



一维链状锰配合物 $[\text{Mn}_3(\text{L})_6(\text{CH}_3\text{OH})_2]_n \cdot 0.5n\text{H}_2\text{O}$ 的水热合成和晶体结构

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关键词: 锰配合物; 晶体结构; 3,5-二甲苯甲酸; 水热合成

中图分类号: O614.7+11

文献标识码: A

文章编号: 1001-4861(2008)09-1535-04

Hydrothermal Synthesis and Crystal Structure of a 1D Manganese(II) Complex: $[\text{Mn}_3(\text{L})_6(\text{CH}_3\text{OH})_2]_n \cdot 0.5n\text{H}_2\text{O}$

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Abstract: The title compound, $[\text{Mn}_3(\text{L})_6(\text{CH}_3\text{OH})_2]_n \cdot 0.5n\text{H}_2\text{O}$ (**1**), where HL=3,5-dimethylbenzoic acid, was synthesized and its crystal structure was determined by X-ray diffraction structure analysis. The crystal is of triclinic, space group $P\bar{1}$ with $a=1.275\ 1(13)$ nm, $b=1.354\ 6(14)$ nm, $c=1.882\ 3(19)$ nm, $\alpha=110.826(1)^\circ$, $\beta=94.358(2)^\circ$, $\gamma=108.038(1)^\circ$, $V=2.825\ 4(5)$ nm³, $Z=1$, $M_r=2\ 265.77$, $D_c=1.332$ g·cm⁻³, $\mu=0.723$ mm⁻¹, $F(000)=1\ 180$, $R_{\text{int}}=0.037$, $R=0.056\ 4$, $wR=0.128\ 5$. In the crystal the manganese atom is six-coordinated by six oxygen atoms, completing an octahedral geometry. The molecules are connected by 3,5-dimethylbenzoic acid to form a 1D chain structure bridged. CCDC: 694097.

Key words: Mn(II) complex; crystal structure; 3,5-dimethylbenzoic acid; hydrothermal synthesis

0 Introduction

The coordination chemistry of manganese complexes has become an attractive research field because of the significant involvement of manganese in various biological systems^[1], especially in oxygen-evolving complex (OEC) of photosystem II (PS II) in green plants^[2]. The syntheses and structures of manganese model complexes have provided a wealth of data for comparison and contrast for the water oxidation complex (WOC)^[3-6]. Moreover, sterically hindered ligands are comm only

used to control the coordination environment of metal ions, and hence their properties through favoring lower coordination numbers and preventing the formation of unwanted polynuclear species that often arise from ligand bridging^[7,8].

In order to continue our studies on the manganese complexes^[9-12], we have chosen 3,5-dimethylbenzoic acid as ligand and investigated its reaction with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. We report herein the synthesis and the crystal structure of the 1D chain manganese (II) complex, $[\text{Mn}_3(\text{L})_6(\text{CH}_3\text{OH})_2]_n \cdot 0.5n\text{H}_2\text{O}$ (**1**).

收稿日期: 2008-03-14. 收修改稿日期: 2008-06-05.

湖南省重点学科建设项目, 衡阳师范学院青年骨干基金(2007)和衡阳市科技局资助项目(No.2007KJ004).

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1 Experimental

1.1 Materials and instruments

All the reagents and solvents were used as commercial sources without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on Shimadzu FTIR-8700 spectrophotometer using KBr discs.

1.2 Synthesis of the title compound

The compound was hydrothermal synthesized under autogenous pressure. A mixture of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.181 g, 0.5 mmol), 3,5-dimethylbenzoic acid (0.115 g, 1 mmol), NaOH (0.041 g, 1 mmol) and $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (9 mL, 2:1) was heated in a 25 mL capacity Teflon-lined reaction vessel at 160 °C for 4 days, the reaction mixture was cooled to room temperature over a period of 24 h. The product was collected by filtration, washed with H_2O and air-dried, Yields based on Mn: 37%. Molecular formula is $\text{C}_{112}\text{H}_{126}\text{Mn}_6\text{O}_{29}$. Elemental analysis (%) C 59.17; H 5.48. Found (%): C 59.32; H 5.56. Main IR bands (cm^{-1}): 3 423s, 1 637s, 1 609s,

1 454ms, 1 114s, 1 087s, 846ms, 725m, 624w.

