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三核锰配合物$[Mn_3O(O_2CCHClCH_3)_6(py)_2(H_2O)]\cdot 2/3H_2O$的合成,晶体结构及磁性

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摘要:用 *N*-*n*-Bu_4MnO_4,醋酸锰,2-氯丙酸在无水乙醇溶剂中合成了三核锰配合物$[Mn_3O(O_2CCHClCH_3)_6(py)_2(H_2O)]\cdot 2/3H_2O$(**1**·2/3$H_2O$)。X-射线单晶衍射确定了其晶体结构。晶体属单斜晶系、*C*2/*c* 空间群。3 个 Mn 原子构成等腰三角形结构。变温磁化率研究表明配合物 **1** 存在反铁磁性交换作用。

关键词:合成;晶体结构;磁性;三核锰配合物
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Synthesis, Crystal Structure and Magnetic Property of A Trinuclear Oxo-Centered Mixed-Valuated Manganese Complex $[Mn_3O(O_2CCHClCH_3)_6(py)_2(H_2O)]\cdot 2/3H_2O$

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Abstract: The reaction of *N*-*n*-Bu_4MnO_4 with $Mn(OAc)_2\cdot 4H_2O$ and 2-chloropropane acid in nonaqueous solvents leads to the formation of the complex $[Mn_3O(O_2CCHClCH_3)_6(py)_2(H_2O)]\cdot 2/3H_2O$ (**1**·2/3H_2O). The crystal structure was determined. The complex crystallizes in monoclinic, space group *C*2/*c*, unit cell parameters, *a*=3.593 5(2) nm, *b*=1.753 40(10) nm, *c*=2.480 9(2) nm, β=124.78(10)°. An isoceles triangle structure of the complex **1** has an antiferromagnetic interaction between the three Mn ions. CCDC: 723814.

Key words: synthesis; crystal structure; magnetic property; trinuclear manganese(Ⅲ) complex

0 Introduction

The synthesis and magnetic properties of oxo-bridge multi-nuclear metal cluster have been a focus of intense research efforts for teens of more than ten years. People have been interesting in them for their characteristics of intramolecular electron transfer and magnetic exchange. Many kinds of multi-nuclear manganese complexes can be made from tri-nuclear manganese complexes of the general formulation $[Mn_3O(O_2CR)_6L_3]^z$ (z=0,+1) with the bridging ligands, such as acetic acid[1~4], benzoic acid[3,4], pivalic acid[5], isobutyric acid[6], X-benzoato acid[7], butyric acid[8], and the terminal ligands, for example, pyridine[1~4,8], halogenated pyridine[2], Imidazole[6], 3-methypyridine[9]or water[3]. In all these complexes very subtle changes in the terminal ligands, bridge and even extra solvent in the crystals can have strong effects on the exact nature of ground and low-lying magnetic states. In order to further understand these states, we have prepared a new mix-valaue trinuclear manganese complex with 2-chloropropane acid.

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1 Experimental

1.1 Materials

All manipulations were performed under aerobic conditions. Reagent grade solvents were used without further purification. The *N*-*n*-Bu_4MnO_4 was prepared according to the literature[3]. It is potentially explosive and should be treated with care.

1.2 Synthesis

$Mn(O_2CMe)_2·4H_2O$ (2.00 g, 8.15 mmol) and 2-chloropropane acid (3.0 mL, 61.4 mmol) were dissolved in a solvent mixture comprising absolute EtOH (20 mL) and pyridine (3 mL), then *N*-*n*-Bu_4MnO_4 (1.14 g, 3.15 mmol) was added in small portions with stirring. The brown-black solution was gained. After a few days, a brown-red precipitate was collected by filtration, washed with EtOH and dried in vacuo. The precipitate was resolved in bichlorine methane layered with hexane. Dark red crystals for X-ray crystallographic analysis were obtained after about one month.

