

## 研究简报

# 混合价三核锰配合物 $Mn_3O(O_2CCCl_3)_6(py)_2(H_2O)$ 的合成、晶体结构及磁性

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## Synthesis, Crystal Structure and Magnetic Property of a New Mixed-Valence Trinuclear Oxo-Centered Manganese Complex $Mn_3O(O_2CCCl_3)_6(py)_2(H_2O)$

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A new mixed-valence trinuclear oxo-centered manganese complex  $Mn_3O(O_2CCCl_3)_6(py)_2(H_2O)$  was prepared by the reaction of  $N^tBu_4MnO_4$  with  $Mn(OAc)_2 \cdot 4H_2O$ , trichloroacetic acid and pyridine in absolute EtOH. The crystal structure was determined. The complex crystallizes in monoclinic, space group  $P2_1/c$ , unit cell parameters,  $a = 14.951(1)$ ,  $b = 20.791(2)$ ,  $c = 17.882(1)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 102.67(1)^\circ$ . Variable temperature solid state magnetic susceptibility study shows that the complex has an antiferromagnetic exchange interaction. CCDC: 183369.

**Keywords:** crystal structure manganese complex mixed valence magnetism

## 0 Introduction

The synthesis and magnetic property of oxo-centered trinuclear manganese complexes have been a focus of intense research efforts for a long time due to their characteristics of intramolecular electron transfer and magnetic exchange<sup>[1]</sup>. They also serve as an excellent starting material to make higher nuclear cluster as single molecule magnet<sup>[2]</sup>. Up to date, there are the well-characterized trinuclear manganese complexes

of the general formulation  $[Mn_3O(O_2CR)_6L_3]^{0,+}$  with the bridging ligands, such as acetic acid<sup>[3~5]</sup>, benzoic acid<sup>[5,6]</sup>, pivalic acid<sup>[7]</sup>, isobutyric acid<sup>[8]</sup>, X-benzoato acid<sup>[5,9]</sup>, butyric acid<sup>[10]</sup>, and with the terminal ligands, such as pyridine<sup>[3~6, 10]</sup>, X-pyridine<sup>[4]</sup>, imidazole<sup>[8]</sup>, 3-methylpyridine<sup>[11]</sup> or water<sup>[5]</sup>. In all these complexes very subtle changes in the terminal and bridging ligands and even extra solvent in the crystals can give some strong effects on the exact nature of ground and

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low-lying magnetic states<sup>[1]</sup>. In this paper, we report the synthesis and crystal structure of  $\text{Mn}_3\text{O}(\text{O}_2\text{CCl}_3)_6(\text{py})_2(\text{H}_2\text{O})$ , together with the results of variable temperature magnetic susceptibility.

## 1 Experimental

### 1.1 Materials and Measurements

All manipulations were performed under aerobic conditions. Reagent grade solvents were used without further purification. The  $\text{N}^{\text{a}}\text{Bu}_4\text{MnO}_4$  was prepared according to the literature report<sup>[5]</sup>.  $\text{N}^{\text{a}}\text{Bu}_4\text{Br}$  (12.00g, 37.2mmol) was added to an aqueous solution of  $\text{KMnO}_4$  (5.00g, 31.6mmol) with vigorous stirring. The immediate purple precipitate was collected by filtration, washed thoroughly with distilled water and diethyl ether and then dried in vacuo at room temperature. Yield > 90%.

Warning!  $\text{N}^{\text{a}}\text{Bu}_4\text{MnO}_4$  is potentially explosive and must be treated with care.

The elemental analysis of carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C at the Analysis and Measurement Center of Nanjing University. IR spectra ( $400 \sim 4000\text{cm}^{-1}$ ) were recorded from KBr pellets in a Bruker Vector 22 FTIR spectrophotometer. The variable temperature (75 ~ 300K) magnetic susceptibility measurements of microcrystalline samples were obtained on a Faraday-type magnetic balance at 0.7T magnetic fields. Diamagnetic corrections were estimated from Pascal's constants and subtracted from the experimental susceptibility data to obtain the molar paramagnetic susceptibility of the complex.

