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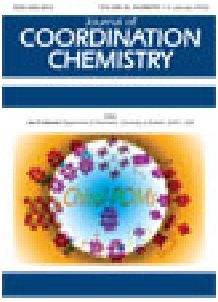

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Syntheses, structures, and fluorescent properties of two new d^{10}-metal coordination polymers containing 1-((benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole ligand

Dong Zhao [a], Yu Xiu [a], Xiao-Li Zhou [b] & Xiang-Ru Meng [a]

[a] Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P.R. China

[b] Experiment Administrative Center, Zhongzhou University, Zhengzhou 450044, P.R. China

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Syntheses, structures, and fluorescent properties of two new d^{10}-metal coordination polymers containing 1-((benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole ligand

DONG ZHAO†, YU XIU†, XIAO-LI ZHOU‡ and XIANG-RU MENG*†

†Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P.R. China
‡Experiment Administrative Center, Zhongzhou University, Zhengzhou 450044, P.R. China

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Two new coordination polymers formulated as $\{[Zn(bdic)(bmt)H_2O]\cdot 0.5H_2O\}_n$ (**1**) and $\{[Cd(bdic)(bmt)(H_2O)_2]\cdot 2H_2O\}_n$ (**2**) ($H_2bdic = 1,3$-benzenedicarboxylic acid, bmt = 1-((benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole) have been synthesized and characterized by elemental analysis, IR, and single-crystal X-ray diffraction. Both coordination polymers exhibit 1-D chain structure where bmt is unidentate and $bdic^{2-}$ bridging. In **1**, bmt hangs at two sides of the main chain, whereas bmt hangs at one side of the main chain in **2**. Fluorescent properties have also been determined.

Keywords: 1-((Benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole); Crystal structure; Fluorescent property

1. Introduction

Coordination polymers attract attention because of intriguing structures, interesting properties, and potential applications in ion exchange, catalysis, luminescence, magnetic, and porous materials [1–3]. A number of coordination polymers have been reported. However, it is still a challenge to control the exact structures of the final products [4]. To further explore the factors that affect the structures and topologies of coordination polymers, coordination polymers based on *N*-heterocyclic ligands, such as imidazole, triazole, tetrazole, benzimidazole, benzotriazole, pyridine, pyrazine, hexahydropyridine, piperazine, and their derivatives, have been reported [5–16], especially those containing symmetrical ligands [17–20]. However, coordination polymers based on unsymmetrical *N*-heterocyclic ligands have rarely been studied. Coordination polymers with d^{10}-metal centers especially zinc or cadmium are promising candidates for photoactive materials [21].

In this work, we select the multidentate unsymmetrical *N*-heterocyclic compound 1-((benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole (bmt) as ligand and investigate the effect of ions on the final structures. Two new coordination polymers

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*Corresponding author. Email: mxr@zzu.edu.cn

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$\{[Zn(bdic)(bmt)H_2O] \cdot 0.5H_2O\}_n$ (**1**) and $\{[Cd(bdic)(bmt)(H_2O)_2] \cdot 2H_2O\}_n$ (**2**) ($H_2bdic = 1,3$-benzenedicarboxylic acid, bmt = 1-((benzotriazol-1-yl) methyl)-1-H-1,2,4-triazole) are obtained and characterized by IR, elemental analysis, fluorescent properties, and X-ray crystallography.

2. Experimental

2.1. *General information and materials*

1-((Benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole (bmt) was synthesized according to the literature method [22]. All chemicals were commercially available and used without purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. The fluorescent spectrum was determined in solid state at room temperature on a Hitachi F-4500 fluorophotometer with the excitation and emission slits of 5 nm and the response time of 1 s (240 nm min^{-1}).

