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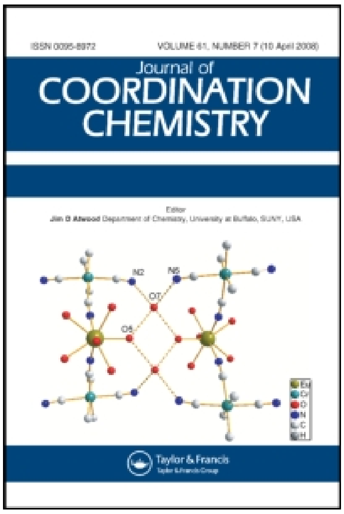

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Synthesis, structure and photoluminescent properties of a new coordination polymer $[Cd_2(pzdc)_2(4,4'\text{-bpy})(H_2O)_2]$<i>_n ($H_2pzdc$ = pyrazine-2,3-dicarboxylic acid, 4,4'-bpy = 4,4'-bipyridine)

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Synthesis, structure and photoluminescent properties of a new coordination polymer $[Cd_2(pzdc)_2(4,4'\text{-bpy})(H_2O)_2]_n$ (H_2pzdc = pyrazine-2,3-dicarboxylic acid, 4,4′-bpy = 4,4′-bipyridine)

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A new 2D coordination polymer, $[Cd_2(pzdc)_2(4,4'\text{-bpy})(H_2O)_2]_n$ (**1**) (pzdc = pyrazine-2,3-dicarboxylic acid, 4,4′-bpy = 4,4′-bipyridine), has been hydrothermally synthesized and characterized by elemental analyses, IR spectra and single crystal X-ray diffraction. X-ray diffraction analysis reveals that **1** features an interesting 2D stair-like layer with linear $[Cd_2(pzdc)_2(H_2O)_2]_n$ ribbons linked by 4,4′-bpy bridges. Furthermore, these layers are packed in an ABAB arrangement to give a 3D supramolecular network via hydrogen bonding and π–π packing interactions. Compound **1** displays strong fluorescent emission in the solid state at room temperature.

Keywords: Synthesis; Crystal structure; Coordination polymer; Photoluminescent properties

1. Introduction

Design and synthesis of inorganic–organic coordination polymers have developed very quickly because of their intriguing topologies and applications as functional materials [1–3]. Many networks with various structural motifs, including honeycomb, brick wall, rectangular grid, bilayer, ladder, herringbone, diamondoid, and octahedral geometries have been documented [4–10]. Heterocyclic carboxylates such as pyridine-, pyrazole-, and imidazole-carboxylic acids have been used in the construction of coordination polymers [11–13]. In particular, pyrazine-2,3-dicarboxylic acid was proved to be a versatile ligand and exhibited various coordination modes [14]. It often acts as chelating bidentate through one nitrogen atom and one oxygen atom of the adjacent carboxylate to form 1D or 2D structures similar to pyridine-2,3-dicarboxylic acid [15]. In this article, we reported on the synthesis, crystal structure and luminescent properties of $[Cd_2(pzdc)_2(4,4'\text{-bpy})(H_2O)_2]_n$ (**1**).

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2. Experimental

2.1. *Materials and methods*

All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer. X-ray power diffraction was recorded with a Bruker AXS D8 advanced automated diffractometer with Cu-Kα radiation. The emission spectra were recorded on a Perkin-Elmer LS50B fluorescence spectrophotometer.

2.2. *Hydrothermal synthesis*

2.2.1. $[Cd_2(pzdc)_2(4,4'\text{-bpy})(H_2O)_2]_n$ (1). A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), H_2pzdc (0.5 mmol), 4,4′-bpy (0.5 mmol), NaOH (1 mmol), and H_2O (10 mL) was mixed in a 23-mL Teflon reactor and stirred for 20 min in air. Then it was heated at 160°C for five days, followed by cooling to room temperature at a rate of 5 K h^{-1}. The resulting yellow block crystals of **1** were isolated. Yield: ca 56%. Anal. Calcd for $C_{22}H_{16}Cd_2N_6O_{10}$ (%): C, 35.27; H, 2.15; N, 11.22; found: C, 35.40; H, 2.06; N, 11.39. IR (KBr, cm^{-1}): 3450(vs), 1641(vs), 1608(vs), 1536(w), 1444(w), 1421(s), 1385(s), 1113(s).