### 1.2 Synthesis of $\text{Mn}_3\text{O}(\text{O}_2\text{CCl}_3)_6(\text{py})_2(\text{H}_2\text{O})$

$\text{Mn}(\text{O}_2\text{CMe})_2 \cdot 4\text{H}_2\text{O}$  (2.00g, 8.15mmol) and trichloroacetic acid (10.00g, 61.4mmol) were dissolved in a solvent mixture comprising absolute EtOH (30mL) and pyridine (3mL). The resulting solution was stirred while solid  $\text{N}^{\text{a}}\text{Bu}_4\text{MnO}_4$  (1.14g, 3.15mmol) was added in small portions to give a deep brown solution. This was allowed to stand undisturbed 4h, and then resulting brown-black precipitate which was collected by filtration, washed thoroughly with EtOH and dried in vacuo.

Yield, 60%. (Based on Mn). Anal. Calcd. for  $\text{C}_{22}\text{H}_{12}\text{Cl}_{18}\text{Mn}_3\text{N}_2\text{O}_{14}$ : C, 19.83; H, 0.90; N, 2.10. Found: C, 19.92; H, 1.02; N, 2.04%. IR Data (main bands,  $\text{cm}^{-1}$ ): 689 (s), 745 (m), 837 (s), 1047(m), 1224(m), 1383(s), 1683(s), 1686(s), 3442(s). Crystals for X-ray crystallographic analysis were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$  solution.

### 1.3 Crystallographic Study

The data were collected on a SMART APEX CCD diffractometer using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $0.71073\text{\AA}$ ) at room temperature (293K). A crystal of dimensions  $0.30 \times 0.20 \times 0.20\text{mm}$  was attached to a thin glass fibre and mounted on the diffractometer. Cell parameters and orientation matrix for data collection were obtained from least-squares refinement. 27704 intensity data, of which 9537 were unique, were collected in the range  $1.90^\circ < \theta < 25.00^\circ$ . The title complex crystallizes in monoclinic, space group  $P2_1/c$ , with  $a = 14.951(1)$ ,  $b = 20.971(2)$ ,  $c = 17.882(1)\text{\AA}$ ,  $V = 5423.2(7)\text{\AA}^3$ ,  $Z = 4$ ,  $D(\text{calc.}) = 1.630(\text{g} \cdot \text{cm}^{-3})$ ,  $F(000) = 2604$ . The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms were added geometrically and not refined.  $R_1$  was 0.0493,  $wR_2$  was 0.1542,  $w = 1/[\sigma^2(F_0)^2 + (0.0900P)^2 + 1.9900P]$  where  $P = (F_0^2 + 2F_c^2)/3$ . The refinement was based on  $F^2$ . Using SHELXTL created the molecular graph. The key crystallographic data and refinement for the complex are given in Table 1.

CCDC: 183369.

## 2 Results and Discussion

### 2.1 Description of the Crystal Structure

The molecular structure of the title complex is shown in Fig. 1. Fractional coordinates and isotropic thermal parameters are listed in Table 2. Selected bond lengths and bond angles are given in Table 3. The charge on the complex is an  $\text{Mn}_2^{III}\text{Mn}^{II}$  description. The complex has distorted octahedral metal geometries and