2.2. *Synthesis of* $\{[Zn(bdic)(bmt)H_2O] \cdot 0.5H_2O\}_n$ *(1)*

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol), H_2bdic (0.1 mmol), bmt (0.1 mmol), water (5 mL), and DMF (2 mL) was placed in a 25 mL Teflon-lined stainless steel vessel and heated at 100°C for 3 days. After the mixture was cooled to room temperature at 10°C h^{-1}, colorless crystals of **1** were obtained. Anal. Calcd for $C_{17}H_{15}N_6O_{5.5}Zn$ (%): C, 44.67; H, 3.28; N, 18.39. Found: C, 43.89; H, 3.14; N, 18.21. Selected IR (cm^{-1}, KBr): 3440(m), 3116(m), 1616(s), 1567(s), 1538(m), 1498(m), 1424(s), 1405(s), 1368(s), 1281(m), 1269(m), 1129(s), 888(w), 774(m), 744(s), 727(s).

2.3. *Synthesis of* $\{[Cd(bdic)(bmt)(H_2O)_2] \cdot 2H_2O\}_n$ *(2)*

The preparation of **2** was similar to that of **1** except that $Cd(NO_3)_2 \cdot 4H_2O$ (0.10 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$. Colorless crystals of **2** were obtained. Anal. Calcd for $C_{17}H_{20}CdN_6O_8$ (%): C, 37.17; H, 3.64; N, 15.30. Found: C, 37.13; H, 3.74; N, 15.22. Selected IR (cm^{-1}, KBr): 3442(s), 3120(w), 1667(s), 1608(s), 1544(s), 1486(m), 1440(s), 1387(s), 1317(m), 1285(s), 1207(s), 1134(s), 904(m), 792(m), 750(s), 727(s).

2.4. *Single-crystal structure determination*

A suitable single crystal of each compound was carefully selected and glued 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-Kα radiation, $\lambda = 0.710\,73$ Å) operating at 50 kV and 40 mA. The data were collected in 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-polarization effects, the structures were solved by direct methods, completed by

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

Coordination polymers	**1**	**2**
Empirical formula	$C_{17}H_{15}N_6O_{5.5}Zn$	$C_{17}H_{20}CdN_6O_8$
Formula weight	456.72	548.79
Temperature (K)	293(2)	293(2) K
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
Unit cell dimensions (Å, °)		
a	19.560(4)	30.936(6)
b	12.428(3)	10.389(2)
c	15.761(3)	18.022(4)
α	90	90
β	105.70(3)	9 125.57(3)
γ	90	90
Volume (Å^3), Z	3688.5(13), 8	4711.4(23), 8
Calculated density (Mg m^{-3})	1.645	1.547
Absorption coefficient (mm^{-1})	1.380	0.979
Reflections collected	13609	19435
Independent reflection	3593 [R(int) = 0.0307]	5580 [R(int) = 0.0431]
F(000)	1864	2208
Crystal sizes (mm^3)	0.20 × 0.18 × 0.15	0.20 × 0.18 × 0.15
Data/restraints/parameters	3593/0/267	5580/2/289
Goodness-of-fit on F^2	1.104	1.093
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0367$, $wR_2 = 0.0775$	$R_1 = 0.0474$, $wR_2 = 0.0993$
R indices (all data)	$R_1 = 0.0413$, $wR_2 = 0.0800$	$R_1 = 0.0602$, $wR_2 = 0.1063$
Largest difference peak and hole (e Å^{-3})	0.304 and −0.271	0.458 and −0.502

difference Fourier syntheses and refined by full-matrix least-squares using the SHELXS-97 program package [23]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. Crystallographic parameters and structural refinements for both coordination polymers are summarized in table 1. Selected bond lengths and angles of the two coordination polymers are listed in table 2 and H-bonds in table 3.