2.3. *X-ray crystallography*

Crystallographic data of **1** were collected at room temperature with a Bruker SMART Apex CCD area-detector diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator using the ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [16]. All non-hydrogen atoms were treated anisotropically. The water H atoms were located in a difference Fourier map and refined with free coordinates and an isotropic displacement parameter fixed at $U_{iso}(H) = 1.5U_{eq}(O)$. The geometry was regularized using restraints for distances O–H = 0.85(1) Å and $H \cdots H = 1.39(1)$ Å. Other hydrogen atoms were added theoretically ride on their parent atoms.

3. Results and discussion

3.1. *Crystal structure*

X-ray structural analysis shows that **1** crystallizes in the monoclinic space group $P2_1/n$ with an asymmetric unit of the unit cell consisting of one Cd, one pzdc, one coordinated water molecule and half a 4,4′-bpy ligand. Each Cd is six-coordinate with four oxygen

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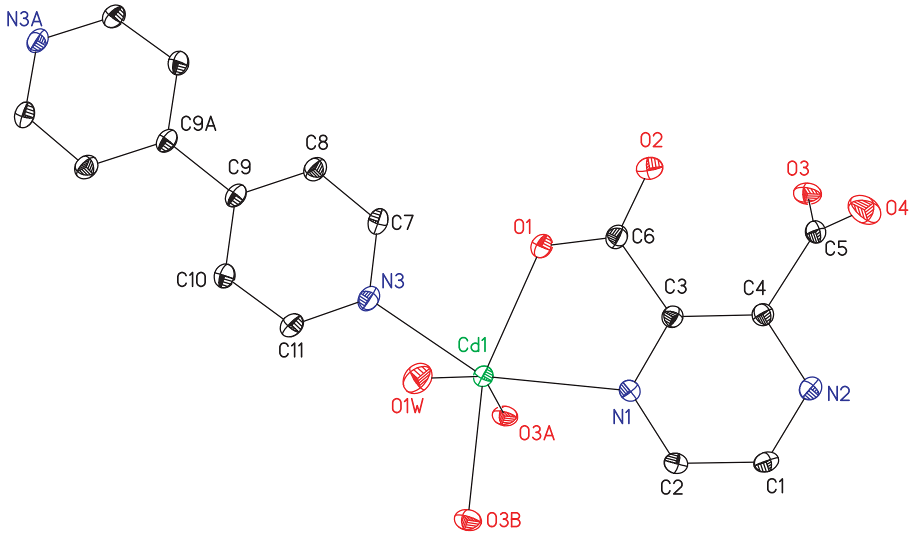
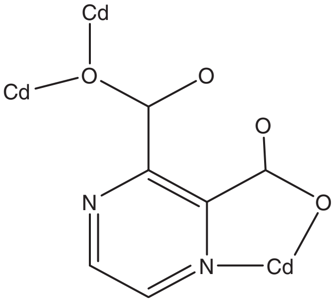


Figure 1. The coordination environment of cadmium in **1**.