Anal. Calcd for $C_{39}H_{45}ClMn_3N_3O_{17}$(%): C, 33.56; H, 3.62; N, 2.80; Found(%): C, 33.34; H, 3.75; N, 2.83; IR (main bands, cm^{-1}): 689(s), 760 (m), 988 (m), 1 072(s), 1 223(m), 1 237(m), 1 408(s), 1 451(s), 1 638(s), 3 043(w).

1.3 Physical measurements

Elemental analyses (C, H, N) of the powder compound **1** were performed on a Perkin-Elmer 240C. The IR spectrum (400~4 000 cm^{-1}) was recorded in a KBr pellet using a Bruker Vector 22 FTIR spectrophotometer. The variable temperature (1.8~310 K) magnetic susceptibility measurements of the powder compound were performed on SQUID MPMS.

1.4 Single-crystal structure determination

All measurements were made on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo $K\alpha$ radiation (0.071 073 nm) at room temperature (291 K). Cell refinement and data reduction were carried out with the SAINT program. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELTL programs. Anisotropic thermal parameters were assigned to all nonhydrogenatoms. The hydrogen atoms were added geometrically and not refined. The essential crystallographic data and experimental details were list in Table 1.

CCDC: 723814.

Table 1　Crystallographic data and experimental details

Empirical formula	[$Mn_3O(O_2CCHClCH_3)_6(py)_2(H_2O)$]·2/3($H_2O$)	Temperature / K	291(2)
Formula weight	1 014.12	*F*(000)	6 164
Crystal system	Monoclinic	Crystal size / mm	0.30×0.26×0.22
Space group	*C*2/*c*	Temperature / K	291(2)
a / nm	3.593 5(2)	θ range for data collection / (°)	1.90~26.00
b / nm	1.753 4(1)	Reflections collected / unique (R_{int})	34 164 / 12 588 (0.013 3)
c / nm	2.480 9(2)	Final R_1 and wR_2 indices ($I>2\sigma(I)$)	0.050 7, 0.151 6
β / (°)	124.78(10)	R_1 and wR_2 indices (all data)	0.071 9, 0.155 0
Volume / nm^3	12.839 1(15)	Largest diff. peak and hole	−0.896, 0.688
Z	4	Data / restraints / parameters	12 588 / 0 / 735
D_c / ($g·cm^{-3}$)	1.574		

2 Results and discussion

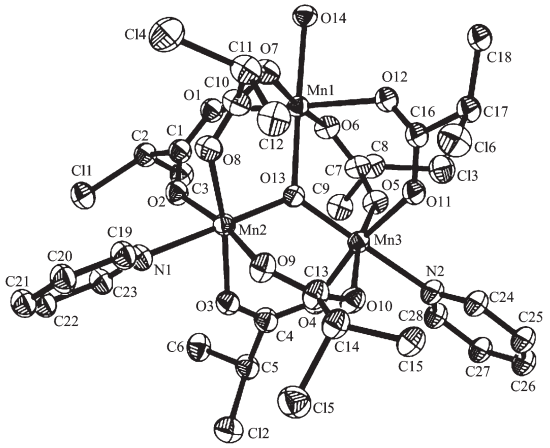
2.1 Description of the crystal structure of the complex 1

The structure of complex **1** is shown in Fig.1. Selected Bond lengths and bond angles are given in Table 2. The compound is composed of Mn_3O cluster and lattic water. The complex has distorted octahedral metal geometries. The central Mn_3O of **1** lost its 3-fold symmetry, because the Mn^{II} ion (Mn1) has a coordinated water molecular, whereas the two Mn^{III} ions (Mn2 and Mn3) each has a coordinated pyridine. The Mn coordination geometries are slightly distorted octahedral with one μ^3-oxygen atom at the center of the Mn_3 triangle, four oxygen atoms from the bridging butenoic acid and one nitrogen atom from the pyridine