3. Results and discussion

3.1. *IR spectroscopy of coordination polymers 1 and 2*

IR spectra show that the absorptions at 3440 cm^{-1} for **1** and 3442 cm^{-1} for **2** can be attributed to O–H stretch. The absorptions at 3116 cm^{-1} for **1** and 3120 cm^{-1} for **2** can be attributed to Ar–H stretch. The separations (Δ) between ν_a(COO) and ν_s(COO) are different for monodentate and chelating coordination polymers. In coordination polymer **1**, carboxylate groups exhibit the ν_a(COO) and ν_s(COO) at 1616 and 1424 cm^{-1} ($\Delta = 192$ cm^{-1}), comparable to those of monodentate carboxylate groups [24]. Different from coordination polymer **1**, carboxylates in **2** coordinate to Cd(II) ions as chelating, and the separations (Δ) between ν_a(COO) and ν_s(COO) are 58 cm^{-1} (1544 cm^{-1}, 1486 cm^{-1}). The above analyses are consistent with the results of the X-ray diffraction.

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

Coordination polymer **1**			
Zn(1)–O(3)#1	1.9467(28)	Zn(1)–O(1)	1.9611(17)
Zn(1)–O(5)	1.9621(18)	Zn(1)–N(1)	2.030(2)
O(3)#1–Zn(1)–O(1)	102.19(7)	O(3)#1–Zn(1)–O(5)	126.53(8)
O(1)–Zn(1)–O(5)	106.30(8)	O(3)#1–Zn(1)–N(1)	109.95(8)
O(1)–Zn(1)–N(1)	104.00(8)	O(5)–Zn(1)–N(1)	105.71(8)
Coordination polymer **2**			
Cd(1)–O(5)	2.304(3)	Cd(1)–N(1)	2.336(4)
Cd(1)–O(6)	2.355(3)	Cd(1)–O(4)#1	2.373(3)
Cd(1)–O(3)#1	2.384(3)	Cd(1)–O(2)	2.389(3)
Cd(1)–O(1)	2.460(3)		
O(5)–Cd(1)–N(1)	164.95(14)	O(5)–Cd(1)–O(6)	85.19(12)
N(1)–Cd(1)–O(6)	81.77(12)	O(5)–Cd(1)–O(4)#1	84.17(13)
N(1)–Cd(1)–O(4)#1	110.53(13)	O(6)–Cd(1)–O(4)#1	136.77(11)
O(5)–Cd(1)–O(3)#1	90.02(12)	N(1)–Cd(1)–O(3)#1	95.86(12)
O(6)–Cd(1)–O(3)#1	83.27(11)	O(4)#1–Cd(1)–O(3)#1	55.00(10)
O(5)–Cd(1)–O(2)	97.66(13)	N(1)–Cd(1)–O(2)	87.98(12)
O(6)–Cd(1)–O(2)	141.42(11)	O(4)#1–Cd(1)–O(2)	81.60(11)
O(3)#1–Cd(1)–O(2)	134.95(11)	O(5)–Cd(1)–O(1)	82.53(13)
N(1)–Cd(1)–O(1)	89.75(12)	O(6)–Cd(1)–O(1)	89.05(11)
O(4)#1–Cd(1)–O(1)	130.58(10)	O(3)#1–Cd(1)–O(1)	169.73(11)
O(2)–Cd(1)–O(1)	53.64(11)		

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

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) (°)
Coordination polymer **1**				
O(5)–H(5A)···O(6)	0.85	1.80	2.652(3)	174.8
O(5)–H(5B)···O(4)#3	0.85	1.79	2.611(3)	163.1
O(6)–H(6A)···N(5)#4	0.85	2.42	3.086(4)	136.3
Coordination polymer **2**				
O(5)–H(5A)···O(6)	0.85	2.31	3.153(5)	179.5
O(7)–H(7A)···O(2)	0.87	1.97	2.837(5)	179.7
O(8)–H(8A)···N(2)	0.85	2.31	2.946(6)	131.7
O(5)–H(5B)···N(6)#3	0.85	2.01	2.816(6)	157.3
O(6)–H(6A)···O(7)#4	0.85	1.93	2.755(5)	163.6
O(6)–H(6B)···O(3)#4	0.85	1.97	2.791(4)	161.5
O(8)–H(8B)···O(5)#5	0.85	2.07	2.854(6)	153.3
O(7)–H(7B)···O(1)#6	0.85	1.90	2.751(5)	179.3

