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A novel $4^4.6^6$ 5-connected metal-organic framework with strong fluorescent emission constructed by *m*-thioacetatebenzoic acid

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ABSTRACT

A novel uninodal 5-connected metal-organic framework (MOF), $[Cd_2L_2(4,4'\text{-bipy})_{3/2}(H_2O)_2]_n$ (H_2L=*m*-thioacetatebenzoic acid and 4,4′-bipy=4,4′-bipyridine), was prepared under hydrothermal condition. It features an unusual brick-wall shape layer by 4,4′-bipy, which consists of right- and left-handed helical chains arrayed alternatively and finally expands by L^{2-} to a rare 5-connected nov ($4^4.6^6$) topology network. Photoluminescence study reveals that it displays intense structure-related fluorescent emission bands (λ_{ex}=355 nm) at 450 nm in the solid state at room temperature.

1. Introduction

In recent years, extensive attention has been focused on the design and synthesis of zinc(II)/cadmium(II) carboxylate metal-organic frameworks (MOFs) for their various geometry chemistry of motifs, photoluminescent properties and other potential applications in molecular-based materials [1–4]. So far, a wide range of one- or multi-dimensional infinite solid-state coordination architectures have been achieved in the last decade [5–17], especially aromatic multibenzenecarboxylate ligands together with neutral N-based ligands such as 4,4′-bipy has been extensively employed in the construction of mixed-ligand MOFs [18–20]. However, the coordination chemistry and structural properties of Cd(II) MOFs based on thioacetatebenzoic acid ligand have been documented very little to date. The thioacetatebenzoic acid ligand includes two different carboxylate systems. The characteristic coordination chemistry of the rigid carboxylate system may facilitate the formation of inorganic–organic materials with high thermal stability and form large channels, while the peculiar coordination chemistry of the flexible carboxylate system employed in the self-assembly reaction has versatile coordination behavior and may be favorable for the formation of the helical structure. What is more, it contains sulfur atom which can also take part in coordination, so it has five potential binding sites when coordinating to a metal center. In addition, 4,4′-bipy has been attracted considerable interests for the formation of extended structures by bridging metal nodes and is very important for the preparation of open frameworks with dimensionalities [21–23]. On the other hand, the d^{10} metals, especially Cd(II) ions, have been extensively used as functional metal centers because of luminescent characteristics arising from 4*d* electrons [24–26].

Lately, the most usual and efficient strategy for synthesizing MOFs is based on a "building block" approach, and the topology of the final structure is greatly dependent on the geometry of the nodes (connection centers) and/or the flexibility of the "building blocks". Among these networks, 3-, 4- and 6-connected MOFs are commonly observed [27–30], 5-, 7-, and 8-connected MOFs remain relatively scarce. According to the design strategy, we have synthesized a new 5-connected luminescent MOF, $[Cd_2L_2(4,4'\text{-bipy})_{3/2}(H_2O)_2]_n$.

2. Experiment section

2.1. Materials and measurements

The ligand of *m*-thioacetatebenzoic acid (H_2L) was prepared according to the method of literature [31]. All other reagents were purchased commercially and used as supplied. Hydrothermal reactions were performed in the 25 mL Teflon-lined stainless-steel Parr bomb. Data collection was performed with Mo*K*α radiation (λ=0.71073 Å) on a Bruker APEX II area-detector diffractometer. Elemental analyses were carried out using a Perkin-Elmer 2400 II

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elemental analyzer. The excitation and luminescence spectra were performed on a HITACHIF-2500 fluorescence spectrometer in solid state at room temperature.

2.2. *Synthesis of [$Cd_2L_2(4,4'\text{-bipy})_{3/2}(H_2O)_2]_n$*

$Cd(CH_3COO)_2 \cdot 2H_2O$ (1.0 mmol, 0.267 g), H_2L (1.0 mmol, 0.212 g), and 4,4’-bipy (0.2 mmol, 0.0396 g) were mixed in 15 mL distilled water. Then the mixture was transferred into a Parr Teflon-lined stainless-steel vessel (25 mL) and heated to 160 °C for 72 h. It was cooled to room temperature over 3 d. Colorless crystals were obtained and collected by filtration, washed with water, then dried in air, 81% yield (based on H_2L). Anal. Calcd. (%) for $C_{33}H_{28}Cd_2N_3O_{10}S_2$: C, 43.14; H, 3.07; N, 4.58; S, 6.97. Found: C, 43.11; H, 3.02; N, 4.61; S, 6.95.

2.3. *Single-crystal structure determination*

The diffraction data was collected on a Bruker APXE II diffractometer equipped with a graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) up to a 2θ limit of 55.0° at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structure was solved by direct methods and expanded with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Except the hydrogen atoms on oxygen atoms were located in successive difference Fourier syntheses, the other hydrogen atoms were generated geometrically. All calculations were performed with SHELXTL-97 package [32]. The crystal data and structure refinement are summarized in Table 1, and the selected bond lengths and bond angles are listed in Table 2.

Table 1
Crystal data and structure refinement.