Scheme 1. Coordination modes of the pzdc ligand.

atoms from three pzdc ligands and an aqua ligand in the equatorial plane (Cd(1)–O(1) 2.288(2) Å, Cd(1)–O(3a) 2.314(2) Å, Cd(1)–O(3b) 2.330(2) Å, Cd(1)–O(1W) 2.298(3) Å) and two nitrogen atoms from one 4,4′-bpy molecule and a pzdc group in the axial positions (Cd(1)–N(1) 2.374(2) Å, Cd(1)–N(3) 2.355(2) Å), forming a distorted octahedral geometry with O–Cd–O bond angles ranging from 72.3(1) to 156.4(2)° (figure 1). The 2-carboxyl group of pzdc chelates to one Cd(II) ion while one μ_2-O(3) atom of 3-carboxyl group connects two other Cd(II) ions with a Cd–O–Cd bond angle of 107.7(1)°. Thus the pzdc group adopts both chelate and monoatomic coordination modes to connect three individual Cd(II) ions, as shown in scheme 1. To the best of our knowledge, this kind of coordination mode has not been previously reported. Pairs of Cd(II) atoms are bridged by two μ_2-O(3) atoms of two pzdc groups to form dinuclear [$Cd_2(pzdc)_2(H_2O)_2$] subunits, which are interconnected through the chelating carboxylate groups of the pzdc ligands to form a linear 1D ribbon (figure 2) with

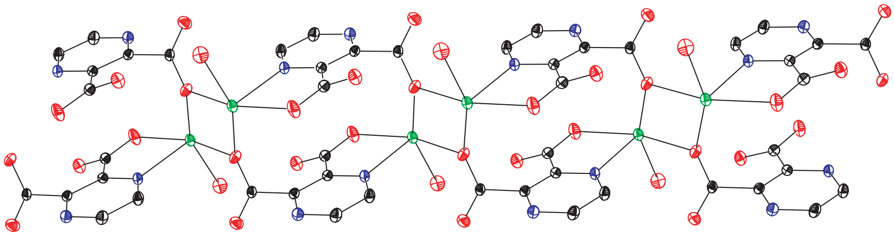


Figure 2. A linear one-dimensional ribbon $[Cd_2(pzdc)_2(H_2O)_2]_n$ assembled by $[Cd_2(pzdc)_2(H_2O)_2]$ subunits and the chelating pzdc groups viewed along the *c* axis.

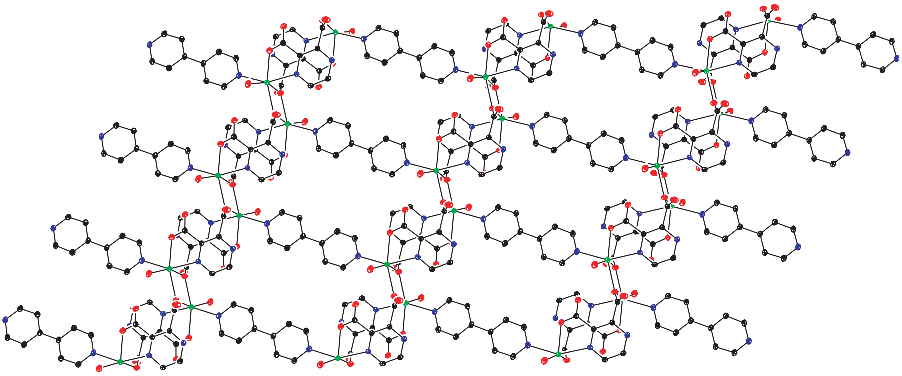


Figure 3. A view of the layer structure of **1**, which may be alternatively described as $[Cd_2(pzdc)_2(H_2O)_2]_n$ chains linked by 4,4′-bpy bridges.

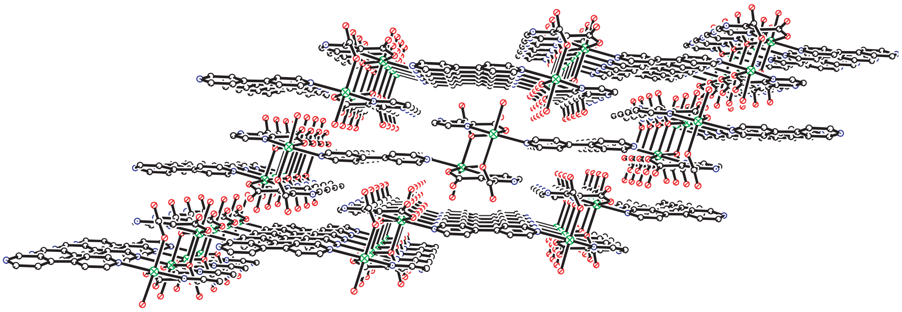


Figure 4. The 3D framework of **1** viewed along the *c* axis.

