

配合物 $[\text{Mn}(2,2'\text{-bipy})(\text{H}_2\text{O})_4]\cdot(m\text{-phth})$ 的水热合成和晶体结构

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Hydrothermal Synthesis and Crystal Structure of an Inclusion Compound $[\text{Mn}(2,2'\text{-bipy})(\text{H}_2\text{O})_4]\cdot(m\text{-phth})$

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Abstract: A mononuclear manganese complex $[\text{Mn}(2,2'\text{-bipy})(\text{H}_2\text{O})_4]\cdot(m\text{-phth})$ ($2,2'\text{-bipy}$ = $2,2'$ -bipyridine, $m\text{-phth}$ =isophthalate) has been synthesized by hydrothermal methods. The crystal structure was determined by single-crystal X-ray diffraction. The crystal is of orthorhombic, space group $Pnna$ with $a=0.766\ 8(8)$ nm, $b=2.050\ 2(2)$ nm, $c=1.247\ 0(13)$ nm, $V=1.960\ 4(4)$ nm³, $Z=4$, $M_r=447.30$, $D_c=1.376$ g·cm⁻³, $\mu=0.722$ mm⁻¹, $F(000)=924$, $R_{\text{int}}=0.027\ 0$, $R=0.028\ 0$ and $wR=0.075\ 5$. In the crystal the manganese atom is six-coordinated by two nitrogen atoms from $2,2'$ -bipyridine and four oxygen atoms from water molecules, completing an octahedral coordination geometry. The isophthalate molecules are included in the lattice and connected to $[\text{Mn}(2,2'\text{-bipy})(\text{H}_2\text{O})_4]$ by hydrogen bonding interactions to form a three-dimensional supramolecular structure. CCDC:286965.

Key words: manganese complex; hydrothermal synthesis; crystal structure; electrochemical property

0 Introduction

As the active sites of several mononuclear enzymes are five- or six-coordinate manganese species containing coordinated carboxylate groups, water and nitrogen-donor molecules research on the coordination compounds of manganese with such coligands has grown^[1,2]. There has been extensive interest in manganese chemistry due to the involvement of manganese in many biosystems and magnetic materials^[3-5]. The isophthalate as a potential bidentate ligand seems

quite suitable for self-assembly systems to construct novel architectures. Furthermore, pronounced interest has recently been focused on the supramolecular chemistry and crystal engineering of coordination compounds organized by coordinate covalent or molecular contacts like hydrogen-bonding, $\pi\text{-}\pi$ interactions^[6]. Herein we report the compound containing isophthalate in the lattice with a 3D supramolecular structure. Its structure is different from those of any other reported compounds.

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1 Experimental

1.1 Materials and instruments

All reagents were purchased from commercial sources and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on FTIR-8700 spectrophotometer using KBr discs.

1.2 Synthesis of the title compound

The compound was hydrothermal synthesized under autogenous pressure. A mixture of $\text{C}_8\text{H}_6\text{O}_4$, NaOH, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 2,2'-bipyridine and H_2O in the mole ratio of 1.0:2.0:1.0:1.0:1 000 was adjusted to pH=6 with $1 \text{ mol} \cdot \text{L}^{-1}$ NaOH, and then heated in a Teflon-lined acid digestion bomb for 120 h at 160°C . After cooling the autoclave to room temperature over 24 h, the mixture gave rise to a needle yellow crystals which were filtered, washed with distilled water and dried at ambient temperature. Yields based on Mn: 36%. Molecular formula is $\text{C}_{18}\text{H}_{20}\text{MnN}_2\text{O}_8$. Elemental analysis (%) Calcd.: C, 48.29; H, 4.47; N, 6.26. Found (%): C,

48.14; H, 4.98; N, 6.63. IR (KBr pellet, cm^{-1}): 3 315.4 (br), 1 718.5(s), 1 602.7(vs), 1 539.1(s), 1 373.2(s), 769.5 (m), 657.7(m).

1.3 X-ray crystallography

A yellow crystal with dimensions of $0.26 \text{ mm} \times 0.24 \text{ mm} \times 0.20 \text{ mm}$ was selected for the measurement. The diffraction data were collected at 294 K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.071\,073 \text{ nm}$). A total of 2 356 reflections were collected in the range of $3.12^\circ \leq \theta \leq 25.46^\circ$ by using an ω -scan mode, of which 150 were unique and used in the succeeding structure calculations. The structure was solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. All calculations were performed with SHELXTL-97 package. Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 286965.

Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$\text{C}_{18}\text{H}_{20}\text{MnN}_2\text{O}_8$	Absorption coefficient / mm^{-1}	0.722
Formula weight	447.30	$F(000)$	924
Temperature / K	294(2)	Crystal size / mm	$0.26 \times 0.24 \times 0.20$
Crystal system	Orthorhombic	$\theta / (^\circ)$	3.12 to 25.46
Space group	$Pnna$	Limiting indices	$-10 \leq h \leq 10, -14 \leq k \leq 27, -16 \leq l \leq 16$
a / nm	0.766 8(8)	Reflections collected / unique	12 269 [R(int)=0.027 0]
b / nm	2.05 02(2)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.247 0(13)	Data / restraints / parameters	2 356 / 0 / 150
V / nm^3	1.960 4(7)	Goodness of fit on F^2	1.068
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.342	Final R indices [$I > 2\sigma(I)$]	$R_1=0.02\,8, wR_2=0.075\,5$
Z	4	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	356 and -248

2 Results and discussion

2.1 IR spectra

The peak of $1\,718.5 \text{ cm}^{-1}$ is observed in IR spectrum of the free isophthalate and assigned to $\nu(\text{C}=\text{O})$ absorption of carboxylic group. However, it disappears in IR spectrum of the title complex, $1\,602, 1\,539, 1\,373 \text{ cm}^{-1}$ are characteristic absorption of 2,2'-bipyridine ligand. The strong broad band around $3\,315 \text{ cm}^{-1}$ in the IR spectra could be ascribed to absorption of co-

ordinated water molecules and H-bonding in the complex. All these results further confirm the structure analysis.

2.2 Crystal structure of the title complex

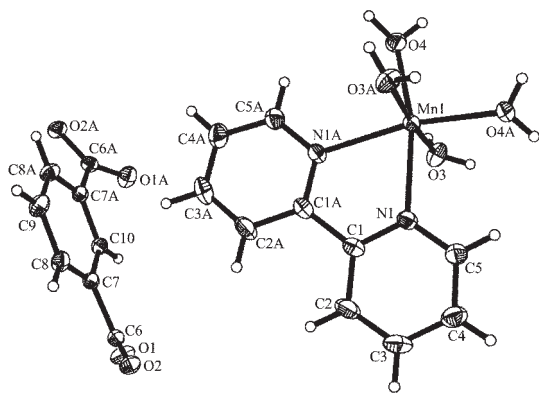
The molecular structure of the title complex is shown in Fig.1, and the packing diagram in Fig.2. The selected bond lengths are given in Table 2. The structure of the complex has crystallographically imposed four-fold and inversion symmetry with the Mn(II) ion locating at the inversion center. The structure unit

Table 2 Selected bond lengths (nm) and bond angle (°)

Mn(1)-O(4)#1	0.214 2(12)	Mn(1)-O(3)#1	0.218 5(12)	Mn(1)-N(1)#1	0.227 4(12)
Mn(1)-O(4)	0.214 2(12)	Mn(1)-O(3)	0.218 5(12)	Mn(1)-N(1)	0.227 4(12)
O(4)#1-Mn(1)-O(4)	99.74(7)	O(4)#1-Mn(1)-N(1)#1	165.23(5)	O(3)#1-Mn(1)-N(1)	96.01(5)
O(4)#1-Mn(1)-O(3)#1	87.82(5)	O(4)-Mn(1)-N(1)#1	94.29(5)	O(3)-Mn(1)-N(1)	87.78(5)
O(4)-Mn(1)-O(3)#1	89.16(5)	O(3)#1-Mn(1)-N(1)#1	87.79(5)	N(1)#1-Mn(1)-N(1)	72.17(7)
O(4)#1-Mn(1)-O(3)	89.16(5)	O(3)-Mn(1)-N(1)#1	96.01(5)	C(5)-N(1)-Mn(1)	123.80(10)
O(4)-Mn(1)-O(3)	87.82(5)	O(4)#1-Mn(1)-N(1)	94.29(5)		
O(3)#1-Mn(1)-O(3)	175.31(7)	O(4)-Mn(1)-N(1)	165.23(5)		

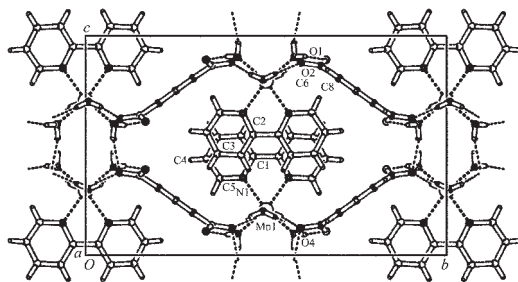
#1: $-x+1/2, -y+1, z$.

