

一个二维锰配位聚合物 $[\text{Mn}_2(\text{L})_2(1,3\text{-BDC})_2] \cdot 0.25\text{H}_2\text{O}$ 的合成、结构和表征

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Synthesis, Structure and Characterization of a Two-dimensional Mn(II) Coordination Polymer: $[\text{Mn}_2(\text{L})_2(1,3\text{-BDC})_2] \cdot 0.25\text{H}_2\text{O}$

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Abstract: The title complex, $[\text{Mn}_2(\text{L})_2(1,3\text{-BDC})_2] \cdot 0.25\text{H}_2\text{O}$ **1** ($\text{L}=2\text{-(2-chloro-6-fluorophenyl)-1H-imidazo}[4,5\text{-f}][1,10]\text{phenanthroline}$ and $1,3\text{-H}_2\text{BDC}=1,3\text{-benzenedicarboxylic acid}$) has been obtained by using hydrothermal synthesis and characterized by elemental analysis, IR and single-crystal X-ray diffraction. It crystallizes in monoclinic, space group $P2_1/n$ with $a=1.751\ 68(6)$ nm, $b=1.160\ 14(4)$ nm, $c=2.585\ 30(8)$ nm, $\beta=104.331(4)^\circ$, $V=5.090\ 3(3)$ nm³, $Z=4$, $\text{C}_{54}\text{H}_{28.50}\text{Cl}_2\text{F}_2\text{Mn}_2\text{N}_8\text{O}_{8.25}$, $M_r=1\ 140.13$, $D_c=1.488$ g·cm⁻³, $F(000)=2\ 306$, $\mu(\text{Mo K}\alpha)=0.673$ mm⁻¹, $R=0.060\ 5$ and $wR=0.161\ 6$. The compound **1** exhibits two-dimensional wavy layer structures, which are further stacked through $\pi\text{-}\pi$ interactions to form three-dimensional supramolecular architectures. CCDC: 760201.

Key words: coordination polymer; crystal structure; 1,10-phenanthroline derivative; 1,3-benzenedicarboxylic acid

0 Introduction

The construction of metal-organic coordination architectures with novel structures and topologies has attracted great interest from chemists due to their potential applications as functional solid materials, as well as their fascinating framework structures^[1-8]. So far, several rational synthetic strategies have been proposed to achieve the metal-organic supramolecular arrays, and one of the most effective approaches is to employ appropriate aromatic N-donor chelating ligands capable

of forming $\pi\text{-}\pi$ interactions^[9-17]. In this regards, 1,10-phenanthroline (phen) has been widely used to build supramolecular architectures because of its excellent coordinating ability and large conjugated system that can easily form $\pi\text{-}\pi$ interactions^[18]. However, relatively less attention has been given to their derivatives. 2-(2-Chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (**L**) as an important phen derivative possesses aromatic systems and is a good candidate for the construction of metal-organic supramolecular architectures. Here, we selected 1,3-benzenedicarboxylate

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dianion (1,3-BDC) as an organic linker and L as a N-donor chelating ligand, generating a new Mn(II) coordination polymer, $[\text{Mn}_2(\text{L})_2(1,3\text{-BDC})_2] \cdot 0.25\text{H}_2\text{O}$ **1**, which will be reported. So far, although several coordination compounds constructed by metal(II) ions, dicarboxylate ligands and phen derivatives have been documented, the two-dimensional structure based on this system are rarely observed^[19].

1 Experimental

1.1 Generals

The L ligand was synthesized according to the reported method^[17] and all other materials were analytical reagent grade and used as received without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; IR spectra were obtained on a Perkin-Elmer 2400LSII spectrometer.