Symmetry transformations used to generate equivalent atoms for **1**: #3: $x-1/2$, $-y+1/2$, $z-1/2$; #4: $-x$, $-y$, $-z$. For **2**: #3: $x+1/2$, $-y+1/2$, $z+1/2$; #4: $-x+1/2$, $y+1/2$, $-z+1/2$; #5 $-x+1/2$, $-y+1/2$, $-z+1$; #6: $-x+1/2$, $y-1/2$, $-z+1/2$.

3.2. *Crystal structure of* $\{[Zn(bdic)(bmt)H_2O]\cdot 0.5H_2O\}_n$ *(1)*

The results of X-ray crystallographic analysis reveal that **1** crystallizes in monoclinic with space group $C2/c$. The asymmetric unit of **1** contains one Zn(II), one bmt, one bdic^{2-}, one coordinated water molecule and a half of an uncoordinated water molecule. As exhibited in figure 1(a), Zn1 is four-coordinate with distorted tetrahedral geometry by one nitrogen (N1) atom from bmt, one oxygen (O5) atom from water and two

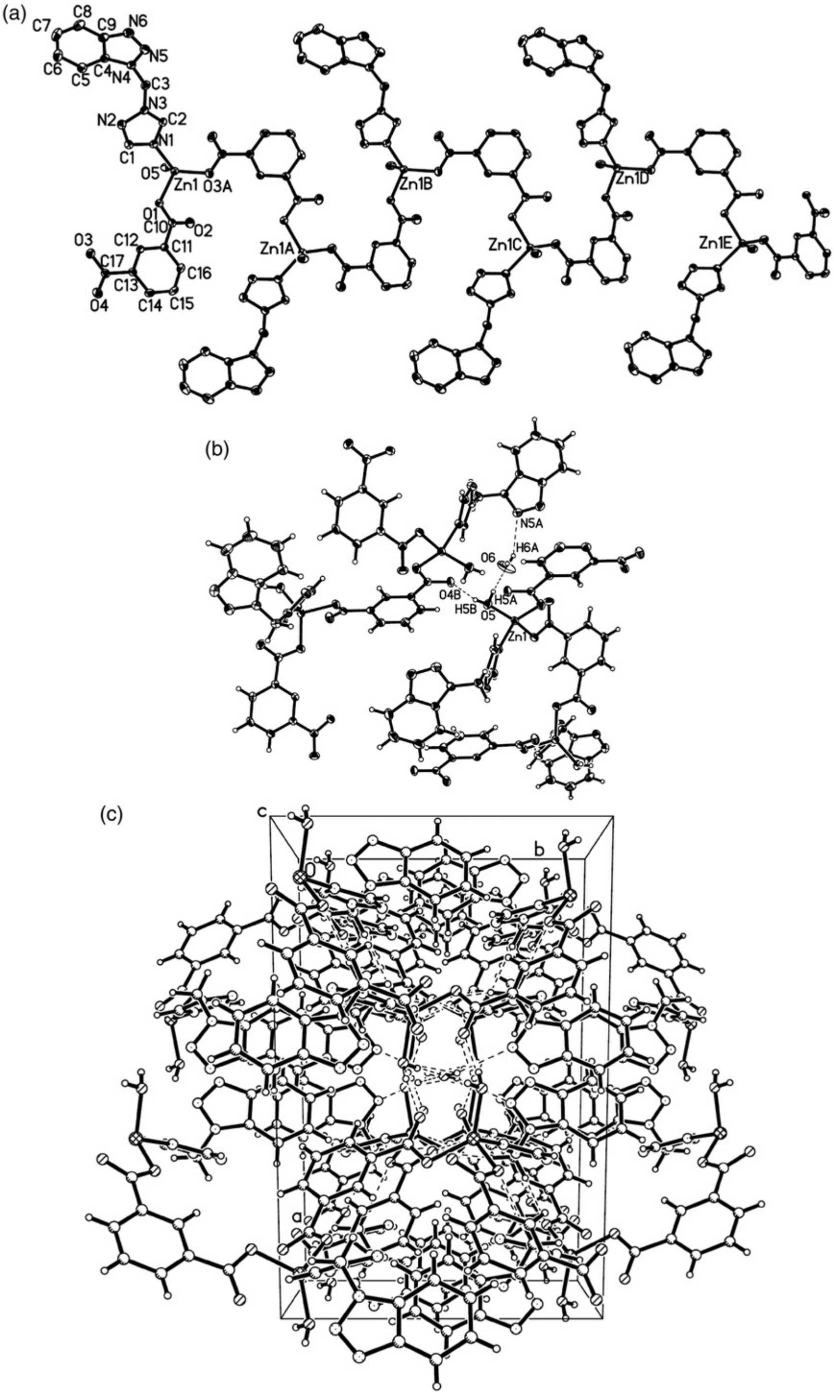

Figure 1. (a) Coordination environment of Zn(II) in **1** with the atom-numbering scheme and the view of the 1-D zigzag chain. Hydrogen atoms and water molecules are omitted for clarity, (b) view of hydrogen bonds in **1** and (c) 3-D structure of **1** linked through hydrogen bonds indicated by dashed lines.