consists of cation $[\text{Mn}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ and one isophthalate anion (Fig.1). The Mn(II) ion is located at the center of an almost ideal octahedron with small distortion of bond distance and bond angle (O(4)A-Mn(1)-O(3)A, 87.82(5)°, O(4)-Mn(1)-O(3)A, 89.16(5)°, O(4)A-Mn(1)-O(3) 89.16(5)°, O(4)-Mn(1)-O(3), 87.82(5)°. The sum of the four angles is 353.96°, typical for the ideal octahedral value of 360°. The Mn-N bond length is 0.227 4(12) nm, which is close to those already found^[7] but a little longer than that of Mn-Oaqua (0.214 2(12) and 0.218 5 nm), and $[\text{Mn}_2(\text{bipy})_4(m\text{-phth})]_n(\text{ClO}_4)_2 \cdot 4n\text{H}_2\text{O}$ (0.226 5 nm)^[8].

**Fig.1** Molecular structure of the title complex

An interesting feature of this structure is the

presence of intrachain hydrogen bonds which are observed between the water O-H groups and carboxylate oxygen atoms, as given in Table 3. Moreover, inter-chain hydrogen bonds occur between water molecules bound to Mn(II) ions in one chain and the noncoordinated oxygen atoms of *m*-phth bridges in other chains, which are analogously found in a hydrogen bonded supramolecular Mn(II) complex^[9]. These hydrogen bonds thus appear to stabilize the asymmetry molecular disposition around the Mn center. The *m*-phth ligand acts in the bridging mode in terms of four carboxylate oxygen linked to the metal ion and the other hydrogen-bonded to the water molecule, as depicted in Fig.2. And they are eventually leading to the formation of a supramolecular extended 3D network structure.

**Fig.2** Packing diagram for the complex in a cell**Table 3** Parameters of hydrogen bonds for the complex (nm, °)

D...H...A	$d(\text{D-H})$ / nm	$d(\text{H-O})$ / nm	$d(\text{D-O})$ / nm	$\angle \text{D-H-A}$ / (°)
O(4)···H(4B)···O(1)#3	0.092(2)	0.170(2)	0.260 8(16)	169(2)
O(4)···H(4A)···O(2)#4	0.082(2)	0.199(2)	0.276 1(17)	157(2)
O(3)···H(3B)···O(2)#5	0.083(2)	0.195(2)	0.277 5(16)	171(2)
O(3)···H(3A)···O(2)#6	0.084(2)	0.192(2)	0.271 5(16)	157(2)
C(5)···H(5)···O(1)	0.092 9	0.258 7	0.340(2)	147.87

#3: $x+1/2, y, -z+1$; #4: $x, y, z-1$; #5: $-x, -y+1, -z+1$; #6: $x-1/2, y, -z+1$.

2.3 Electrochemistry studies

Cyclic voltammogram of the title compound is presented in Fig.3. In the solution of DMF, the electrochemical experiment of the title complex ($2.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) was carried out with a glass carbon (GC) working electrode, a Pt plate auxiliary electrode and a saturated calomel (SCE) reference electrode. All the potentials are reported against SCE. The scanning rate was $50 \text{ V} \cdot \text{s}^{-1}$. HAc-NaAc (pH=4.74) was used as buffer solution. The cyclic voltammogram of the title complex shows there is only one pair of redox peaks, which probably corresponds to the redox couple of

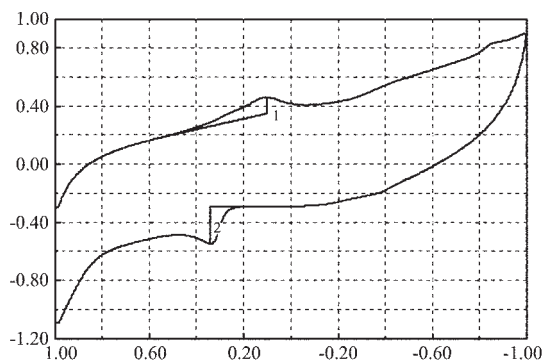


Fig.3 Cyclic voltammogram curve of the complex

Mn(III) / Mn(II). The redox potential is 0.347 V ($E_{\text{pa}} = 0.347 \text{ V}$), while the cathodic peak potential (E_{pc}) is 0.104 V. The average formal potential [$E_{1/2} = (E_{\text{pa}} + E_{\text{pc}}) / 2$] is 0.226 V, and the separation between the anodic and cathodic peaks ΔE_p is 0.243 V. These features are indicative of a quasi-reversible electrode process.

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