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# 基于三核锰(Ⅲ)结构单元的二维配位聚合物的合成、结构和磁性研究

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**摘要**: 新合成了钠离子桥联三核锰结构单元的配位聚合物{[$NaMn^{Ⅲ}_3O(sao)_3(tfbdc)(H_2O)_4$]·$0.5H_2O$·$2CH_3CH_2OH$}$_n$(1) ($H_2$tfbdc=2, 3, 5, 6-四氟对苯二甲酸;$H_2$sao=水杨醛肟),对其进行了元素分析、红外光谱、热重分析和单晶 X-射线衍射结构分析。配合物属于三斜晶系,空间群 $P\bar{1}$。该配合物是一个由三核锰结构单元[$Mn_3O$]构成的、钠离子和四氟对苯二甲酸桥联的二维配位聚合物。磁学性质研究表明,该配合物中锰离子之间存在着反铁磁性耦合作用。

**关键词**: 三核锰(Ⅲ)结构单元; 配位聚合物; 晶体结构; 磁性质
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## A Two-Dimensional Manganese(Ⅲ) Coordination Polymer Constructed from [$Mn_3O$] Units: Synthesis, Crystal Structure and Magnetic Properties

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**Abstract**: A 2D coordination polymer, namely {[$NaMn^{Ⅲ}_3O(sao)_3(tfbdc)(H_2O)_4$]·$0.5H_2O$·$2CH_3CH_2OH$}$_n$(1) ($H_2$tfbdc= 2, 3, 5, 6-tetrafluoroterephthalic acid, $H_2$sao=salicylaldoxime), was synthesized and structurally characterized by elemental analysis, IR spectrum, thermogravimetric analysis, and single-crystal X-ray diffraction. This complex crystallizes in triclinic space group $P\bar{1}$, and exhibits a two-dimensional polymeric structure constructing from [$Mn_3O$] units bridged by sodium cations and tetrafluoroterephthalate. Variable-temperature magnetic susceptibility analysis indicates that antiferromagnetic interaction exists between the manganese(Ⅲ) ions in the [$Mn_3O$] unit. CCDC: 934761.

**Key words**: trinuclear manganese(Ⅲ) unit; coordination polymer; crystal structure; magnetic properties

## 0 Introduction

Coordination polymers and metal-organic frameworks based on polycarboxylate ligands have attracted great interest owing to their intriguing structural motifs [1-4] and potential applications such as separation[5], catalysis[6], magnetism[7], and gas storage[8-10]. In particular, benzenedicarboxylic acids are widely used in the preparation of coordination polymers owing to their rich coordination modes. The derivatives of benzenedicarboxylic acid with substituent groups such as methyl[11], chlorine[12], and bromine[13] are signicant to assemble coordination polymers with transition-metals. Moreover, organo-fluorine compounds have been widely

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used in pharmaceutical, agrochemical and catalytic materials, due to the peculiar characteristics of fluorine element including high electronegativity, low polarizability and small covalent radius [14-21]. Tetrauoroterephthalic acid, as a fluorine-containing versatile ligand and acceptor/donor of hydrogen bond, is a good candidate for the construction of coordination polymers with interesting structures and peculiar properties. Theoretical investigation predicts that coordination polymers using 2, 3, 5, 6-tetrafluoro-terephthalate as linker have superior $H_2$ adsorbing properties [22-24]. To date, several coordination polymers employing tetrauoroterephthalate ($tfbdc^{2-}$) have been reported [25-37]. Previous studies were mainly focused on single metal center connected by tetrauoroterephthalate. In this work, we report the preparation, structure and magnetism of a novel 2D coordination polymer based on trinuclear [$Mn_3O$] cluster bridged by tetrauoroterephthalate and sodium cation.

## 1 Experimental

### 1.1 Materials and measurements

All chemicals were of reagent grade and used as received without further purification. Elemental analyses for carbon, hydrogen, and nitrogen were carried out with a Vario EL-Ⅲ elemental analyzer. Infrared spectrum was recorded with a Nicolet A370 FTIR spectrometer using KBr pellets in the 400~4 000 $cm^{-1}$ region. TGA experiment was performed with a Shimadzu DT-20B thermo gravimetric analyzer from 20 to 800 ℃ at a heating rate of 10 ℃·$min^{-1}$ in nitrogen. Variable-temperature magnetic susceptibility measurement was taken at an applied field of 2 kOe on a Quantum Design MPMS-XL7 SQUID magnetometer working in 300~1.8 K temperature range. Diamagnetic corrections were applied by using Pascals constants.