unidentate carboxylate oxygen atoms (O1 and O3A) from two $bdic^{2-}$ groups. The Zn1–N distance is 2.030(2) Å and the Zn1–O distances are 1.9611(17), 1.9467(18) and 1.9621(18) Å. These bond lengths are close to those in $[Zn_3(L)(btc)_2(H_2O)_2] \cdot 3H_2O$ (L = 1,2,4,5-tetrakis(imidazol-1-ylmethyl)benzene; btc = 1,3,5-benzenetricarboxylic acid) [25].

As exhibited in figure 1(a), each $bdic^{2-}$ bridges two Zn(II) ions to form a 1-D chain ($\cdots$Zn-$bdic^{2-}$–Zn-$bdic^{2-}\cdots$) *via* Zn1–O bonds. The distance of Zn(II)–Zn(II) bridged by $bdic^{2-}$ groups is 8.260 Å; bmt coordinates monodentate to zinc and hang at two sides of the main chain. All benzotriazole rings on the same side are parallel and the distance between the neighboring benzotriazole rings is 12.248 Å. As shown in figure 1(b), there are hydrogen-bonding interactions between coordinated water molecules and uncoordinated water molecules, between the coordinated water molecules and carboxylate and between uncoordinated water and nitrogen of bmt. The existence of hydrogen-bonding further stabilizes the 3-D structure as illustrated in figure 1(c).

