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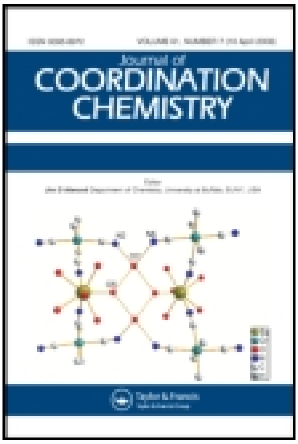

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Syntheses and structures of Cd(II) and Co(II) compounds of 4-[(3-pyridyl)methylamino]benzoate anion

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Syntheses and structures of Cd(II) and Co(II) compounds of 4-[(3-pyridyl)methylamino]benzoate anion

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Three coordination polymers containing Cd(II) and Co(II), connected *via* 4-[(3-pyridyl) methylamino]benzoate (L^-), have been synthesized in hydrothermal conditions. In $[Cd(L)Cl]_n$ (**1**), adjacent Cd(II) cations are linked by carboxylates to give a dinuclear cluster. Pairs of L^- bridge the dinuclear cluster to form double helical chains, and these chains are further linked by Cl^- to produce a 4-connected net with $(4^2 \cdot 6^3 \cdot 8)$ topology. $[CdL_2]_n$ (**2**) contains 1-D ladder-like chains. The packing structure displays a 3-D supramolecular structure, with $\pi \cdots \pi$ interactions stabilizing the framework. $[CoL_2]_n$ (**3**) has a 2-D extended supramolecular structure *via* $\pi \cdots \pi$ interactions of 1-D coordination polymers of **3**. The crystal structures of **1**–**3** have been determined by single-crystal X-ray diffraction. Luminescent properties for **1** and **2** are discussed.

Keywords: Cadmium; Cobalt; Coordination polymers; Topology

1. Introduction

Metal–organic extended structures receive attention because of intriguing architectures and topologies and potential applications such as catalysis, electrical conductivity, host–guest chemistry, and magnetism [1–4]. Therefore, the design and construction of coordination polymers has become a particularly important subject. High-dimensional networks can be obtained by assembly of lower dimensional coordination polymers *via* non-covalent intermolecular forces such as hydrogen-bonding, π–π, C–H$\cdots\pi$, S$\cdots$S interactions, etc. [5–7]. Transition metal ions [8, 9] with pyridine-carboxylates and their derivatives have been widely utilized to build metal–organic extended structures [10]. To gain better understanding of the factors that influence the 2-D and 3-D network structures built from pyrdidine-carboxylate bridging ligands, we use 4-((3-pyridyl) methylamino)benzoic acid (HL) as a bridging ligand for the construction of cadmium

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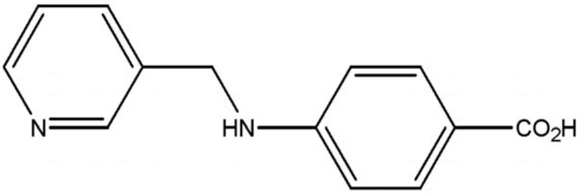
and cobalt coordination networks. Herein, we report the syntheses and structures of $[Cd(L)Cl]_n$ (**1**), $[CdL2]_n$ (**2**), and $[CoL_2]_n$ (**3**).



HL

2. Experimental

2.1. *Preparation*

All reagents and solvents for syntheses were purchased from commercial sources and used as received.

2.1.1. Synthesis of HL. 10 mmol of *p*-aminobenzoic acid (1.37 g) was dissolved in 50 mL of absolute methanol with refluxing and pyridine-3-carbaldehyde (10 mmol, 1.08 g) in 50 mL of absolute methanol was added slowly to give a clear yellowish solution. The mixture was refluxed for 3 h and stirred overnight at ambient temperature. Then an excess of $NaBH_4$ (2 g) was added in small portions with stirring at room temperature. The mixture was allowed to stand overnight with stirring and then the methanol was removed by evaporation. To the mixture was added 50 mL of deionized water, adjusted to pH = 6 with HCl and eventually the white product (HL) formed was filtered off, washed thoroughly with water, and dried in vacuum (yield 54%).