### 1.2 Synthesis of $\{[NaMn^{Ⅲ}_3O(sao)_3(tfbdc)(H_2O)_4]\cdot 0.5H_2O\cdot 2CH_3CH_2OH\}_n$ (1)

A mixture of $MnCl_2\cdot 4H_2O$ (20.0 mg, 0.1 mmol), 2,3,5,6-tetrafluoroterephthalic acid (11.9 mg, 0.05 mmol) and salicylaldoxime (13.7 mg, 0.1 mmol) were dissolved in a mixed solvent of water (3 mL) and ethanol (6 mL) with stirring. Additional NaOH solution (1 mol·$L^{-1}$) was added to adjust the value of pH to 8, and the mixture turned dark green. After stirring for 10 min, the mixture was filtered and the filtrate was left undisturbed three weeks to give dark-green block crystals of **1** in 30% yield based on Mn. Anal. Calcd. for $C_{66}H_{72}F_8Mn_6N_6Na_2O_{35}$ (%): C, 38.91; H, 3.56; N, 4.12. Found (%): C, 38.56; H, 3.52; N, 3.96. IR data (KBr, $cm^{-1}$): 3 500(s), 1 622(s), 1 597(s), 1 543(m), 1 472(m), 1 440(m), 1 374(s), 1 280(s), 1 029(m), 987(m), 919(s), 679(s), 648(m).

### 1.3 X-ray crystallography

The well-shaped single crystal of **1** was selected for X-ray diffraction study. Data collections were performed with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) on a Bruker Smart Apex-II CCD diffractometer, using the φ-ω scan technique. Data reduction was made with the Bruker SAINT

**Table 1 Crystal data and structure refinements for complex 1**

| | | | |
|---|---|---|---|
| Formula | $C_{66}H_{72}F_8Mn_6N_6Na_2O_{35}$ | $D_c$ / (g·$cm^{-3}$) | 1.478 |
| Formula weight | 2 036.92 | $\mu$ / $mm^{-1}$ | 0.910 |
| Crystal system | Triclinic | $F$(000) | 1 034 |
| Space group | $P\bar{1}$ | $\theta$ range for data collection / (°) | 2.44 to 25.99 |
| $a$ / nm | 1.188 91(19) | Indices range ($h$, $k$, $l$) | $-14\leqslant h\leqslant 14$, $-17\leqslant k\leqslant 15$, $-15\leqslant l\leqslant 19$ |
| $b$ / nm | 1.406 68(17) | Reflections collected / unique | 20 510/8 869 |
| $c$ / nm | 1.581 96(11) | $R_{int}$ | 0.025 1 |
| $\alpha$ / (°) | 112.635(2) | Data / restraints / parameters | 8 869/0/598 |
| $\beta$ / (°) | 103.240(3) | GOF on $F^2$ | 1.059 |
| $\gamma$ / (°) | 98.954(2) | $R_1$, $wR_2$ ($I>2\sigma(I)$) | 0.057 9, 0.144 5 |
| $V$ / $nm^3$ | 2.287 8(5) | $R_1$, $wR_2$ (all data) | 0.070 6, 0.146 3 |
| $Z$ | 1 | $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·$nm^{-3}$) | 734, −430 |