3.3. *Crystal structure of $\{[Cd(bdic)(bmt)(H_2O)_2] \cdot 2H_2O\}_n$ (2)*

Since the structures of complexes can be influenced by various factors including metal centers [26], we introduced Cd(II) to the reaction system and coordination polymer **2** was obtained. As Cd(II) radius is larger than Zn(II), the Cd(II) in **2** is seven-coordinate by one bmt, two $bdic^{2-}$ and two coordinated water molecules. Carboxylates of $bdic^{2-}$ coordinate to Cd(II) ion in chelating mode, as opposed to monodentate in **1**. Single-crystal X-ray analysis reveals that **2** crystallizes in monoclinic space group $C2/c$. The central Cd(II) (figure 2a) is in a distorted pentagonal bipyramidal coordination environment with one nitrogen (N1) atom from one bmt and six oxygen atoms from two chelating carboxylates (O1, O2, O3A, O4A) and two water molecules (O5, O6). The Cd–N bond lengths (2.336(4) Å) are similar to those in $\{[CdCl(pbbm)_2]Cl \cdot CH_3OH\}_n$ (pbbm = 1,10-(1,5-pentamethylene) *bis*-1 H-benzimidazole) [27]. The overall structure of **2** is an infinite 1-D chain presented in figure 2(b). The bmt using nitrogen from triazole coordinates monodentate to Cd(II). The $bdic^{2-}$ groups bridge the Cd(II) to form a 1-D chain ($\cdots$Cd-$bdic^{2-}$–Cd-$bdic^{2-}\cdots$). The Cd(II)–Cd(II) distance separated by bridging $bdic^{2-}$ is 9.723 Å. In **2**, bmt ligands hang at one side of the main chain. In addition, there are hydrogen-bonding interactions between coordinated water and uncoordinated water, between coordinated water and carboxylate and between uncoordinated water and nitrogen of bmt (figure 2c). These 1-D chains are further connected into a 3-D supramolecular framework through hydrogen-bonding indicated by the dashed lines in figure 2(d).

3.4. *Fluorescent properties*

Investigating through the literature, we find that metal–organic frameworks constructed from d^{10}-metal centers and conjugated organic linkers are promising candidates for photoactive materials [28, 29]. The fluorescence of free bmt, H_2bdic, **1**, and **2** are determined in the solid state at room temperature. As shown in figure 3, excitation at 320 nm leads to emission bands at 359 nm for **1** and 362 nm for **2** under the same conditions; H_2bdic exhibits band emissions with maximum intensity at 378 nm upon excitation at 320 nm. Free bmt exhibits very weak emissions. The fluorescent