2.1.2. Synthesis of $[Cd(L)Cl]_n$ (1). A mixture of $CdCl_2 \cdot 2H_2O$ (0.066 g, 0.30 mmol), L (0.069 g, 0.30 mmol), NaOH (0.012 g, 0.30 mmol), and $C_2H_5OH : H_2O$ (1 : 2 ratio) (10 mL) was stirred for 10 min in air. The mixture was heated at 140°C for 3 days and then gradually cooled to room temperature at $10°C\,h^{-1}$. Colorless block crystals of **1** were collected from the reaction by filtration, washed several times with ethanol, and dried in air at ambient temperature (Yield: 38%). Anal. Calcd for $C_{13}H_{11}CdClN_2O_2$ (375.09): C, 41.63; H, 2.96; N, 7.46. Found: C, 41.84; H, 2.82; N, 7.64. IR (cm^{-1}): 3521 (s), 3382 (m), 2921 (s), 1607 (w), 1519 (w), 1477 (w), 1432 (w), 1388 (w), 1281 (m), 1180 (m), 1138 (s), 1082 (s), 1050 (s), 1030 (s), 993 (s), 859 (s), 840 (s), 785 (s), 743 (s), 702 (m), 646 (s), 624 (s), 522 (s).

2.1.3. $[CdL_2]_n$ (2). The same synthetic procedure as that for **1** was used except that $CdCl_2 \cdot 2H_2O$ was replaced by $Cd(OAc)_2 \cdot 2H_2O$ (0.080 g, 0.30 mmol) giving colorless block crystals of **2** collected from the final reaction system by filtration, washed several times with ethanol, and dried in air at ambient temperature (Yield: 46%). Anal. Calcd for $C_{26}H_{22}CdN_4O_4$ (566.88): C, 55.09; H, 3.91; N, 9.88. Found: C, 55.18; H, 3.72; N, 9.84. IR (cm^{-1}): 3336 (s), 1607 (s), 1529 (s), 1389 (s), 1268 (s), 1177 (s), 1101 (m), 1052 (s), 852 (s), 781 (s), 694 (s), 614 (s).

2.1.4. $[CoL_2]_n$ (3). The same synthetic procedure as that for **2** was used except that $Cd(OAc)_2 \cdot 2H_2O$ was replaced by $Co(OAc)_2 \cdot 2H_2O$ (0.075 g, 0.30 mmol) giving purple block crystals of **3** collected from the final reaction system by filtration, washed several times with ethanol, and dried in air at ambient temperature (Yield: 45%). Anal. Calcd for $C_{26}H_{22}CoN_4O_4$ (513.41): C, 60.83; H, 4.32; N, 10.91. Found: C, 60.78; H, 4.40; N, 10.74. IR (cm^{-1}): 3308 (w), 3041 (s), 2931 (s), 1605 (w), 1524 (m), 1485 (w), 1413 (w), 1334 (m), 1313 (w), 1281 (w), 1192 (m), 1171 (m), 1134 (m), 1107 (m), 1080 (s), 1052 (s), 1030 (s), 860 (s), 838 (s), 807 (s), 785 (w), 701 (m), 620 (m), 502 (s).

2.2. *Physical measurements and X-ray crystallography*

The C, H, and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded as KBr pellets from 4000 to 400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The excitation-emission spectra and the decay curve were measured on an Edinburgh Instruments Flsp920 spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from 30°C to 800°C under nitrogen. The phase purities of the bulk samples were identified by X-ray powder diffraction on a Siemens D5005 diffractometer.

Single-crystal X-ray diffraction data for **1–3** were collected on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using multiscan technique. The structures were solved with the direct method of SHELXS-97 [11] and refined with full-matrix least-squares using SHELXL-97 [12] within WINGX [13]. Non-hydrogen atoms were refined anisotropically. N-bonded hydrogens were located in a difference map and their positions freely refined. Hydrogens bonded to carbon were positioned geometrically (C–H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C,N)$. The crystal data and details of the data collection and structure refinement are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure*

Selected geometric parameters for **1–3** are given in table 2.

