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Two 2D cadmium coordination polymers with 3,4-pyridinedicarboxylic acid

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Abstract

Two 2D cadmium coordination polymers $\{[Cd(pda)(2,2'\text{-bpy})(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Cd(pda)(4,4'\text{-bpy})(H_2O)]\cdot 2H_2O\}_n$ (**2**) ($H_2pda = 3,4$-pyridinedicarboxylic acid; 2,2′-bpy = 2,2′-bipyridine; 4,4′-bpy = 4,4′-bipyridine) have been synthesized and characterized by elemental analysis, infrared spectroscopy and X-ray single crystal diffraction. The 3D supramolecular structures of both **1** and **2** are constructed by hydrogen bonds between the 2D layers. Importantly, there are intramolecular $\pi\cdots\pi$ stacking interactions in both of the compounds. Crystallographic data for **1**: Orthorhombic, *Pbca*, $a = 15.5977(12)$ Å, $b = 12.6063(10)$ Å, $c = 16.9891(13)$ Å, $Z = 8$, $R_1 = 0.0202$, $wR_2 = 0.0504$; for **2**: Monoclinic, *C2/c*, $a = 27.345(4)$ Å, $b = 11.2530(16)$ Å, $c = 12.1068(16)$ Å, $\beta = 104.197(2)°$, $Z = 8$, $R_1 = 0.0269$, $wR_2 = 0.0625$.

Keywords: Cadmium(II) complex; 3,4-Pyridinedicarboxylic acid; Coordination polymer; $\pi\cdots\pi$ interaction

1. Introduction

Pyridinedicarboxylic acids have been widely used as organic ligands to the construction of metal organic frameworks (MOFs), which is of intense interests in recent years [1–6] for their potential application in molecular sieve, optoelectronics, magnetism, chemical sensors and so on [7]. This type of ligands combines the advantages of both organic multi-carboxylic acid and aromatic compound. In coordination compounds, the multi-carboxylic acids as ligand always show varieties of coordination modes for both transition metal and rare-earth metal complexes. The compounds with aromatic rings such as pyridine, 2,2′-bipyridine, 4,4′-bipyridine, 1,10-phenanthroline and interrelated derivatives can be used as the antenna for energy absorption in photoluminescent materials [8,9]. Furthermore, $\pi\cdots\pi$ interaction could exist in the complexes when the mutual distance and position of aromatic rings are appropriate. The $\pi\cdots\pi$ interaction of the aromatic rings existed in the complexes may help to stabilize the framework and often show intriguing structures. On the other hand, the weak interactions such as hydrogen bond and $\pi\cdots\pi$ stacking interaction play important roles in molecular recognition and self-organization of molecules in supramolecular structures [10].

In this contribution, two coordination polymers $\{[Cd(pda)(2,2'\text{-bpy})(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Cd(pda)(4,4'\text{-bpy})(H_2O)]\cdot 2H_2O\}_n$ (**2**) ($H_2pda = 3,4$-pyridinedicarboxylic acid; 2,2′-bpy = 2,2′-bipyridine; 4,4′-bpy = 4,4′-bipyridine) with different novel topological frameworks have been obtained by reacting the ligands with cadmium(II) perchlorate in water at room temperature. The $\pi\cdots\pi$ stacking interactions between the pyridine rings in the coordination polymers have been observed and discussed in detail.

2. Experimental section

2.1. Materials and methods

The organic compounds 3,4-pyridinedicarboxylic acid, 2,2′-bipyridine and 4,4′-bipyridine were purchased

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commercially and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded with a Bruker Tensor 27 FTIR spectrophotometer (KBr pellets, range in 4000–400 cm^{-1}). The X-ray diffraction data were collected on a Bruker SMART 1000 CCD area detector. The fluorescence spectra were determined on a Cary Eclipse fluorescence spectrophotometer.

Caution! Mixing organic ligand with cadmium(II) perchlorate is potentially explosive. Only a small amount of materials should be handled with care.