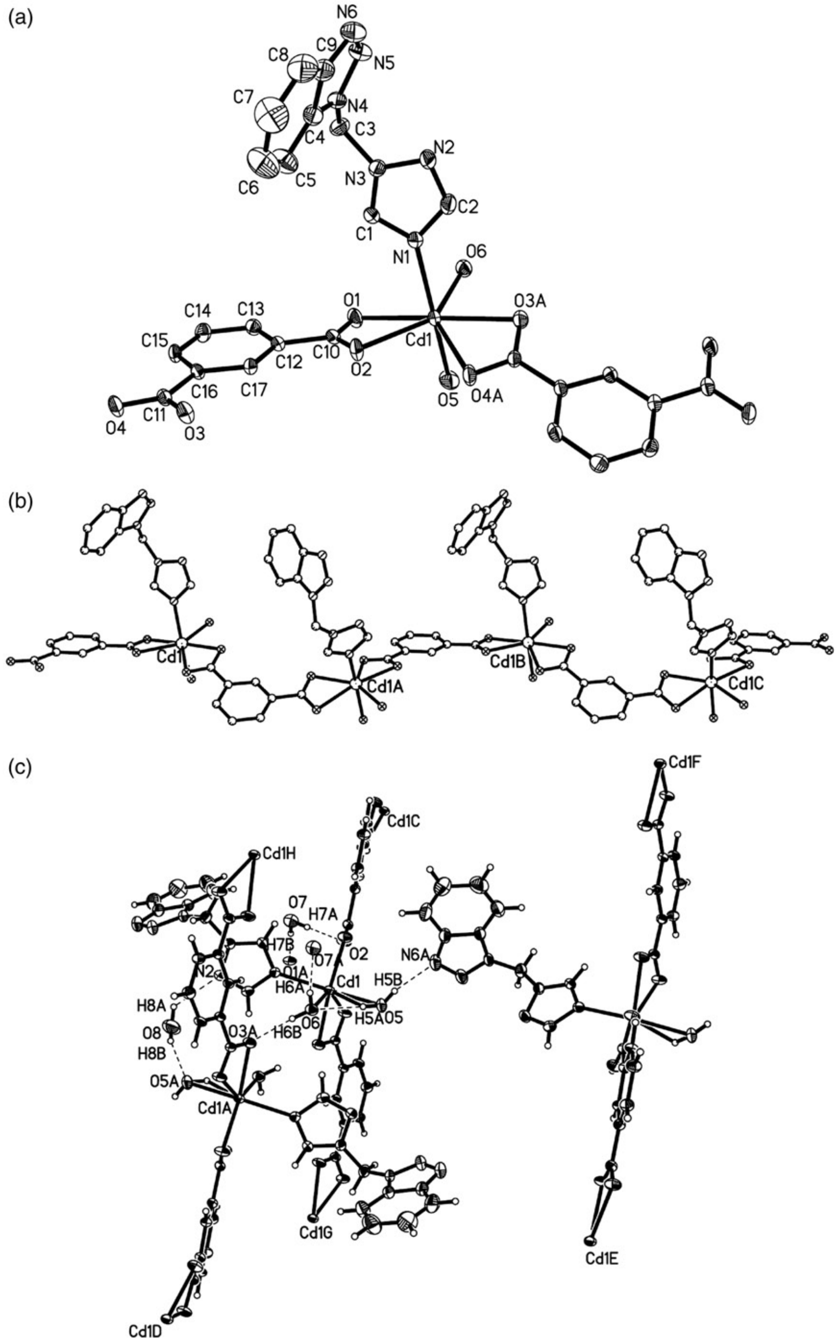

Figure 2. (a) View of coordination sphere around Cd(II) in **2**. Hydrogen atoms and water molecules are omitted for clarity, (b) view of the 1-D chain of **2**. Hydrogen atoms and water molecules are omitted for clarity, (c) view of hydrogen bonds in **2** and (d) 3-D structure of **2** in the solid state supported by hydrogen bonds.

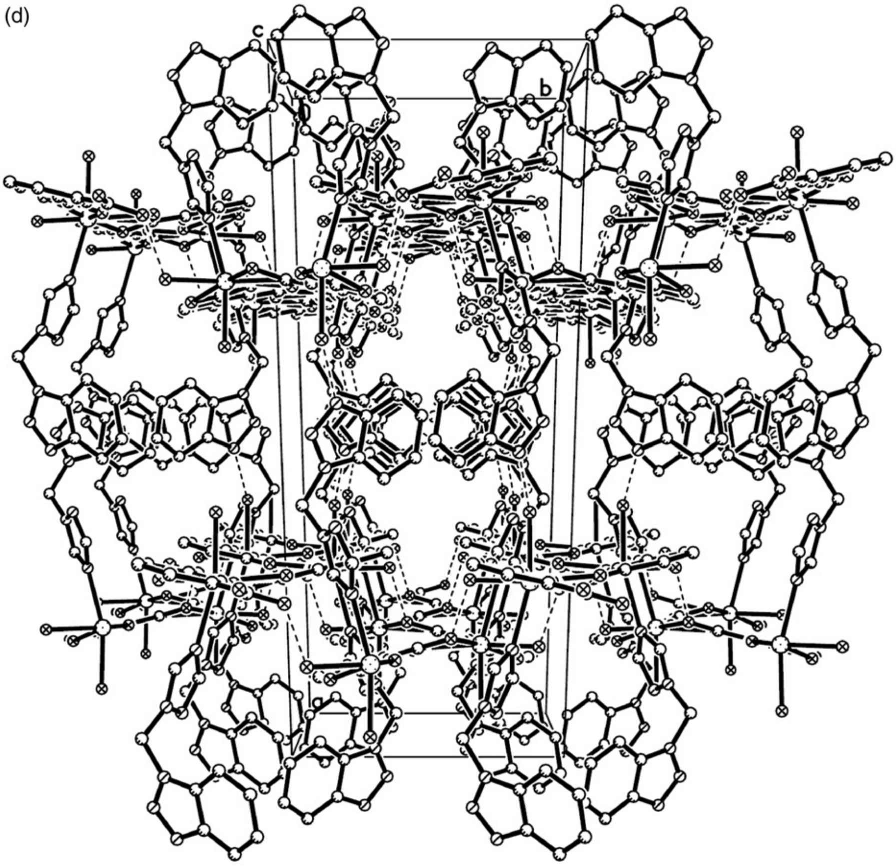

Figure 2. Continued.

