be regarded as a four-connected node. In this method, the 3-D supramolecular structure can be rationalized as a (3,4)-connected InS net with a Schäfli symbol of $(6^3)\cdot(6^5\cdot8)$, which is the first example of an InS net formed *via* hydrogen-bonding interactions (figure 1d).

3.1.2. [Cd(L_2)(bib)$_{0.5}$]$_n$ (2). In [Cd(L2)(bib)$_{0.5}$]$_n$ (**2**), each Cd^{II} is also six-coordinate by five oxygen atoms from L_2 [Cd–O bond lengths varying from 2.265(15) to 2.404(16) Å] and one nitrogen atom from one bib [Cd(1)–N(1) = 2.206(17) Å], showing a distorted

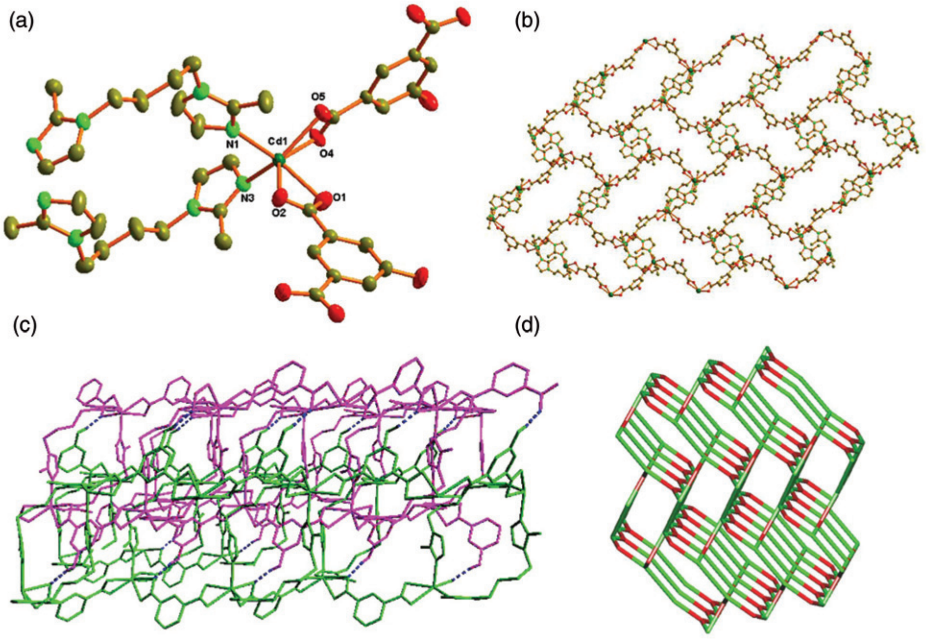

Figure 1. (a) Coordination environment of Cd(II) in **1**. Hydrogen atoms are omitted for clarity; (b) the 2-D layer structure; (c) 3-D supramolecular structure *via* hydrogen bonds; and (d) the InS network of the $(6^3)\cdot(6^5\cdot8)$ topology for the 3-D supramolecular structure.

octahedral geometry (figure 2a). Each L_2 is bis-monodentate and chelating/bridging modes, forming a binuclear Cd unit ($d_{Cd-Cd} = 3.280$ Å). The dimers are bonded to four L_2 and thus can be regarded as a four-connected node to generate a (4,4) 2-D layer (figure 2b). The 2-D layers are further bridged by bib to generate a 3-D framework. From a topological view, the dimeric unit can be treated as a six-connected node with L_2 and bib as linkers; the 3-D structure can be classified as a pcu-related net (α-Po topology). Due to the absence of guest molecules to fill the large void space in the 3-D framework during assembly, the potential voids in **2** are filled *via* mutual interpenetration of two identical 3-D nets, which directly leads to formation of a two-fold interpenetrated network (figure 2c).

3.2. *X-ray powder diffraction*

XRPD was used to confirm the phase purity of bulk materials of **1** and **2** at room temperature, indicating that the synthesized **1** and **2** are homogeneous systems (figure S1, Supplementary material).

3.3. *Photoluminescent properties*

Luminescent properties of **1** and **2** were investigated in the solid state at room temperature. Complexes **1** and **2** exhibit fluorescent emission bands with maxima at