1.3 Crystal structure determination

A colorless block crystal with dimensions of 0.20 mm \times 0.26 mm \times 0.32 mm was selected for the measurement. The diffraction data were collected at 291(2) K on a Bruker Smart Apex CCD single crystal diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). A total of 26 125 reflections were collected in the range of $1.18^\circ \leq \theta \leq 26.00^\circ$ by using an ω -scan mode, of which 10 868 were unique with $R_{\text{int}}=0.037$, 7 546 were considered as observed ($I>2\sigma(I)$) and used in the structural analysis and refinement. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically and Hydrogen atoms were localized in their calculation positions and refined by using the riding model. All calculations were performed by the SHELXTL program version 5.1. Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 694097.

Table 1 Crystal data and structure parameters for the title complex

Empirical formula	$\text{C}_{112}\text{H}_{126}\text{Mn}_6\text{O}_{29}$	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.332
Formula weight	2 265.77	Z	1
Temperature / K	291(2)	Absorption coefficient / mm^{-1}	0.723
Crystal system	Triclinic	$F(000)$	1 180
Space group	$P\bar{1}$	Crystal size / mm	0.20 \times 0.26 \times 0.32
a / nm	1.2751(13)	$\theta / (^\circ)$	1.18 to 26.00
b / nm	1.354 6(14)	Limiting indices	$-15 \leq h \leq 15, -16 \leq k \leq 16, -23 \leq l \leq 16$
c / nm	1.882 3(19)	Reflections collected / unique	26 125 ($R_{\text{int}}=0.037$)
$\alpha / (^\circ)$	110.826(1)	Data / restraints / parameters	10 868 / 693 / 0
$\beta / (^\circ)$	94.358(2)	Goodness of fit on F^2	0.92
$\gamma / (^\circ)$	108.038(1)	Final R indices [$I>2\sigma(I)$]	$R_1=0.054\ 6, wR_2=0.128\ 5$
V / nm^3	2.825 4(5)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	261 and -557

2 Results and discussion

2.1 Crystal structure of the title complex

The molecular structure of the title complex is shown in Fig.1, and the selected bond lengths and bond angle are given in Table 2.

X-ray analyses revealed that the structure of the complex consists of infinite 1D coordination chains

$[\text{Mn}_3(\text{L})_6(\text{CH}_3\text{OH})_2]_n \cdot 0.5n\text{H}_2\text{O}$. The asymmetric unit contains three Mn^{2+} cations, six 3,5- $\text{Me}_2\text{PhCO}_2^-$ anions, half H_2O molecule and two methanol molecules. As depicted in Fig.1, the Mn1 atom is octahedrally coordinated by five O atoms of four different ligands and one O atoms of one methanol molecule. We can presume that the equatorial plane is composed of O2, O12, O13, and O1B, which the sum of bond angles O(2)-Mn(1)-O(12)

Table 2 Selected bond lengths (nm) and bond angle ($^\circ$)