**Table 2　Selected bond lengths (nm) and angles (°) for complex 1**

| | | | | | |
|---|---|---|---|---|---|
| Mn(1)-O(1) | 0.188 6(3) | Mn(1)-O(2) | 0.186 0(3) | Mn(1)-N(1) | 0.197 9(4) |
| Mn(1)-O(7) | 0.191 5(3) | Mn(1)-O(4W) | 0.228 5(3) | Mn(1)-O(8) | 0.223 4(3) |
| Mn(2)-O(1) | 0.188 2(3) | Mn(2)-O(4) | 0.186 1(3) | Mn(2)-N(2) | 0.200 7(4) |
| Mn(2)-O(3) | 0.191 5(3) | Mn(2)-O(1W) | 0.229 3(3) | Mn(2)-O(3W) | 0.227 9(3) |
| Mn(3)-O(1) | 0.186 9(3) | Mn(3)-O(6) | 0.186 6(3) | Mn(3)-N(3) | 0.199 2(4) |
| Mn(3)-O(5) | 0.193 3(3) | Mn(3)-O(10)A | 0.228 1(3) | Mn(3)-O(2W) | 0.227 4(3) |
| Na(1)-O(7) | 0.234 2(3) | Na(1)-O(7)B | 0.234 2(3) | Na(1)-O(9)B | 0.238 7(3) |
| Na(1)-O(9) | 0.238 7(3) | Na(1)-O(2) | 0.244 2(3) | Na(1)-O(2)B | 0.244 2(3) |
| Na(2)-O(11)A | 0.233 3(3) | Na(2)-O(11)C | 0.233 3(3) | Na(2)-O(6) | 0.241 6(3) |
| Na(2)-O(6)D | 0.241 6(3) | Na(2)-O(5)D | 0.242 6(3) | Na(2)-O(5) | 0.242 6(3) |
| | | | | | |
| Mn(1)-N(1)-O(3)-Mn(2) | 23.06(2) | Mn(2)-N(2)-O(5)-Mn(3) | -26.00(1) | Mn(3)-N(3)-O(7)-Mn(1) | 9.29(7) |

Symmetry codes: A: *x*−1, *y*, *z*; B: 2−*x*, 2−*y*, 1−*z*; C: 2−*x*, 1−*y*, −*z*; D: 1−*x*, 1−*y*, −*z*

**Table 3　Hydrogen bonding parameters for complex 1**

| D-H…A | d(D-H) | d(H…A) | d(D…A) | <DHA |
|---|---|---|---|---|
| O(1W)-H(1Y)…O(8) | 0.096 | 0.181 | 0.271 2(4) | 155 |
| O(1W)-H(1X)…O(2W) | 0.096 | 0.244 | 0.293 2(5) | 112 |
| O(2W)-H(2Y)…O(8) | 0.085 | 0.251 | 0.329 0(4) | 153 |
| O(2W)-H(2X)…O(14) | 0.086 | 0.230 | 0.288 9(5) | 126 |
| O(3W)-H(3X)…F(1)A | 0.096 | 0.248 | 0.326 4(4) | 139 |
| O(3W)-H(3X)…O(10)A | 0.096 | 0.246 | 0.327 1(5) | 142 |
| O(3W)-H(3Y)…O(12)D | 0.085 | 0.245 | 0.294 0(8) | 118 |
| O(4W)-H(4Y)…O(13) | 0.096 | 0.254 | 0.346 0(8) | 161 |
| O(4W)-H(4X)…F(1)A | 0.096 | 0.240 | 0.312 3(4) | 132 |
| O(4W)-H(4X)…O(10)A | 0.096 | 0.198 | 0.277 4(4) | 139 |
| O(6W)-H(6Y)…O(4)E | 0.085 | 0.250 | 0.303 2(9) | 122 |
| O(6W)-H(6X)…O(3)E | 0.085 | 0.206 | 0.274 9(9) | 138 |
| O(12)-H(12X)…O(3W)D | 0.084 | 0.249 | 0.294 0(8) | 115 |
| O(13)-H(13X)…O(9)B | 0.096 | 0.225 | 0.283 0(8) | 118 |
| O(14)-H(14X)…O(11)C | 0.085 | 0.227 | 0.269 7(4) | 111 |

Symmetry codes: A: *x*−1, *y*, *z*; B: 2−*x*, 2−*y*, 1−*z*; C: 2−*x*, 1−*y*, −*z*; D: 1−*x*, 1−*y*, −*z*; E: 1−*x*, 2−*y*, −*z*