Table 1 Crystallographic and Refinement

formula	$C_{22}H_{12}Cl_{18}Mn_3N_2O_{14}$	formula weight	1331.26
crystal system	monoclinic	space group	$P2_1/c$
$a/\text{\AA}$	14.951(1)	$b/\text{\AA}$	20.791(2)
$c/\text{\AA}$	17.882(1)	$\alpha, \gamma/(\text{^\circ})$	90
$\beta/(\text{^\circ})$	102.67(1)	$V/\text{\AA}^3$	5423.2(7)
Z	4	$D(\text{calc.})/(g \cdot \text{cm}^{-3})$	1.630
$\mu(\text{Mo K}\alpha)/\text{mm}$	1.624	$F(000)$	2604
crystal size/mm	0.30 × 0.20 × 0.20	temperature/K	293
radiation/ $\text{\AA}$	0.71073	$\theta$ range for data collection/( $\text{^\circ}$ )	1.90 to 25.00
limiting indices	$-17 \leq h \leq 17, 0 \leq k \leq 24, 0 \leq l \leq 21$	No. of reflections measured	27704
No. of independent reflections	9537	$R(\text{int})$	0.073
observed data [ $I > 2.0\sigma(I)$ ]	6917	final $R$ indices	$R_1 = 0.0493, wR_2 = 0.1542$
goodness of fit indicator	1.02	largest diff. peak and hole/(e · $\text{\AA}^{-3}$ )	0.69, -0.59

Table 2 Fractional Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\text{\AA}^2 \times 10^3$ )

atom	x	y	z	$U(\text{eq})$	atom	x	y	z	$U(\text{eq})$
Mn1	991(3)	4961(3)	6399(1)	42(4)	Mn2	1329(3)	3799(8)	7795(5)	45(8)
Mn3	3125(6)	4435(9)	7297(8)	51(1)	Cl1	-1010(8)	2586(1)	6098(6)	98(5)
Cl2	-1750(4)	3666(1)	5197(9)	95(7)	Cl3	-1772(6)	3609(2)	6809(9)	107(5)
Cl4	-661(9)	6130(1)	8047(9)	154(4)	Cl5	-1085(2)	5000(5)	8633(3)	194(5)
Cl6	522(2)	5504(7)	9249(9)	163(2)	Cl7	3654(4)	6542(7)	8220(3)	190(9)
Cl8	2282(9)	7085(1)	7004(8)	162(5)	Cl9	3831(3)	6587(4)	6702(4)	334(4)
Cl10	2796(3)	3475(2)	823(9)	207(7)	Cl11	3753(9)	4640(1)	4760(9)	141(8)
Cl12	1938(6)	4501(5)	3945(5)	141(8)	Cl13	2537(1)	4328(2)	10348(3)	230(2)
Cl14	4248(3)	3973(9)	10180(3)	161(9)	Cl15	3673(3)	5200(8)	9892(5)	240(2)
Cl16	2162(2)	2188(8)	6195(2)	187(8)	Cl17	2940(2)	1781(9)	7679(2)	189(7)
Cl18	4089(3)	2365(8)	6754(2)	77(8)	O1	1867(9)	4361(1)	2237(1)	53(1)
O2	141(2)	5594(9)	5582(1)	64(1)	O3	-83(1)	4223(7)	6016(1)	63(5)
O4	287(2)	3511(6)	6903(4)	63(7)	O5	264(3)	5269(7)	7246(2)	91(5)
O6	491(3)	4494(9)	8083(2)	91(3)	O7	1929(3)	5763(1)	6672(3)	96(3)
O8	3101(3)	5382(6)	7450(2)	93(1)	O9	1590(2)	4659(4)	5458(5)	72(8)
O10	3012(2)	4512(7)	6118(2)	80(1)	O11	2218(3)	4012(2)	8790(4)	96(6)
O12	3478(2)	4374(2)	8524(2)	97(1)	O13	2120(2)	3050(1)	7567(2)	80(5)
O14	3283(2)	3486(2)	7188(2)	83(1)	N1	762(3)	3184(2)	8445(2)	72(8)
N2	4490(3)	4511(3)	7348(3)	89(7)	C1	-224(3)	3746(2)	6357(3)	58(7)
C2	-1147(3)	3430(2)	6133(2)	59(3)	C3	209(5)	5019(3)	7830(3)	97(3)
C4	-187(5)	5457(3)	8383(3)	112(3)	C5	2618(5)	5825(3)	7154(4)	101(2)
C6	3019(5)	6495(3)	7228(5)	135(4)	C7	2402(4)	4514(3)	5508(3)	80(2)
C8	2713(4)	4309(3)	4800(3)	90(2)	C9	2984(4)	4212(4)	8955(3)	101(3)
C10	3350(5)	4397(4)	9795(3)	113(3)	C11	2795(4)	3038(3)	7312(4)	80(8)
C12	3041(4)	2372(3)	7035(4)	89(2)	C13	572(4)	2566(2)	8192(3)	73(4)
C14	163(4)	2138(3)	8598(3)	75(5)	C15	33(4)	2323(2)	9273(3)	76(9)
C16	251(4)	2953(2)	9564(3)	76(2)	C17	560(4)	3345(3)	9103(3)	74(4)
C18	5001(3)	4911(3)	7837(3)	91(2)	C19	5868(3)	5070(3)	837(3)	93(2)
C20	6330(3)	4710(3)	7352(3)	94(2)	C21	5811(3)	4289(3)	6880(3)	92(2)
C22	4895(3)	4193(3)	6891(3)	90(2)					