2.2. Syntheses of the compounds

2.2.1. $\{[Cd(pda)(2,2'\text{-}bpy)(H_2O)]\cdot H_2O\}_n$ (**1**)

$Cd(ClO_4)_2\cdot 6H_2O$ (0.0420 g, 0.1 mmol), H_2pda (0.0167 g, 0.1 mmol) and 2,2′-bpy (0.0192 g, 0.1 mmol) were added into 30 mL water by the molar ratio of 1:1:1 at room temperature and filtered after stirring for an hour. The filtrate was kept at room temperature for about 3 weeks, and the colorless block crystals were obtained in 60% yield. Anal. Calcd. for $C_{17}H_{15}CdN_3O_6$ (%): C, 43.47; H, 3.22; N, 8.95. Found (%): C, 43.32; H, 3.40; N, 9.40. IR (KBr, cm^{-1}): 3379(s), 1598(s), 1476(ms), 1439(s), 1396(s), 1160(w), 1063(ms), 1018(ms), 874(ms), 819(ms), 767(s), 714(ms), 677(ms), 445(ms).

2.2.2. $\{[Cd(pda)(4,4'\text{-}bpy)(H_2O)]\cdot 2H_2O\}_n$ (**2**)

The synthetic methods are the same as **1** except that the 2,2′-bpy was replaced by 4,4′-bpy. Light-yellow flake crystals were obtained in 65% yield. Anal. Calcd. for $C_{17}H_{17}CdN_3O_7$ (%): C, 41.86; H, 3.51; N, 8.62. Found (%): C, 41.64; H, 3.66; N, 8.72. IR (KBr, cm^{-1}): 3316(s), 1623(s), 1561(s), 1392(s), 1171(w), 1126(w), 1070(w), 830(ms), 715(ms), 681(ms), 598(w), 460(w).

2.3. X-ray crystallography

Diffraction data for **1** and **2** were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated MoKα radiation with a radiation wavelength of 0.71073 Å using the $\omega-\varphi$ scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [11]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.

Crystallographic data for the two compounds are listed in Table 1 and the selected bond lengths and angles are listed in Table 2. The data for hydrogen bonds are listed in Table 3.

Table 1
Crystallographic data for **1** and **2**

	1	2
Empirical formula	$C_{17}H_{15}N_3O_6Cd$	$C_{17}H_{17}N_3O_7Cd$
M	469.72	487.74
T (K)	294(2)	294(2)
λ (Å)	0.71073	0.71073
Cryst system	Orthorhombic	Monoclinic
Space group	*P*bca	*C*2/*c*
a (Å)	15.5977(12)	27.345(4)
b (Å)	12.6063(10)	11.2530(16)
c (Å)	16.9891(13)	12.1068(16)
α (°)	90	90
β (°)	90	104.197(2)
γ (°)	90	90
V (Å) ^{3}	3340.6(4)	3611.6(9)
Z	8	8
μ (mm^{-1})	1.350	1.256
R_1 [$I > 2\sigma(I)$]	0.0202	0.0269
wR_2	0.0504	0.0625

3. Results and discussions

3.1. Description of structures

An ORTEP view of **1** is shown in Fig. 1. Single crystal X-ray structure analysis shows that the Cd(II) ion center is octahedrally coordinated with three nitrogen atoms from 2,2′-bpy and pda, and three oxygen atoms from one water molecule and the carboxylic groups of pda. The bond lengths of Cd–N are 2.3267(19), 2.4203(18), and 2.3615(18) Å, and that of Cd–O are 2.2336(15), 2.2510(16), and 2.3739(17) Å, respectively. The bond angles of N–Cd–N range from 71.26(6)° to 95.53(6)°, while the O–Cd–N range from 83.15(6)° to 170.59(6)° and the O–Cd–O from 87.59(6)° to 100.96(6)°. Four Cd(II) ions and four pda molecules formed an interesting rectangular ring, as shown in Fig. 2. In the ring there are two nearly parallel 2,2′-bpy molecules. At the same time a small ring was formed by two Cd(II) ions and two pda molecules at the four angles of the rectangular ring. A two-dimensional framework was formed by these two kinds of rings, as shown in Fig. 3. Recently, Qin et al. [12] reported another compound of $[Cd(pda)(2,2'\text{-}bpy)]_n$ (**1a**) obtained by hydrothermal method using similar chemical reagents. By comparing the composition of **1** with that of **1a**, one coordinated water molecule and one lattice water molecule were lost in **1**. The Cd(II) ion in **1a** is five coordinated, while the Cd(II) ion is six coordinated in **1**. The difference between the structures of **1** and **1a** may be attributed to the different reacting conditions since the reagents are similar. Compound **1** was synthesized at room temperature and average pressure, while **1a** was synthesized at high temperature with auto-generated pressure in hydrothermal conditions. As a thermodynamics consequence, high temperature can reduce the small coordination molecules from the metal ions. It is a useful method to control the number of small ligands coordinated to metal ions, and we have successfully used this method to