emissions of **1** and **2** can be tentatively assigned to intraligand fluorescence emission, since a similar emission can also be observed for the free 1,3-benzenedicarboxylic acid. Emissions of the two coordination polymers may be attributable to intraligand $n \rightarrow \pi^*$ transitions within 1,3-benzenedicarboxylate group [30].

4. Conclusion

A number of symmetrical *N*-heterocyclic ligands coordinated to metal ions with bridging mode have been reported [12–14, 16]. Most unsymmetrical *N*-heterocyclic ligands coordinate to metal ions chelating or monodentate [9, 13, 15]. Through self-assemblies of a flexible unsymmetrical *N*-heterocyclic ligand 1-((benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole (bmt) with Zn(II) or Cd(II) in the presence of H_2bdic, we obtained two new coordination polymers $\{[Zn(bdic)(bmt)H_2O] \cdot 0.5H_2O\}_n$ (**1**) and $\{[Cd(bdic)(bmt)(H_2O)_2] \cdot 2H_2O\}_n$ (**2**). Similar with reported complexes, unsymmetrical bmt ligands coordinate monodentate in both polymers; bmt can bridge metal ions under suitable conditions [31]. Change of ions can influence the coordination

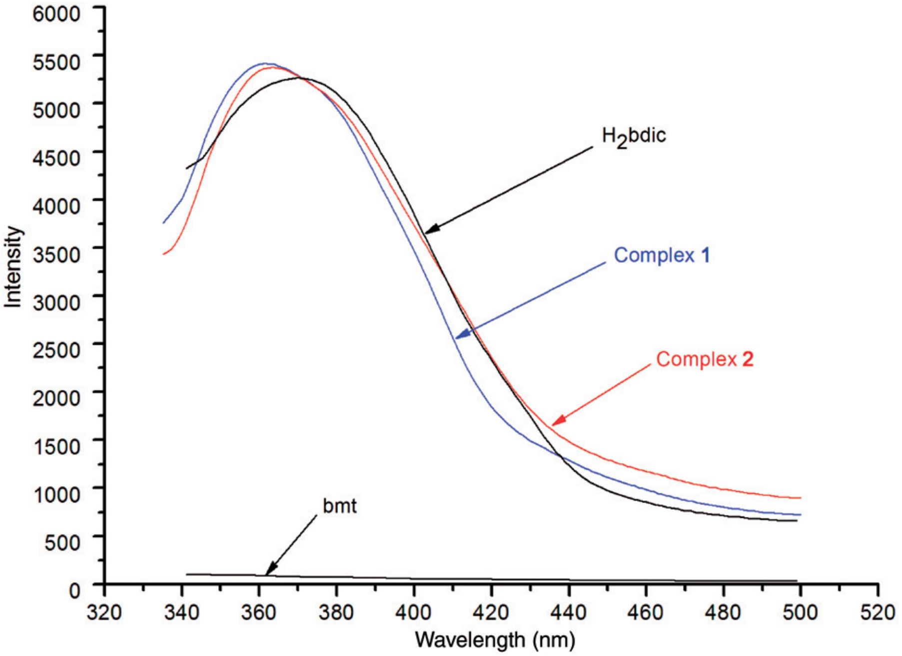

Figure 3. Solid-state photoluminescence spectra of free bmt, free H_2bdic, **1,** and **2** at room temperature.

environment of the metal centers and the conformation of bmt, and thus influence the detailed architecture of the coordination polymers.

Supplementary material

Crystallographic data for the structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC 837493 and 837492 for **1** and **2**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk).

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