Mn(1)-O(1)	0.245 4(3)	Mn(2)-O(4)	0.211 6(3)	Mn(3)-O(6)	0.212 7(3)
Mn(1)-O(2)	0.226 3(3)	Mn(2)-O(2)	0.226 4(2)	Mn(3)-O(8)	0.215 6(3)
Mn(1)-O(3)	0.211 1(3)	Mn(2)-O(5)	0.212 3(3)	Mn(3)-O(9)	0.234 0(3)
Mn(1)-O(12)	0.216 5(3)	Mn(2)-O(7)	0.210 8(3)	Mn(3)-O(10)	0.237 9(3)
Mn(1)-O(13)	0.223 5(3)	Mn(2)-O(9)	0.221 8(2)	Mn(3)-O(14)	0.221 6(3)
Mn(1)-O(1B)	0.214 0(3)	Mn(2)-O(11)	0.212 1(3)	Mn(3)-O(10A)	0.217 3(3)
O(1)-Mn(1)-O(3)	170.69(10)	O(4)-Mn(2)-O(11)	86.86(10)	O(5)-Mn(3)-O(10)	124.07(9)
O(2)-Mn(1)-O(12)	88.98(10)	O(5)-Mn(2)-O(7)	90.19(11)	O(5)-Mn(3)-O(14)	92.58(9)
O(2)-Mn(1)-O(13)	87.15(10)	O(7)-Mn(2)-O(11)	91.89(11)	O(5)-Mn(3)-O(10A)	153.86(10)
O(1B)-Mn(1)-O(12)	85.42(10)	O(5)-Mn(2)-O(9)	82.57(10)	O(6)-Mn(3)-O(10)	171.23(10)
O(1B)-Mn(1)-O(13)	83.16(10)	O(4)-Mn(2)-O(7)	172.89(10)	O(8)-Mn(3)-O(9)	92.53(10)
O(1)-Mn(1)-O(4)	123.78(9)	O(5)-Mn(2)-O(11)	176.35(10)	O(8)-Mn(3)-O(14)	162.86(10)
O(1)-Mn(1)-O(12)	83.40(9)	O(7)-Mn(2)-O(9)	87.23(10)	O(8)-Mn(3)-O(10A)	84.53(10)
O(1)-Mn(1)-O(13)	78.36(10)	O(7)-Mn(2)-O(11)	91.89(11)	O(10)-Mn(3)-O(14)	79.58(10)
O(1)-Mn(1)-O(1B)	79.22(9)	O(9)-Mn(2)-O(11)	94.53(10)	O(10)-Mn(3)-O(10A)	80.62(9)
O(2)-Mn(1)-O(3)	123.08(10)	O(5)-Mn(3)-O(6)	52.96(10)	O(9)-Mn(3)-O(10)	54.73(9)
O(2)-Mn(2)-O(9)	177.84(10)	O(5)-Mn(3)-O(8)	103.71(9)	O(9)-Mn(3)-O(14)	88.05(10)
O(4)-Mn(2)-O(5)	91.44(11)	O(5)-Mn(3)-O(9)	69.85(9)	O(9)-Mn(3)-O(10A)	135.35(9)

A: $-x, 2-y, -z$; B: $-x, 2-y, 1-z$.

88.98(10) $^\circ$, O(12)-Mn(1)-O(1B) 85.42(10) $^\circ$, O(1B)-Mn(1)-O(13) 83.16(10) $^\circ$ and O(13)-Mn(1)-O(2) 87.15(10) $^\circ$ is 344.71 $^\circ$, and the Mn-O bond distances fall in the region 0.211 1~0.245 4 (3) nm, which is comparable to those in related complexes^[3,13]. Furthermore, the angle

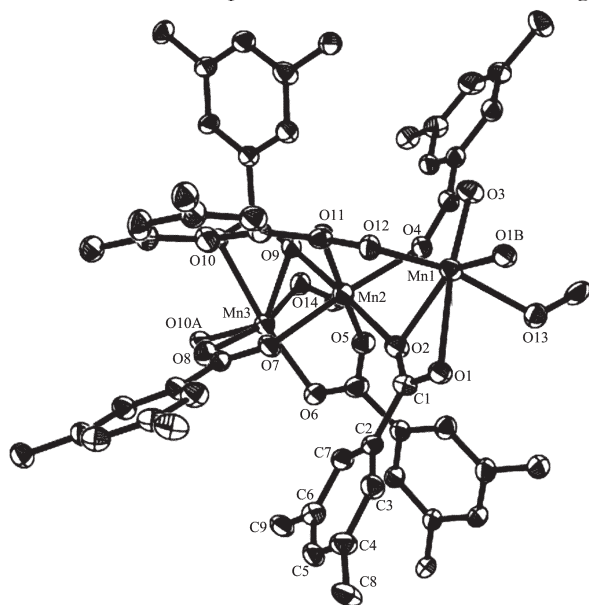
Code: A: $-x, 2-y, -z$; B: $-x, 2-y, 1-z$; A water molecule is omitted for clarity

Fig.1 Ortep view of the complex with displacement ellipsoids (30% probability)

O(1)-Mn(1)-O(3) being in axial place is 170.69(10) $^\circ$, these data indicate that the Mn1 atom of the complex is in distorted octahedron environment. The Mn3 atom is similar to the Mn1, while Mn2 is a little different from them. Around it is six O atoms which come from six 3,5-Me₂PhCO₂⁻ anions. The distance of Mn(1)···Mn(2) 0.34 nm, Mn(1)···Mn(1A) 0.35 nm is much longer than that of Mn(1)···Mn(2) 0.329 3(9) nm^[6], so there exists no weak mental bond between the adjacent Mn atoms. In addition, Fig.2 also clearly reveals the true relationship of the two manganese centers (Mn1 Mn1A); that is, the two Mn centers form two edge-sharing octahedral.