3.1.1. Structure of $[Cd(L)Cl]_n$ (1). As illustrated in figure 1(a), the independent unit of **1** contains one Cd^{II}, one L^-, and one Cl^-. The Cd^{II} is a distorted octahedral $[CdO_3NCl_2]$ environment by coordinating to one nitrogen of one L^- through pyridyl (Cd–N = 2.284(4) Å), two chelating carboxylate oxygens of one L^-, one carboxylate oxygen of another L^- (Cd–O = 2.213(4)–2.745(5) Å), and two Cl^- anions. All of the coordination bonds are within normal distances [14]. The carboxylate group bridges

Table 1. Crystal data and structure refinements for **1–3**.

	1	**2**	**3**
Formula	$C_{13}H_{11}CdClN_2O_2$	$C_{26}H_{22}CdN_4O_4$	$C_{26}H_{22}CoN_4O_4$
M	375.09	566.88	513.41
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*P2₁/c*	*P2₁/c*
Unit cell dimensions (Å, °)			
a	11.0897(4)	17.1894(4)	32.051(7)
b	11.1038(5)	11.0845(2)	10.630(4)
c	21.1775(7)	12.4761(3)	9.490(3)
α	90	90	90
β	98.808(4)	95.892(2)	111.857(6)
γ	90	90	90
Volume (Å^3), *Z*	2578.04(17), 8	2364.57(9), 4	1118.99(10), 2
Calculated density (g cm^{-3})	1.933	1.592	1.524
F(000)	1472	1144	530
θ range (°)	4.69–20.20	4.59–29.80	4.37–29.20
R_{int}	0.0204	0.0224	0.0516
Reflections collected/unique	7026/3024	14,003/5905	5034/2605
Goodness-of-fit on F^2	0.994	0.979	0.909
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0291, 0.0804	0.0271, 0.0633	0.0449, 0.0840
$R_1{}^a$, $wR_2{}^b$ (all data)	0.0346, 0.0830	0.0436, 0.0672	0.1025, 0.0911

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

two metal centers, and each L$^-$ is tridentate linking three metals. The two adjacent Cd ions are joined into a binuclear kernel consisting of a four-membered {CdOCdO} ring by bridging carboxylates of L$^-$; this sort of carboxylate bridged unit has been reported before [14a–c]. The Cd···Cd distance across the binuclear unit is 4.202(3) Å. Neighboring dinuclear clusters are connected to each other by two Cl$^-$ anions to form a 1-D chain (figure 1b). The Cd···Cd distance separated by Cl$^-$ is 3.385(5) Å. Dinuclear clusters are also linked by pairs of antiparallel L$^-$ anions *via* the pyridyl nitrogen and carboxylate oxygens to produce double helical chains with an opposite Cd···Cd distance of 12.090(3) Å, which are further propagated by Cl$^-$ into an interesting 3-D framework (figure 1c). From a topological view, if the dinuclear cluster are taken as four-connected node and L$^-$ anions are considered as connected line, the 3-D framework can be simplified as a 4-connected zeolite ABW net (also named as **sra**) with the vertex symbol ($4^2 \cdot 6^3 \cdot 8$) topology (figure 1d) [15]. The 4-connected nets with tetrahedral nodes, **dia** (diamond) net has been reported widely, while the **sra** net is relatively rare [16].

3.1.2. Structure of [CdL$_2$]$_n$ (2).

Compounds **1** and **2** are synthesized under similar conditions; however, the structures are quite different. When $CdCl_2 \cdot 2H_2O$ is replaced by $Cd(OAc)_2 \cdot 2H_2O$, **2** is obtained. As shown in figure 2(a), the independent unit of **2** contains one Cd^{II} and two L$^-$. Cd^{II} is located in the center of a distorted octahedral geometry (CdN_2O_4) by coordinating to two nitrogens from pyridyl (Cd1–N1 = 2.270(2) Å, Cd1–N3 = 2.267(2) Å, N1–Cd1–N3 = 99.54(6)°) of two L$^-$ and four carboxyl oxygens (Cd–O = 2.285(3)–2.456(3) Å) from two L$^-$. The carboxylate groups are bidentate chelating and each L$^-$ is a linear bridging unit linking two metals. Two *trans* L$^-$ anions and two Cd(II) cations are connected to form a {Cd–L–Cd–L}

Table 2. Selected bond distances (Å) and angles (°) for **1–3**.