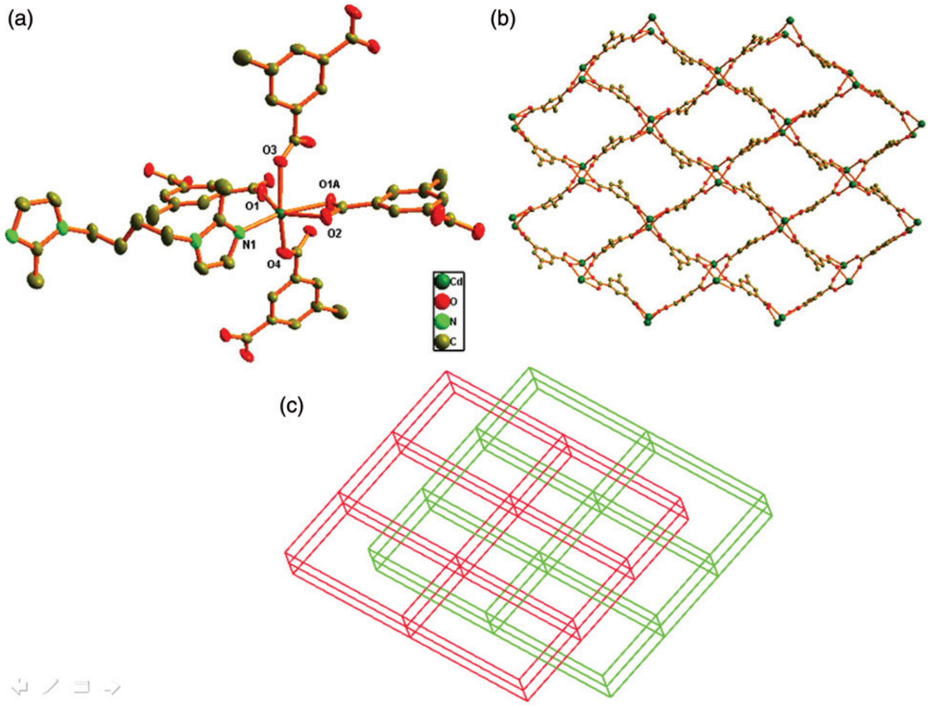

Figure 2. (a) Coordination environment of Cd(II) in **2**. Hydrogen atoms and free water are omitted for clarity; (b) the 2-D layer formed by carboxylates; and (c) the two-fold interpenetrated pcu net.

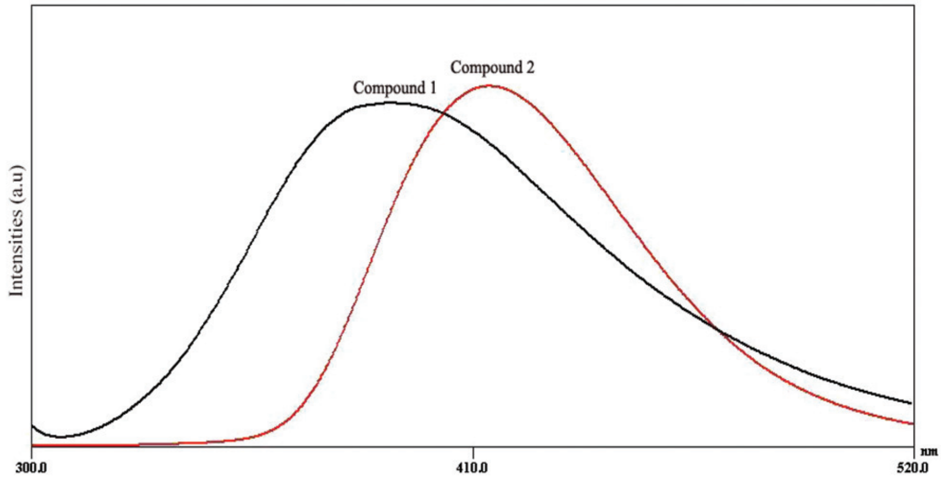

Figure 3. Solid-state emission spectra of **1** and **2** at room temperature.

386 nm and 409 nm upon excitation at 334 nm and 340 nm, respectively. To understand the nature of these emissions, we compared the emission spectra of the two compounds and those of free H_2L1, H_2L2, and bib which exhibit broad weak fluorescent emission centered on 350 nm ($\lambda_{ex} = 280$ nm) [24], 380 nm ($\lambda_{ex} = 280$ nm) [30], and 465 nm ($\lambda_{ex} = 280$ nm) [31] (figure 3). The emissions of **1** and **2** are tentatively assigned to intraligand transition due to their similarity to ligands. Cd is difficult to oxidize or reduce [32–34]. The different emission positions and intensities of **1** and **2** may be due to the different structures because enhancement of luminescence is associated with coordination of ligands to metal [35, 36].

4. Conclusion

We synthesized two new coordination polymers. Compound **1** shows a 3-D supramolecular structure with InS topology *via* hydrogen bonds. Compound **2** is a two-fold pcu topology. Changing the 5-position substituent, the structures from a 2-D net into a 3-D framework affects the structure of coordination polymers. In comparison with **1** and **2**, using the same N-donor ligand, the carboxylates have a critical impact on the construction of different MOFs due to their steric and/or electronic effect at the 5-position. When –OH is changed to $–CH_3$, the structures are changed from 2-D layer to 3-D pcu network. Compounds **1** and **2** also exhibit emission in the solid state at room temperature.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference numbers: 862572 and 862573. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk or Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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