1.2 Synthesis and crystal growth

A mixture of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.098 g, 0.5 mmol), 1,3- H_2BDC (0.083 g, 0.5 mmol), L (0.165 g, 0.5 mmol), NaOH (0.008 g, 0.2 mmol) and deionized water (12 mL) was heated to 190 °C for one week in a 25 mL Teflon-lined stainless steel vessel under autogenous pressure. Subsequently, it was cooled to room temperature at a rate of 10 °C \cdot h⁻¹. Pale yellow crystals of **1** was isolated by filtration and washed with water and dried at ambient temperature. IR (KBr, cm^{-1}): 3 047m, 1 612s, 1 584m, 1 459m, 1 341m, 845m, 773s, 730w, 700m, 622w. Anal. Calcd. For $\text{C}_{54}\text{H}_{28.50}\text{Cl}_2\text{F}_2\text{Mn}_2\text{N}_8\text{O}_{8.25}$ (%): C, 56.84; H, 2.50; N, 9.82. Found (%): C, 56.78; H, 2.70; N, 10.11.

1.3 X-ray structure determination

A single crystal with dimensions of 0.30 mm \times 0.26 mm \times 0.19 mm was selected and mounted on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ ($\lambda = 0.071\,073$ nm) radiation by using an φ - ω scanning method at a temperature of 20 \pm 2 °C. Out of the total 25 510 reflections collected in the 2.13° $\leq \theta \leq$ 26.37° range, 10 415 were independent with $R_{\text{int}} = 0.046\,9$, of which 5 292 were considered to be observed ($I > 2\sigma(I)$) and used in the succeeding refinement. The structure was solved by Direct Method with SHELXS-97 program^[20] and refined

with SHELXL 97^[21] by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The H atoms of water molecule were not located from difference Fourier map. The final $R = 0.060\,5$ and $wR = 0.161\,6$ ($w = 1/[\sigma^2(F_o^2) + (0.037\,7P)^2 + 0.28P]$, where $P = (F_o^2 + 2F_c^2)/3$). $S = 0.894$, $(\Delta\rho)_{\text{max}} = 1.111$, $(\Delta\rho)_{\text{min}} = -0.959$ e \cdot nm⁻³ and $(\Delta/\sigma)_{\text{max}} = 0.000$.

CCDC: 760201.

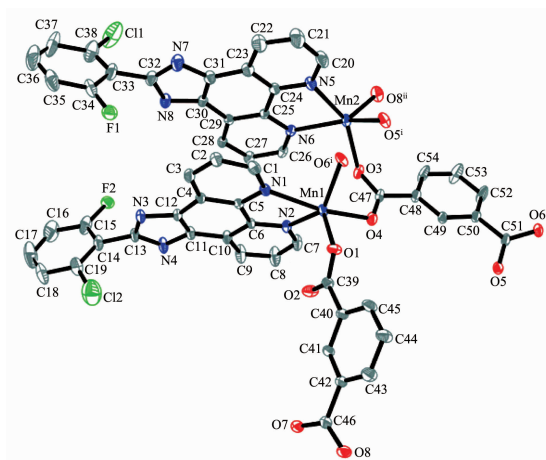
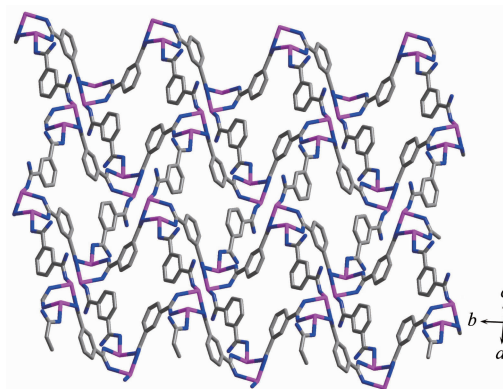
2 Results and discussion