1			
N(1)–Cd(1)$^{\rm i}$	2.283(2)	Cd(1)–O(1)$^{\rm ii}$	2.213(2)
O(1)–Cd(1)$^{\rm ii}$	2.213(2)	Cd(1)–N(1)$^{\rm i}$	2.283(2)
O(2)–Cd(1)	2.355(2)	Cd(1)–Cl(1)	2.523(1)
O(1)$^{\rm ii}$–Cd(1)–N(1)$^{\rm i}$	121.05(9)	O(1)$^{\rm ii}$–Cd(1)–Cl(1)$^{\rm iii}$	91.88(7)
O(1)$^{\rm ii}$–Cd(1)–O(2)	108.21(8)	N(1)$^{\rm i}$–Cd(1)–Cl(1)$^{\rm iii}$	89.69(7)
N(1)$^{\rm i}$–Cd(1)–O(2)	84.54(8)	O(2)–Cd(1)–Cl(1)$^{\rm iii}$	159.21(6)
O(1)$^{\rm ii}$–Cd(1)–Cl(1)	103.10(7)	Cl(1)–Cd(1)–Cl(1)$^{\rm iii}$	84.52(3)
N(1)$^{\rm i}$–Cd(1)–Cl(1)	135.65(7)	Cd(1)–Cl(1)–Cd(1)$^{\rm iii}$	95.48(3)
O(2)–Cd(1)–Cl(1)	85.72(6)		
2			
Cd(1)–N(3)	2.267(2)	Cd(1)–O(2)$^{\rm ii}$	2.2891(15)
Cd(1)–N(1)	2.270(2)	Cd(1)–O(3)$^{\rm i}$	2.4032(15)
Cd(1)–O(4)$^{\rm i}$	2.285(2)	Cd(1)–O(1)$^{\rm ii}$	2.456(2)
N(3)–Cd(1)–N(1)	99.54(6)	O(4)$^{\rm i}$–Cd(1)–O(3)$^{\rm i}$	55.60(5)
N(3)–Cd(1)–O(4)$^{\rm i}$	95.74(6)	O(2)$^{\rm ii}$–Cd(1)–O(3)$^{\rm i}$	101.02(5)
N(1)–Cd(1)–O(4)$^{\rm i}$	141.12(6)	N(3)–Cd(1)–O(1)$^{\rm ii}$	87.12(6)
N(3)–Cd(1)–O(2)$^{\rm ii}$	136.02(6)	N(1)–Cd(1)–O(1)$^{\rm ii}$	101.40(6)
N(1)–Cd(1)–O(2)$^{\rm ii}$	107.73(7)	O(4)$^{\rm i}$–Cd(1)–O(1)$^{\rm ii}$	114.94(6)
O(4)$^{\rm i}$–Cd(1)–O(2)$^{\rm ii}$	84.23(7)	O(2)$^{\rm ii}$–Cd(1)–O(1)$^{\rm ii}$	54.48(5)
N(3)–Cd(1)–O(3)$^{\rm i}$	115.12(6)	O(3)$^{\rm i}$–Cd(1)–O(1)$^{\rm ii}$	155.50(5)
N(1)–Cd(1)–O(3)$^{\rm i}$	85.58(6)		
3			
N(1)–Co(1)$^{\rm i}$	2.126(3)	O(1)–Co(1)	2.127(2)
O(2)–Co(1)	2.145(2)	Co(1)–O(1)$^{\rm ii}$	2.127(2)
Co(1)–N(1)$^{\rm iii}$	2.126(3)	Co(1)–O(2)$^{\rm ii}$	2.145(2)
O(1)$^{\rm ii}$–Co(1)–O(1)	180.00(4)	O(1)$^{\rm ii}$–C(o1)–N(1)$^{\rm iii}$	88.69(9)
O(1)–Co(1)–N(1)$^{\rm iii}$	91.31(9)	O(1)–Co(1)–N(1)$^{\rm iv}$	88.69(9)
N(1)$^{\rm iii}$–Co(1)–N(1)$^{\rm iv}$	180.0(4)	O(1)$^{\rm ii}$–Co(1)–O(2)	118.07(8)
O(1)–Co(1)–O(2)	61.93(8)	N(1)$^{\rm iii}$–Co(1)–O(2)	89.30(9)
O(1)$^{\rm ii}$–Co(1)–O(2)$^{\rm ii}$	61.93(8)	O(1)–Co(1)–O(2)$^{\rm ii}$	118.07(8)
N(1)$^{\rm iii}$–Co(1)–O(2)$^{\rm ii}$	90.70(9)	O(2)–Co(1)–O(2)$^{\rm ii}$	180.0