$U(\text{eq}) = 1/3$  of the trace of the orthogonalized  $U$  tensor.

the overall “ basic metal carboxylate ” structure. The central O-atom O(1) lies in the plane of the Mn3 triangle. The O(1)-Mn distances are 1.848(3)  $\text{\AA}$  for Mn(2), 1.862(3)  $\text{\AA}$  for Mn(3) and 2.145(3)  $\text{\AA}$  for Mn(1) (which has the  $H_2O$  molecule as terminal lig-

and). The Mn-O(1)-Mn angles are  $Mn(2)-O(1)-Mn(3) = 124.68(15)\text{^\circ}$ ;  $Mn(1)-O(1)-Mn(3) = 117.09(13)\text{^\circ}$  and  $Mn(1)-O(1)-Mn(2) = 118.22(13)\text{^\circ}$ , respectively. The Mn coordination geometries are slightly distorted octahedra consisting of the oxygen of the

Table 3 Select Bond Lengths ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ )

Mn1-O1	2.145(3)	Mn1-O2	2.161(3)	Mn1-O3	2.218(3)	Mn1-O5	2.147(4)
Mn1-O7	2.164(4)	Mn1-O9	2.164(3)	Mn2-O1	1.848(3)	Mn2-O4	2.060(3)
Mn2-O6	2.051(4)	Mn2-O11	2.022(3)	Mn2-O13	2.051(3)	Mn2-N1	2.035(4)
Mn3-O1	1.862(3)	Mn3-O8	1.988(4)	Mn3-O10	2.085(3)	Mn3-O12	2.144(3)
Mn3-O14	2.003(4)	Mn3-N2	2.028(5)				
O1-Mn1-O2	177.93(11)	O13-Mn2-N1	88.06(15)	O1-Mn1-O7	91.44(14)	O1-Mn3-O12	94.91(12)
O2-Mn1-O5	88.91(13)	O8-Mn3-O10	93.60(15)	O3-Mn1-O5	88.84(13)	O8-Mn3-N2	88.1(2)
O5-Mn1-O7	90.81(17)	O10-Mn3-N2	84.08(17)	O1-Mn2-O4	95.89(12)	O14-Mn3-N2	86.7(2)
O1-Mn2-O13	91.69(13)	Mn2-O1-Mn3	124.68(15)	O4-Mn2-O13	89.76(13)	O6-Mn2-O13	174.97(15)
O11-Mn2-N1	84.88(16)	O1-Mn1-O5	90.94(12)	O1-Mn3-O10	94.44(12)	O2-Mn1-O3	86.21(11)
O1-Mn3-N2	178.45(18)	O2-Mn1-O9	86.19(12)	O8-Mn3-O14	174.37(16)	O3-Mn1-O9	87.39(12)
O10-Mn3-O14	87.80(15)	O7-Mn1-O9	92.33(16)	O12-Mn3-N2	86.57(17)	O1-Mn2-O11	93.85(14)
Mn1-O1-Mn3	117.09(13)	O4-Mn2-O6	89.94(14)	O4-Mn2-N1	85.40(14)	O6-Mn2-N1	86.91(16)
O1-Mn-O3	95.85(11)	O1-Mn3-O8	92.51(16)	O1-Mn1-O9	94.07(11)	O1-Mn3-O14	92.81(12)
O2-Mn1-O7	86.50(14)	O8-Mn3-O12	85.82(15)	O3-Mn1-O7	172.70(15)	O10-Mn3-O12	170.65(12)
O5-Mn1-O9	174.01(14)	O12-Mn3-O14	91.91(15)	O1-Mn2-O6	93.34(14)	Mn1-O1-Mn2	118.22(13)
O1-Mn2-N1	178.69(15)	O4-Mn2-O11	169.92(15)	O6-Mn2-O11	86.87(16)	O11-Mn2-O13	92.57(16)