2.1 Description of crystal structure

The selected bond distances and angles are listed in Table 1. The asymmetric unit of **1** consists of two unique Mn(II) atoms, two unique L molecules, two unique 1,3-BDC ligands, and one quarter lattice water molecule (Fig.1). Each Mn(II) atom is five-coordinated by three carboxylate oxygen atoms from two different 1,3-BDC ligands and two nitrogen atoms from one chelating L ligand in a square-pyramidal geometry. The two 1,3-BDC ligands display different coordination modes: one connects two Mn(II) atoms, while the other is bonded to four Mn(II) atoms. In these coordination modes, dinuclear unit is formed in which two Mn(II) atoms are bridged by the carboxylate groups of the 1,3-BDC ligands (Fig.1). The backbones of the 1,3-BDC ligands further linked the dinuclear units to generate a two-dimensional wavy layer structure (Fig.2). The L ligands are attached on both sides of the wavy layer. So far, although several coordination compounds constructed by metal(II) ions, dicarboxylate ligands and phen derivatives have been reported, most of these reported compounds show discrete or one-dimensional chain structures^[18]. However, the present two-dimensional wavy layer structure based on this system has not been observed^[19]. It is noteworthy that the adjacent layers are further connected through the aromatic π - π interactions between L ligands with the face-to-face distance *ca.* 0.342 nm, resulting in a three-dimensional supramolecular architecture. It should be pointed out that the structure of **1** is different from the related structure $[\text{Pb}(1,3\text{-BDC})(\text{dpdp})] \cdot \text{H}_2\text{O}$ (dpdp=dipyrido[3,2-a:2',3'-c]-phenazine)^[19]. In that reported structure, the 1,3-BDC

Table 1 Selected bond distances (nm) and angles ($^\circ$)

Mn(1)-N(1)	0.228 9(4)	Mn(1)-N(2)	0.217 7(3)	Mn(2)-N(5)	0.225 0(4)
Mn(2)-N(6)	0.223 7(3)	Mn(1)-O(1)	0.205 2(3)	Mn(2)-O(3)	0.210 6(3)
Mn(1)-O(4)	0.212 2(3)	Mn(1)-O(6) ⁱ	0.209 4(3)	Mn(2)-O(8) ⁱⁱ	0.204 0(3)
Mn(2)-O(5) ⁱ	0.215 9(3)				
O(1)-Mn(1)-O(6) ⁱ	104.25(13)	O(1)-Mn(1)-O(4)	94.89(13)	O(6) ⁱ -Mn(1)-O(4)	91.75(14)
O(1)-Mn(1)-N(2)	117.82(13)	O(6) ⁱ -Mn(1)-N(2)	135.44(13)	O(4)-Mn(1)-N(2)	98.32(14)
O(1)-Mn(1)-N(1)	102.04(13)	O(6) ⁱ -Mn(1)-N(1)	84.78(13)	O(4)-Mn(1)-N(1)	163.06(12)
N(2)-Mn(1)-N(1)	73.25(13)	O(8) ⁱⁱ -Mn(2)-O(3)	97.40(15)	O(8) ⁱⁱ -Mn(2)-O(5) ⁱ	97.40(12)
O(3)-Mn(2)-O(5) ⁱ	95.40(13)	O(8) ⁱⁱ -Mn(2)-N(6)	116.64(12)	O(3)-Mn(2)-N(6)	88.26(13)
O(5) ⁱ -Mn(2)-N(6)	145.04(12)	O(8) ⁱⁱ -Mn(2)-N(5)	113.42(15)	O(3)-Mn(2)-N(5)	148.68(14)
O(5) ⁱ -Mn(2)-N(5)	86.43(14)	N(6)-Mn(2)-N(5)	73.40(13)		

Symmetry codes: ⁱ 1/2-x, y-1/2, 3/2-z; ⁱⁱ x-1/2, 1/2-y+, z-1/2.Symmetric codes: ⁱ 1/2-x, y-1/2, 3/2-z; ⁱⁱ x-1/2, 1/2-y, z-1/2Fig.1 Coordination environments of Mn(II) atoms in complex **1** (displacement ellipsoids at the 30% probability level)Fig.2 View of the wavy layer structure of complex **1** (L ligands are omitted for clarity)

ligands connect Pb(II) centers to form a chain structure.

2.2 IR analysis

In the IR spectrum, the C-H stretching mode for the phenyl ring is relatively weak and is observed at about $3\,047\text{ cm}^{-1}$. Peaks at $1\,612$, $1\,584$ and $1\,459\text{ cm}^{-1}$ could be attributed to $\nu(\text{C}=\text{C})$ vibration of aromatic ring. The peak at $1\,341\text{ cm}^{-1}$ is ascribed to the $\nu(\text{C}=\text{N})$ vibration of L.

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