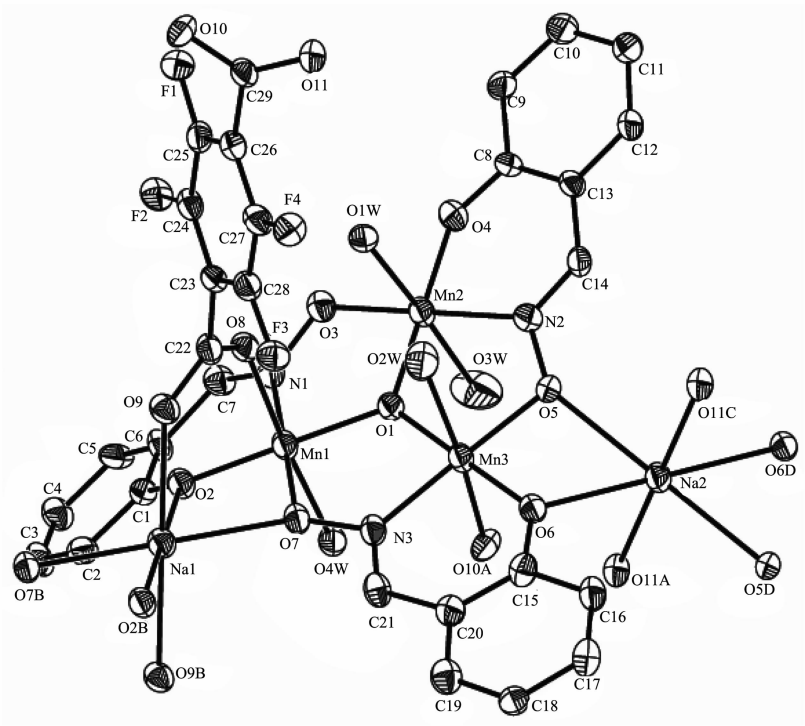
package. Absorption correction was performed using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ with SHELXTL-2000 program package [38]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position. Crystallographic data and details on refinements are summarized in Table 1. Selected bond distances and angles are listed in Table 2. Hydrogen bonds are given in Table 3.

CCDC: 934761.

## 2　Results and discussion

### 2.1　Description of the crystal structure

Single-crystal X-ray structural analysis reveals that complex **1** crystallizes in triclinic space group $P\bar{1}$. The complex **1** comprises a two-dimensional polymeric framework based on triangular-shaped $[Mn_3O]$ units linked by $tfbdc^{2-}$ and $Na^+$ cations to each other. The $tfbdc^{2-}$ ligand acts as a $\mu_2$-bridge and connects two $Mn^{III}$ ions and two $Na^+$ ions through carboxyl oxygen donors. As shown in Fig.1, the asymmetric unit contains three



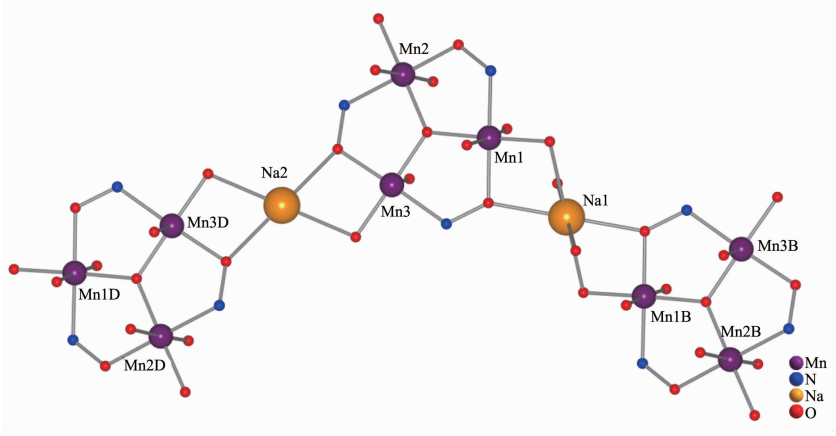

Hydrogen atoms, lattice water and ethanol molecules have been omitted for clarity; Symmetry codes: A: $x-1, y, z$; B: $2-x, 2-y, 1-z$; C: $2-x, 1-y, -z$; D: $1-x, 1-y, -z$

Fig.1 Asymmetric unit and coordination environment of Mn(Ⅲ) in **1** with ellipsoids drawn at 30% probability level