Empirical formula	$C_{33}H_{28}Cd_2N_3O_{10}S_2$
Formula weight	915.50
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.4510(1)
b (Å)	18.3188(2)
c (Å)	16.2454(2)
β (°)	104.080(1)
V (Å^3)	3305.40(6)
Z	4
D_c (mg/m^3)	1.840
μ (mm^{-1})	1.477
F(0 0 0)	1820
θ range	1.70–27.43
Reflections collected, unique, R_{int}	28760, 7523, 0.0301
Reflections observed [$I > 2\sigma(I)$]	6363
Parameters refined	463
Goodness-of-fit on F^2	1.033
R/wR [$I > 2\sigma(I)$]	0.0255, 0.0545
R/wR (all data)	0.0338, 0.0578
Max., Min.$\Delta\rho$ (eÅ^{-3})	0.342, −0.406

3. Results and discussion

3.1. *Crystal structure*

A single-crystal X-ray diffraction study reveals that the title compound is a unique three-dimensional (3D) open framework consisting of two crystallographically independent Cd(II), two individual L^{2-} ligands, one and half distinct 4,4′-bipy and two water molecules, as shown in Fig. 1. Cd(1) is coordinated to four oxygen atoms from flexible carboxylic groups of two individual L^{2-} ligands (Cd–O 2.2697(16)–2.4041(18) Å), two N atoms belonging to different 4,4′-bipy (Cd–N 2.3266(18) and 2.388(2) Å) and one water molecule (Cd–O 2.2854(17) Å) in a slightly distorted pentagonal-bipyramidal geometry. Cd(2) is coordinated to three oxygen atoms from rigid carboxylic groups of two individual L^{2-} ligands, one oxygen atom from flexible carboxylic group (Cd–O 2.2616(17)–2.5253(16) Å), one N atom of 4,4′-bipy (Cd–N 2.3032(19) Å) and one water

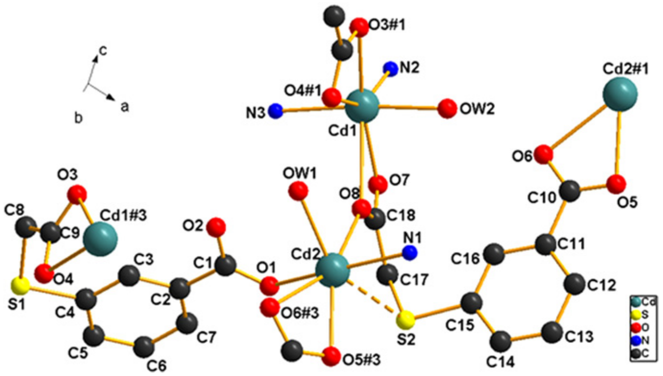

Fig. 1. Ball-and-stick representation (symmetry codes: #1 $x+1/2, -y+1/2, z+1/2$; #2 $-x+3/2, y+1/2, -z+3/2$; #3 $x-1/2, -y+1/2, z-1/2$).

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

Cd(1)–O(7)	2.2697(16)	Cd(1)–N(1)	2.3266(18)	Cd(1)–N(3)#2	2.388(2)
Cd(1)–O(2W)	2.2854(17)	Cd(1)–O(3)#1	2.3390(17)	Cd(1)–O(4)#1	2.4041(18)
Cd(2)–O(1)	2.2616(17)	Cd(2)–O(1W)	2.3743(19)	Cd(2)–O(5)#3	2.3353(18)
Cd(2)–N(2)	2.3032(19)	Cd(2)–O(8)	2.3905(16)	Cd(2)–O(6)#3	2.5253(16)
Cd(2)–S(2)	2.9984(6)				
O(7)–Cd(1)–O(2W)	86.79(7)	O(3)#1–Cd(1)–O(4)#1	54.90(6)	N(1)–Cd(1)–O(4)#1	89.65(7)
O(7)–Cd(1)–N(1)	88.86(6)	N(3)#2–Cd(1)–O(4)#1	151.77(6)	O(1)–Cd(2)–O(6)#3	86.57(6)
O(2W)–Cd(1)–N(1)	175.19(7)	O(1)–Cd(2)–N(2)	166.41(7)	N(2)–Cd(2)–O(6)#3	106.47(7)
O(7)–Cd(1)–O(3)#1	170.36(6)	O(1)–Cd(2)–O(5)#3	93.16(7)	O(5)#3–Cd(2)–O(6)#3	53.38(6)
O(2W)–Cd(1)–O(3)#1	83.86(7)	N(2)–Cd(2)–O(5)#3	91.72(7)	O(1W)–Cd(2)–O(6)#3	80.38(6)
N(1)–Cd(1)–O(3)#1	100.40(7)	O(1)–Cd(2)–O(1W)	98.01(7)	O(8)–Cd(2)–O(6)#3	155.01(5)
O(7)–Cd(1)–N(3)#2	85.11(6)	N(2)–Cd(2)–O(1W)	88.16(7)	O(1)–Cd(2)–S(2)	85.27(5)
O(2W)–Cd(1)–N(3)#2	89.70(8)	O(5)#3–Cd(2)–O(1W)	131.59(6)	N(2)–Cd(2)–S(2)	82.99(5)
N(1)–Cd(1)–N(3)#2	91.98(7)	O(1)–Cd(2)–O(8)	82.24(6)	O(5)#3–Cd(2)–S(2)	80.99(4)
O(3)#1–Cd(1)–N(3)#2	97.17(6)	N(2)–Cd(2)–O(8)	87.08(6)	O(1W)–Cd(2)–S(2)	146.61(5)
O(7)–Cd(1)–O(4)#1	123.10(6)	O(5)#3–Cd(2)–O(8)	149.20(6)	O(8)–Cd(2)–S(2)	68.32(4)
O(2W)–Cd(1)–O(4)#1	91.00(8)	O(1W)–Cd(2)–O(8)	79.16(6)	O(6)#3–Cd(2)–S(2)	133.00(4)

Symmetry codes: #1 $x+1/2, -y+1/2, z+1/2$; #2 $-x+3/2, y+1/2, -z+3/2$; #3 $x-1/2, -y+1/2, z-1/2$.