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

Mn1-O13	0.213 7(3)	Mn2-O13	0.182 9(3)	Mn3-O13	0.182 6(3)
Mn1-O1	0.218 9(3)	Mn1-O6	0.214 7(3)	Mn2-O2	0.202 0(3)
Mn2-O3	0.208 0(3)	Mn3-O4	0.201 8(3)	Mn3-O5	0.216 1(3)
Mn1-O14	0.219 8(3)	Mn2-N1	0.208 0(4)	Mn3-N2	0.208 4(4)
O13-Mn1-O1	92.45(12)	O1-Mn1-O6	86.66(12)	O6-Mn1-O7	173.67(13)
O13-Mn1-O6	94.69(12)	O1-Mn1-O7	93.50(13)	O6-Mn1-O12	93.57(13)
O13-Mn1-O14	177.65(12)	O1-Mn1-O12	178.20(13)	O7-Mn1-O12	84.50(19)
O13-Mn1-O7	91.62(12)	O1-Mn1-O14	89.72(12)	O7-Mn1-O14	86.07(13)
O13-Mn1-O12	89.31(12)	O6-Mn1-O14	86.32(12)	O12-Mn1-O14	88.55(17)
O13-Mn2-O2	92.99(13)	O2-Mn2-O3	86.87(13)	O3-Mn2-O8	169.59(13)
O13-Mn2-O3	94.50(13)	O2-Mn2-O8	96.08(13)	O3-Mn2-O9	90.03(14)
O13-Mn2-N1	178.52(17)	O2-Mn2-O9	170.51(14)	O8-Mn2-O9	85.46(14)
O13-Mn2-O8	95.31(13)	O2-Mn2-N1	85.54(15)	O8-Mn2-N1	85.01(15)
O13-Mn2-O9	96.20(14)	O3-Mn2-N1	85.26(15)	O9-Mn2-N1	85.27(15)

or one oxygen atom from the coordinated water. In the molecular, The distances of Mn1-O1 (0.219 nm), Mn1-O6 (0.215 nm), Mn1-O13 (0.214 nm) and Mn1-O14 (0.220 nm) are all about the same. The distances of Mn2-O2 (0.202 nm), Mn2-O3 (0.208 nm) and Mn2-N1 (0.208 nm) are about the same too, but the Mn2-O13 distance (0.183 nm) is shorter apparently. The angles of O13-Mn1-O14 (177.65°) and O13-Mn2-N1 (178.52°) are little smaller than 180°. The planes of the pyridine moleculars are nearly at right angles to that of Mn1Mn2Mn3. The three Mn atoms form an isoceles triangle, with the two equal distances of Mn2-O13 and Mn3-O13, but a longer distance of Mn1-O13, which are nearly same with those in the benzoic acid counterpart $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]\cdot 0.5MeCN$[3].

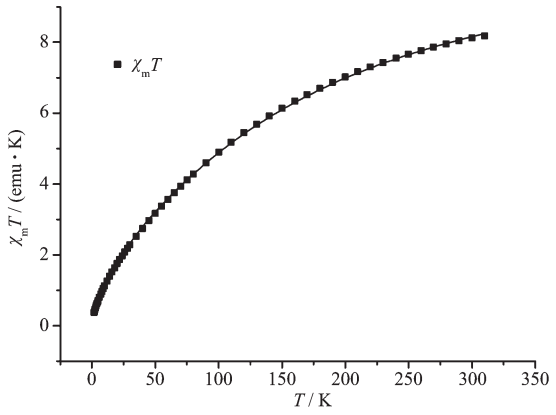


H atoms and lattice waters have been omitted

Fig.1 Structure of sample **1**, showing the atom-numbering scheme, thermal ellipsoids at 30% probability level