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

ring with Cd $\cdots$ Cd distance of 10.223(6) Å. Adjacent rings share L^- anions *via* Cd to generate an infinite 1-D ladder-like framework. The distance of adjacent rings separated by the L^- linker is 12.476(3) Å (figure 2b). The approximately parallel orientation of the pyridyl rings allow neighboring chains to generate a 2-D supramolecular layer through $\pi \cdots \pi$ stacking interactions (with face-to-face distances of 3.408(3) Å and centroid-to-centroid distance of 3.599(3) Å, figure 2c). There are also $\pi \cdots \pi$ stacking interactions (with face-to-face distance of 3.574(7) Å and centroid-to-centroid distance of 3.816(6) Å, figure 2d) among the 2-D supramolecular layers. Finally, a 3-D supramolecular structure is obtained. The $\pi \cdots \pi$ stacking interactions play an important role in the formation and stabilization of the 3-D supramolecular structure [17].

3.1.3. Structure of $[CoL_2]_n$ (3).

The independent unit of **3** consists of half a Co^{II} cation and one L^- (figure 3a). The Co^{2+} is on a center of symmetry with a distorted octahedral (CoN_2O_4) geometry with two nitrogens from pyridyl of two symmetry-related L^- anions *trans* and four carboxyl oxygens from two symmetry-related L^- anions in the equatorial plane. The mean Co–O and Co–N distances in **3** are 2.135 and 2.125 Å, respectively.