Cd $\cdots$ Cd distances of 3.750(2) Å. These ribbons are alternatively bridged by 4,4′-bpy molecules via Cd(II) centers to form a 2D stair-like layer (figure 3).

In the packing arrangement of **1** (figure 4), the 2D layers are almost parallel and packed in an ABAB arrangement to furnish a 3D network via π–π packing interactions

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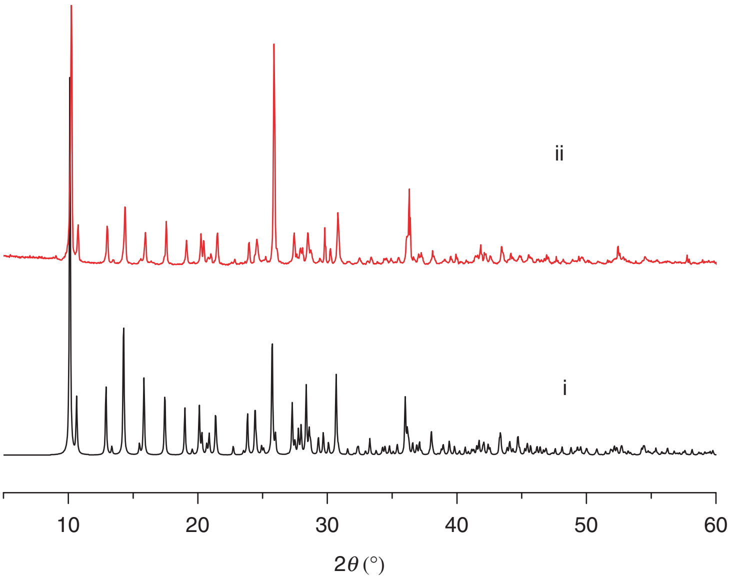

Figure 5. Simulated (i) and experimental (ii) X-ray powder diffraction patterns of **1**.

between aromatic groups of pzdc ligands and 4,4′-bpy molecules with face-to-face distances of ca 3.49 Å [17]. Furthermore, adjacent layers are connected through strong hydrogen-bonding interactions between carboxylate groups of pzdc ligands and the coordinated water. Typical hydrogen bonds are O1W ⋯ O2(x, $y-1$, z) 2.892(4) Å and O1W ⋯ O1($-x+3/2$, $y-1/2$, $-z+3/2$) 2.958(3) Å. The hydrogen bonding and π–π stacking interactions enhance the stability of the compound.

3.2. *IR spectrum and XRPD patterns*

The IR spectrum of **1** shows characteristic bands of carboxylate groups at 1641 and 1608 cm^{-1} for the antisymmetric stretching and at 1385 cm^{-1} for symmetric stretching. The separations (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ indicate the presence of monoatomic (256 cm^{-1}) and monodentate (223 cm^{-1}) coordination modes [18]. The absence of strong characteristic peaks around 1720 cm^{-1} indicates that all carboxylate groups are completely deprotonated [17, 19], consistent with the results of the X-ray analysis. The simulated and experimental XRPD patterns of **1** are shown in figure 5. Their peak positions are in good agreement with each other, indicating the phase purity of the product. The differences in intensity may be due to the preferred orientation of the powder samples.