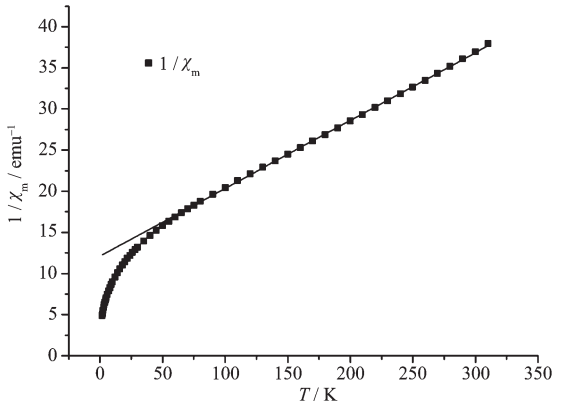
2.2 Magnetic susceptibility

Variable temperature (1.8 to 310 K) magnetic susceptibility data were collected for the crystal. The $\chi_m T$ and $1/\chi_m$ versus temperature plots are shown in Fig. 2 and Fig.3. The Weiss constant (θ=147 K) is obtained from a linear fit of the $1/\chi_m$ data between 70~300 K. The negative value of the Weiss constant θ indicates that there are antiferromagnetic exchange interactions between the Mn ions. The product of $\chi_m T$ decreases gradually from 8.17 $cm^3\cdot K\cdot mol^{-1}$ at 310 K to 0.37 $cm^3\cdot K\cdot mol^{-1}$ at 1.8 K. This fact leads us to believe that some degree of antiferromagnetic exchange interactions do exist in the compound. This interaction is chiefly propagated by both the oxide and the carboxylate



Solid lines represent a least-squares fit of the date to the reference[3]

Fig.2 Plot $\chi_m T$ vs temperature for sample **1**



Solid lines represent a least-squares fit of the date to the Curies-Weiss Theory

Fig.3　Plot 1/χ_m vs temperature for sample **1**

bridge. The similar results have also been reported for other analog trinuclear oxo-centered manganese complex [3,7~9]. See in the Fig.4, J_{ij} express the exchange interaction between Mn_i and Mn_j. We have tried to fit the data based on the spin Hamiltonian:

$$\hat{H}=-[J_{12}(\hat{S}_1\cdot\hat{S}_2)+J_{23}(\hat{S}_2\cdot\hat{S}_3)+J_{31}(\hat{S}_3\cdot\hat{S}_1)]$$

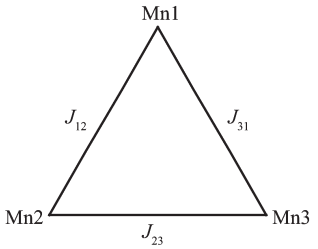


Fig.4　Exchange interactions between Mn_i

In this casing, $J=J_{12}=J_{13}$ for the Mn^{II}-Mn^{III} interactions and $J'=J_{23}$ for the Mn^{III}-Mn^{III} interaction, then we get g=2.11, J=−7.39 cm^{-1}, J'=−10.8 cm^{-1} by the simulation. The parameters resulting from least-squares fitting of sample **1** and some analogues are list in Table 3. We can find that g is about 2.1 in $Mn^{III}_2Mn^{II}$. The Mn^{III}-Mn^{III} interaction (J'=−10.8) is closed to the interaction in the [$Mn_3O(O_2CPh)_6(py)_2(H_2O)$]·0.5MeCN ($J'$=−10.9)[3].

Table 3　Parameters resulting from least-squares fitting of magnetic susceptibility data

Compound	J / cm^{-1}	J' / cm^{-1}	g
[$Mn_3O(O_2CCH_3)_6(py)_3$]·ClO_4[3]	−10.2		1.81
[$Mn_3O(O_2CCH_3)_6(py)_3$]·py[3]	−5.1	−8.3	2.13
[$Mn_3O(O_2CCH_3)_6(py)_3$][3]	−7.7	−5.7	2.10
[$Mn_3O(O_2CPh_3)_6(py)_2(H_2O)$]·0.5MeCN[3]	−7.3	−10.9	2.11
[$Mn_3O(O_2CCHClCH_3)_6(py)_2(H_2O)$]·2/3$H_2O$	−7.39	−10.8	2.11

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