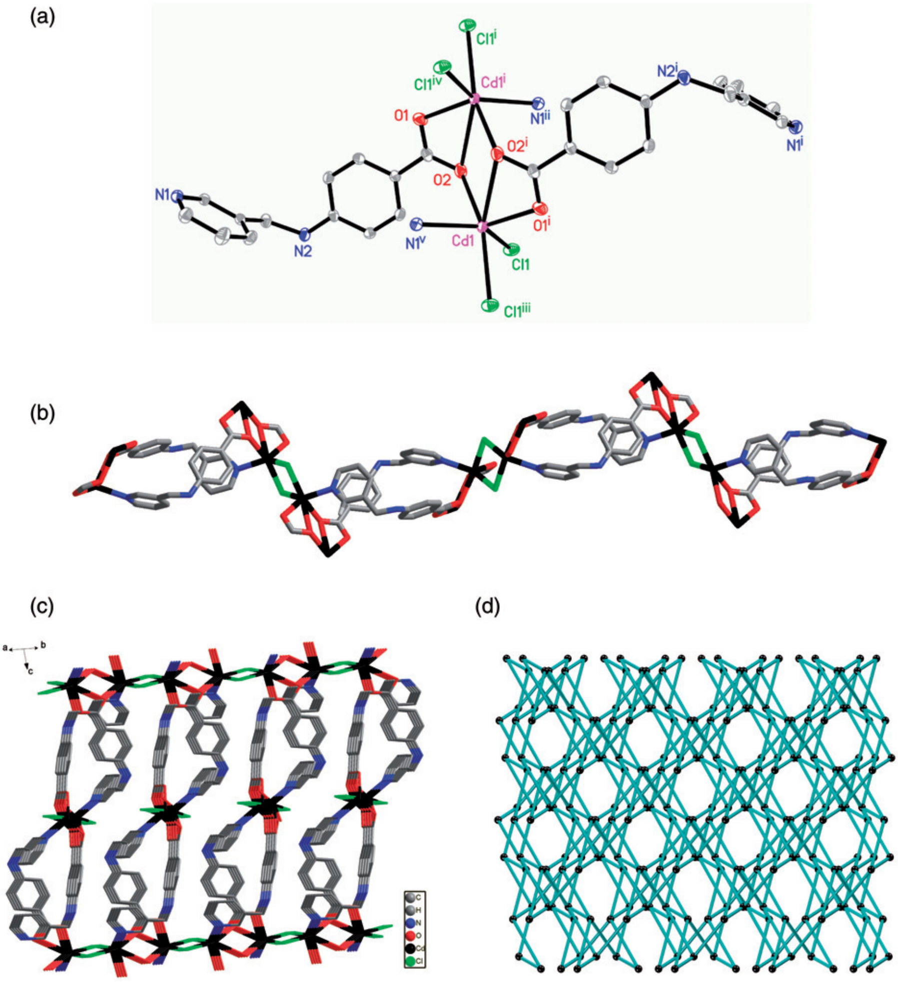


Figure 1. (a) A view of the local coordination environment of Cd^{II} in **1**; (b) 1-D chain based on neighboring dinuclear clusters and Cl^- anions; (c) view of the 3-D metal-organic framework through double helix chains and Cl^- anions; (d) schematic diagram (OLEX) showing the 4-connected network with a $(4^2 \cdot 6^3 \cdot 8)$ topology along the *c*-axis. Symmetry codes: (i) $3/2-x$, $1/2-y$, $1-z$; (ii) $x-1/2$, $1/2-y$, $z-1/2$; (iii) $1-x$, $-y$, $1-z$; (iv) $x+1/2$, $y+1/2$, z; (v) $2-x$, y, $3/2-z$.

The carboxylate is bidentate chelating and each Co^{II} is bridged by pairs of L^- to form a 1-D polymeric structure, with adjacent $Co \cdots Co$ separation distance of 10.5834(6) Å. The approximately parallel orientation of the pyridyl rings allow neighboring chains to generate a 2-D supramolecular layer through $\pi \cdots \pi$ stacking interactions (with face-to-face distances of 3.527(3) Å and centroid-to-centroid distance of 3.838(3) Å, figure 3b).

Compounds **2** and **3** were hydrothermally synthesized at the same conditions. Compound **2** has an infinite 1-D ladder-like framework, further stacked by $\pi \cdots \pi$ interactions to yield a 3-D supramolecular structure. Compound **3** contains a 1-D double zigzag chain, which is further connected through $\pi \cdots \pi$ stacking interactions to

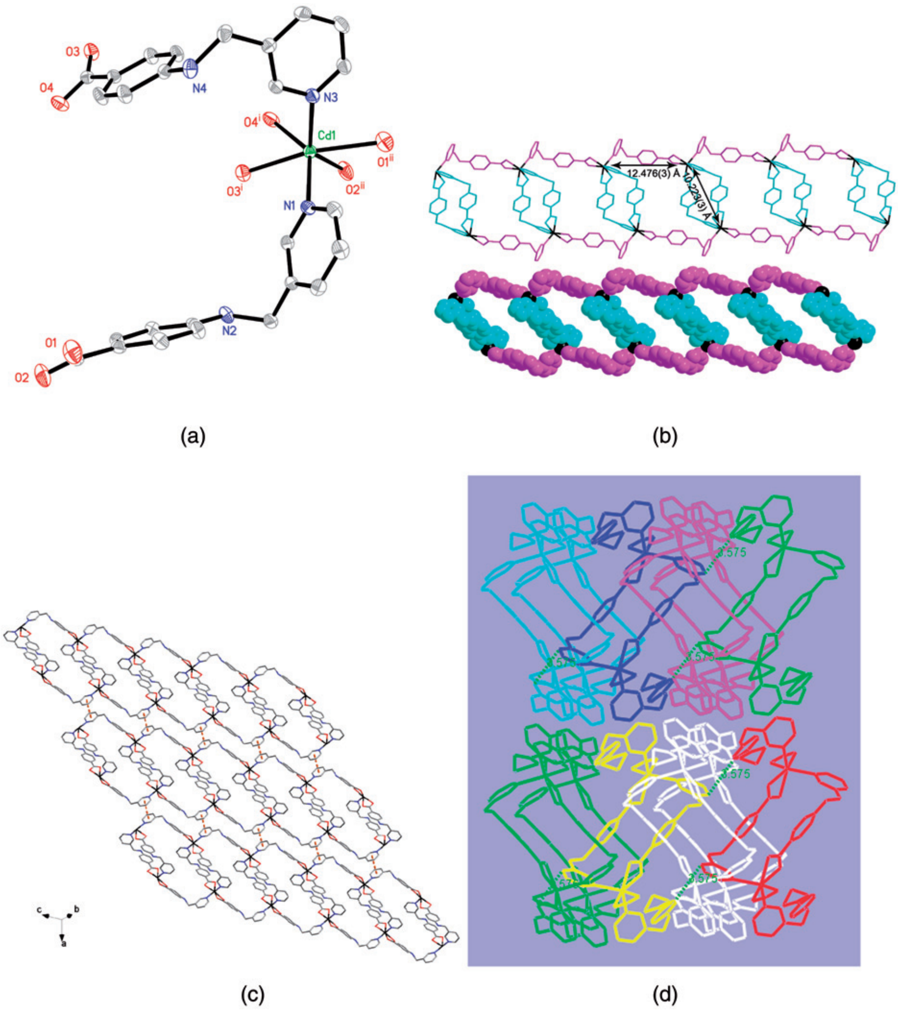
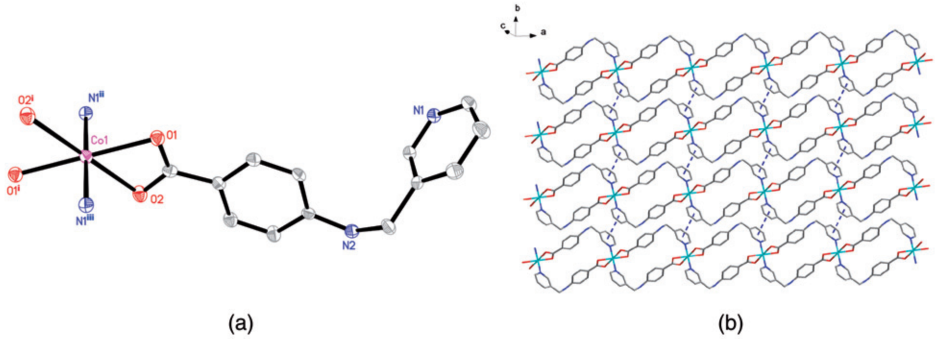