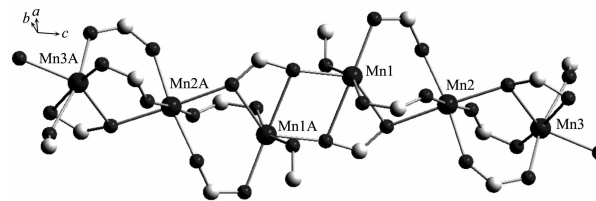
Code: A $-x, 2-y, -z$; Benzene ring of 3,5-dimethylbenzoate is omitted for clarity

Fig.2 1D infinite chain constructed by 3,5-dimethylbenzoate

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. These hydrogen bonds thus appear to stabilize the asymmetry

molecular disposition around the Mn center.

Table 3 Parameters of hydrogen bonds for the complex

D...H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H-O}) / \text{nm}$	$d(\text{D-O}) / \text{nm}$	$\angle \text{D-H-A} / (^\circ)$
O(13)···H(13E)···O(12) ^a	0.091(4)	0.192(4)	0.280 0(4)	163(4)
O(14)···H(14A)···O(8) ^b	0.084(5)	0.203(5)	0.282 0(4)	157(5)
O(15)···H(15A)···O(4) ^c	0.084(10)	0.237(10)	0.284 3(7)	116(8)

^a $-x, 2-y, 1-z$; ^b $-x, 2-y, -z$; ^c $1+x, y, z$.

2.2 Spectra characteristics and cyclic voltammetry

The infrared spectra of the title complex has been recorded and some important assignments are shown above. One feature of the IR data is the separation between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, which have often been used to diagnose the coordination modes in the carboxylate ligands. The separation for monodentate carboxylate groups is $>200 \text{ cm}^{-1}$, whereas it is $<200 \text{ cm}^{-1}$ in bidentate groups [14]. The separation (Δ) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ is 183 cm^{-1} for **1**, indicating bidentate coordinating modes for the coordinated carboxylate groups, these IR results are coincident with the crystallographic structural analyses. In the IR spectra, the band at 3423 cm^{-1} , due to the $\nu(\text{O-H})$ absorptions of methanol molecules.

In the CV measurement, tri-electrode system was used with glass/C as working electrode, Pt as auxiliary electrode and SCE as reference electrode. The solvent is the mixture of methanol and water with complex condensation of $1.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. KCl is used as the supporting electrolyte and HAc-NaAc buffer solution is adopted. The scanning range is $-1.500 \sim -2.000 \text{ V}$ and scanning rate $100 \text{ mV} \cdot \text{s}^{-1}$. Electron transfer in the

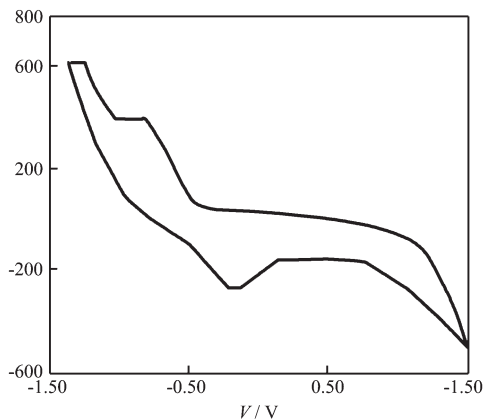


Fig.3 Cyclic voltammograms of the title complex

electrode reaction is irreversible. The peak potential of our complex could be comparable with that of Mn(II)/Mn ($E = -1.034 \text{ V}$) under standard conditions, so we can deduce that the oxidizability of Mn(II) in the title complex has been strengthened.

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