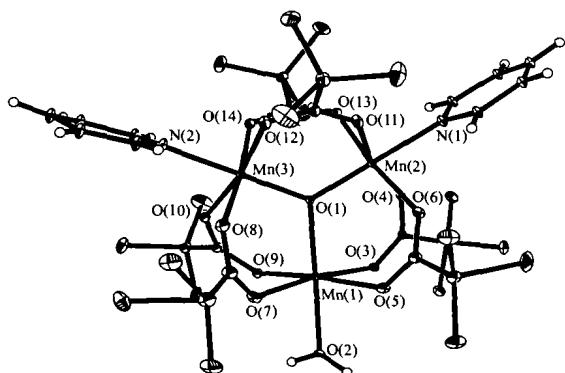
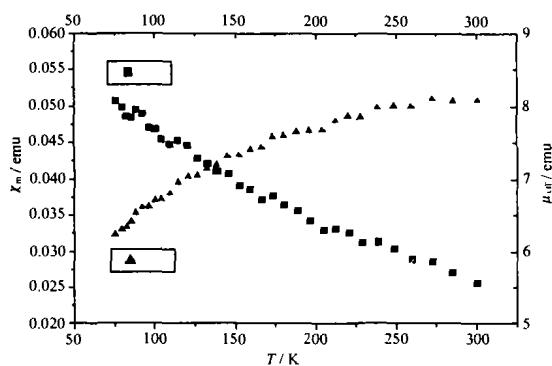


Fig. 1 Molecular structure of the title complex

central triangle, four oxygen atoms from bridging trichloroacetic acid ligands, and a terminal oxygen ( $\text{H}_2\text{O}$ ) or nitrogen (pyridine) atom. The average values for the five Mn-O bond distances are 2.168  $\text{\AA}$  for Mn (1), 2.006  $\text{\AA}$  for Mn(2), and 2.016  $\text{\AA}$  for Mn(3), respectively. This asymmetry is most noticeable in the Mn<sub>3</sub> triangle being essentially isosceles rather than equilateral. The Mn(2)-Mn(3) distance (3.287  $\text{\AA}$ ) is significantly shorter than the Mn(2,3)-Mn(1) distance (3.431  $\text{\AA}$  and 3.422  $\text{\AA}$ ). The Mn(1) atom can be assigned as Mn<sup>II</sup> center since all Mn(1) distances are longer than those for Mn(2) and Mn(3), as expected for the lower oxidation state. The same situation has been reported for the benzoate<sup>[5]</sup> and X-benzoate analog<sup>[9]</sup>.

## 2.2 Magnetic Susceptibility

Variable temperature (75 to 300 K) magnetic susceptibility data were collected for microcrystalline sample of the compound. The  $\mu_{\text{eff}}$  versus  $T$  plots is shown in Fig. 2. The effective magnetic moment decreases gradually from 7.85 (c. g. s. emu) at 300 K to 5.53 (c. g. s. emu) at 75 K. The similar results have been reported for other analogous trinuclear oxo-centered manganese complex<sup>[5, 9~11]</sup>, implying the existence of an antiferromagnetically coupling of the Mn<sub>3</sub> core of the title complex.

Fig. 2 Plots of effective magnetic moment per Mn<sub>3</sub>O molecule and molar paramagnetic susceptibility vs temperature

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