Figure 2. (a) A view of the local coordination environment of Cd^{II} in **2**; (b) linear and space filling representations of the chainlike structure of **2**; (c) the extended 2-D supramolecular structure of **2** formed through $\pi\cdots\pi$ interactions; (d) the 3-D supramolecular structure of **2**. Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) x, y, $z-1$.

form a 2-D supramolecular layer. The structural differences between them imply that cations make an important role in the formation of the structure.

3.2. *Luminescent properties*

Recently, polymeric Cd^{II} complexes have been investigated for fluorescence properties and potential applications as new luminescent materials [18]. The solid-state luminescence properties of **1** and **2** as well as the free HL ligand were investigated at room temperature (figure 4). The strongest emission peak for HL is observed at 510 nm upon



(a) (b)

Figure 3. (a) The local coordination environment of Co^{II} in **3**; (b) The extended 2-D supramolecular structure of **3** formed through $\pi\cdots\pi$ interactions; Symmetry codes: (i) $2-x$, $-y$, $1-z$; (ii) $x-1$, y, z; (iii) $-x+3$, $-y$, $1-z$.

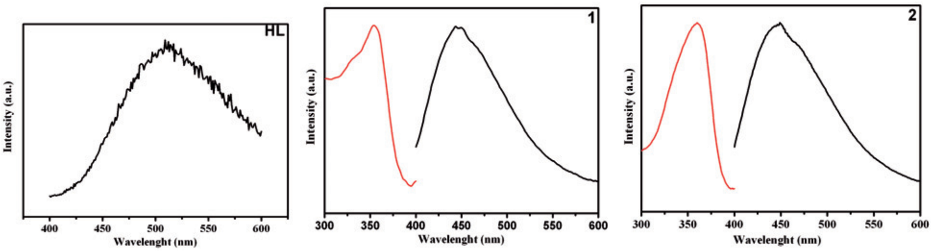


Figure 4. Solid-state photoluminescence spectra of HL, **1** and **2** at room temperature.

excitation at 255 nm, which is probably attributable to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transition [19]. Complexes **1** and **2** both exhibit intense blue photoluminescence. The emission spectra of **1** had the emission maxima at 449 nm, whereas that of **2** was 450 nm upon excitation at 354 and 364 nm, respectively. Emission maxima of **1** and **2** are similar because of the slight difference in structures. These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT), since Cd^{II} is difficult to oxidize or reduce due to the d^{10} configuration [20]. In comparison to that of the free HL, most of the emission maxima of **1** and **2** are significantly shifted. The shifts of the emission bands are attributed to both the deprotonated effect of HL ligand and the coordination interactions of the organic ligand to Cd(II) [21].