3.3. *Photoluminescent properties*

The photoluminescence spectrum of **1** is shown in figure 6. Strong photoluminescent emission bands at 408 and 544 nm ($\lambda_{ex} = 306$ nm) are observed in the solid state

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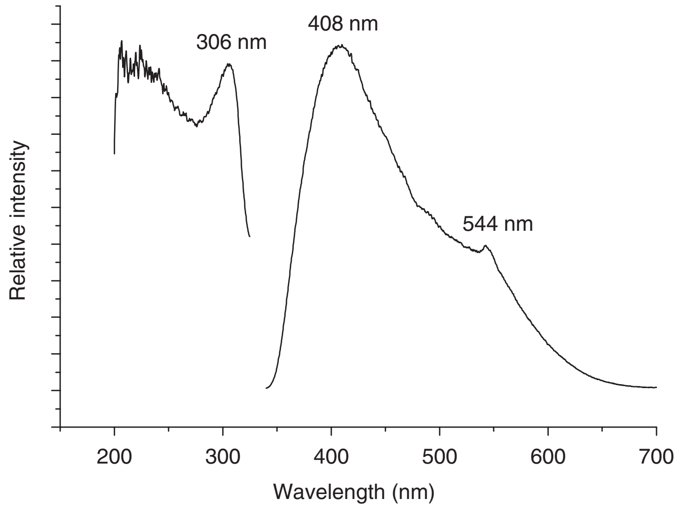

Figure 6. The photoluminescent spectrum of **1** in the solid state at room temperature.

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Table 1. Crystallographic data for **1**.

Empirical formula	$C_{22}H_{16}Cd_2N_6O_{10}$
Formula weight	374.60
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	10.8808(18)
b	7.5579(18)
c	13.719(2)
β	92.954(12)
V (Å^3)	1126.7(4)
Z	4
D_c (g cm^{-3})	2.208
μ (mm^{-1})	1.964
F(000)	732
Crystal size (mm^3)	0.36 × 0.24 × 0.22
θ range for data collection (°)	2.33–27.50
Reflections collected	2584
Independent reflections (R_{int})	2179 (0.0232)
Max., min. transmission	0.6775, 0.5415
T (K)	293(2)
Goodness-of-fit on F^2	1.072
Data/restraints/parameters	2584/3/187
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0274$, $wR_2 = 0.0679$
R indices (all data)	$R_1 = 0.0358$, $wR_2 = 0.0727$
Largest diff. peak and hole (e Å^{-3})	0.705, −0.803

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

at room temperature. There is no obvious emission observed for free H_2pzdc under the same experimental conditions, while free 4,4′-bpy presents weak fluorescent emission at 486 nm. Therefore, the fluorescent emissions of **1** may be attributed to the charge transition of pzdc ligands to cadmium atoms (LMCT) [13, 20].

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

Cd(1)–O(1)	2.288(2)	Cd(1)–O(1W)	2.298(3)
Cd(1)–O(3)#1	2.314(2)	Cd(1)–O(3)#2	2.330(2)
Cd(1)–N(3)	2.355(2)	Cd(1)–N(1)	2.374(2)
O(1)–Cd(1)–O(1W)	94.90(10)	O(1)–Cd(1)–O(3)#1	161.38(8)
O(1W)–Cd(1)–O(3)#1	88.22(9)	O(1)–Cd(1)–O(3)#2	107.84(9)
O(1W)–Cd(1)–O(3)#2	156.39(9)	O(3)#1–Cd(1)–O(3)#2	72.28(9)
O(1)–Cd(1)–N(3)	82.32(9)	O(1W)–Cd(1)–N(3)	84.87(9)
N(3)–Cd(1)–O(3)#1	116.27(9)	N(3)–Cd(1)–O(3)#2	91.83(9)

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

Supplementary data

Crystallographic data and experimental details for structural analysis are summarized in table 1. Selected bond lengths and angles are listed in table 2. CCDC reference number 631994. Copy 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; Email: deposit@ccdc.cam.ac.uk].

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