The luminescence decay curves of **1** and **2** at room temperature (figure 5) are well fit into a single-exponential function as $I = A\exp(-t/\tau) + y_0$ (the black circles represent experimental data and the solid red lines represent fitting results). The luminescent lifetimes τ are 11.12 ns for **1** and 8.82 ns for **2**. The luminescence components may come from HL (**1** and **2**). The luminescence lifetimes of **1** and **2** are much shorter than ones from a triplet state ($>10^{-3}$ s), so the emissions should arise from a singlet state [22].

3.3. *Thermal analysis*

To characterize the compounds more fully, their thermal behaviors were studied by TGA. The experiments were performed on samples consisting of numerous single

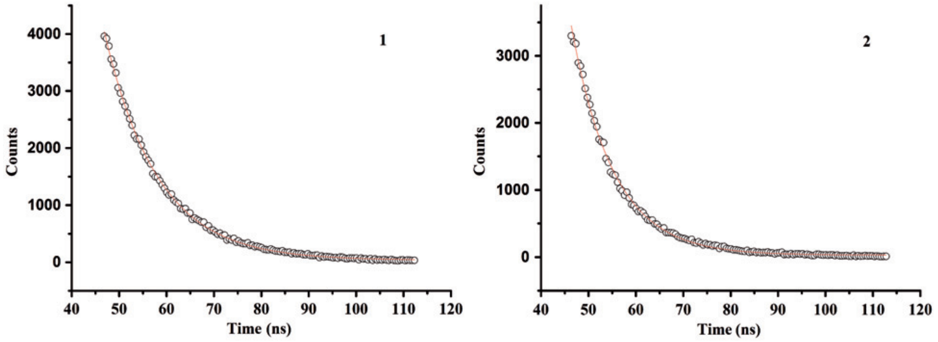


Figure 5. Luminescence decay curves for **1** ($\lambda_{ex} = 354$ nm; $\lambda_{em} = 449$ nm) and **2** ($\lambda_{ex} = 364$ nm; $\lambda_{em} = 450$ nm).

crystals of **1–3** under N_2 with a heating rate of 10° min^{-1} (Supplementary material). The networks remain intact until 320°C, 190°C, and 336°C, respectively, and then begin to collapse. For **1**, the weight loss corresponding to the release of organic component is from 320°C to 724°C (Obsd 65.73%, Calcd 65.77%). Compound **2** loses its organic component between 190°C and 668°C (Obsd 76.44%, Calcd 77.35%). In the case of **3**, weight loss of 84.93% (Calcd 85.41%) between 336 and 511°C is attributed to the release of organic component. The remaining weight of **1**–**3** corresponds to the formation of CdO or Co_2O_3.

3.4. *X-ray powder diffraction analysis*

As shown in "Supplementary material", the experimental powder XRD patterns are in good agreement with the corresponding simulated ones except for the relative intensity variation because of the preferred orientations of the crystals. Therefore, the phase purity of the as-synthesized products is substantiated.

4. Conclusion

Three structurally different coordination frameworks based on 4-[(3-pyridyl) methylamino]benzoate have been prepared and characterized by single-crystal X-ray diffraction. These compounds display coordination features with 1-D or 3-D frameworks. The structures of **1** and **2** are greatly affected by metal salts. In **1**, $CdCl_2$ is further extended into a 3-D framework. When $Cd(OAc)_2$ is used, a 3-D supramolecular structure of **2** was obtained. In **2**, OAc^- does not participate in coordination. When $Cd(OAc)_2$ is replaced by $Co(OAc)_2$, a 2-D supramolecular structure of **3** was obtained. The structural difference between **2** and **3** was caused by the metal cations.

Supplementary material

X-ray crystallographic files in CIF format for **1–3** have been deposited at the Cambridge Crystallographic Data Center with deposition number CCDC

776659−776661. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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