$Mn^{Ⅲ}$ ions, one $Na^+$, one $tfbdc^{2-}$ and three $sao^{2-}$ ligands together with four coordinated water molecules, half of a lattice water molecule and two ethanol molecules. The Mn(1), Mn(2) and Mn(3) centers adopt similar distorted octahedral geometry, six-coordinated by five oxygen atoms and one nitrogen atom. The four coordinate sits on equatorial plane in each $Mn^{Ⅲ}$ octahedron are occupied by two oxygen atoms and one nitrogen atom from two $sao^{2-}$ ligands as well as the center oxide O (1). However, the Jahn-Teller axises of three Mn(Ⅲ)octahedra are obviously different. The axial positions of Mn(2) are occupied by two coordinate water molecules, while Mn (1) is occupied by coordinated water O(4W) and carboxyl O(8). Similar to Mn(1), the axial positions of Mn (3) are occupied by coordinated water O(2W) and carboxyl O(10A). The equatorial Mn-O and Mn-N bond lengths around three Mn(Ⅲ) atoms are about 0.190 and 0.200 nm respectively. While the axial Mn-O distances are signicantly longer (from 0.223 4(3) to 0.229 3(3) nm, see Table 2). This phenomenon is also found in reported Mn(Ⅲ) complexes[39]. Interestingly, the Na (1) and Na(2) cations also adopt a six-coordinated octahedral geometry, bound by two phenoxo oxygen and two oximato oxygen donors from four $sao^{2-}$ ligands as well as two carboxyl oxygen atoms from two $tfbdc^{2-}$, which is similar to one complex reported by us[40]. In the complex **1**, the asymmetric unit contains two half $Na^+$ cation, Na (1) and Na (2), which is different from the reported complex. The Na-O bond distances range from 0.233 3 (3) to 0.244 2 (3) nm, which are normal as expected[41]. In addition, the Mn-N-O-Mn torsion angles are 23.06 (2)°, −26.00 (1)° and 9.29 (7)°, which are important parameters to influence magnetic couple between Mn(Ⅲ) centers. Both terminal carboxyl groups of 2, 3, 5, 6-tetrafluoroterephthalate adopt monodentate coordination mode. The tetrauorinated phenyl ring of $tfbdc^{2-}$ is inclined to the carboxylate group with the dihedral angles of 55.947° and 56.809° . This was attributed to an electrostatic repulsion between the fluorine atoms and the carboxyl oxygen atoms as well as a decrease in aromatic character of the carboxyl group due to the electron-withdrawing nature of the fluorine

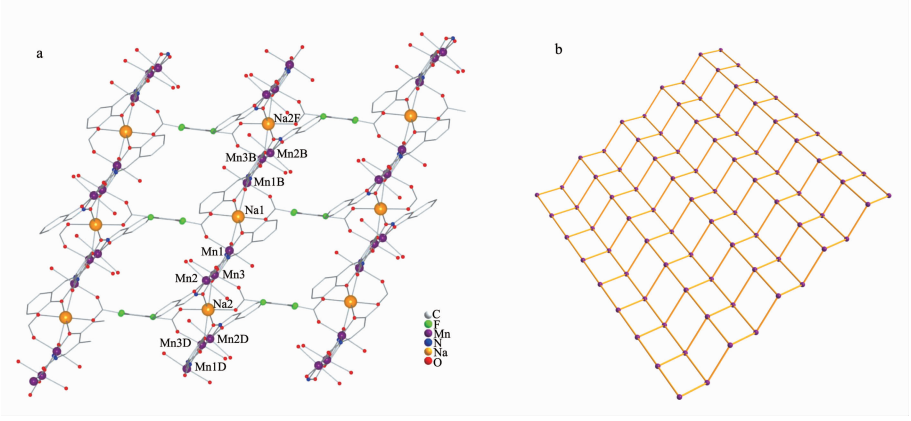
atoms[42-43].

In complex **1**, sodium cation as bridge links adjacent [$Mn_3O$] units to form a 1D zigzag chain (Fig.2). Furthermore, the neighboring 1D array is connected by $tfbdc^{2-}$ ligands to form a 2D coordination polymer (Fig. 3a). In the 2D polymeric network, the [$Mn_3O$] units as nodes construct a four-connected (4,4) topologic network (Fig.3b). In the crystal structure, several intramolecular and intermolecular hydrogen bonds are observed (Table 3), originating from the interactions between fluorine atoms, carboxyl oxygen, coordinated water and lattice water. All the H-bonding interactions assemble the 2D polymeric network of **1** into a 3D supramolecular architecture.




Symmetry codes: B: 2–$x$, 2–$y$, 1–$z$; D: 1–$x$, 1–$y$, –$z$

Fig.2　Sodium-bridging 1D zigzag chain formed by [$Mn_3O$] units




Symmetry codes: B: 2–$x$, 2–$y$, 1–$z$; D: 1–$x$, 1–$y$, –$z$; F: 1+$x$, 1+$y$, 1+$z$

Fig.3　Structure of 2D polymeric network (a), and the (4,4) topologic network in which [$Mn_3O$] units as nodes (b)

## 2.2　IR spectrum

The IR spectrum of complex **1** exhibits the characterization absorptions of salicylaldoxime, $H_2$ tfbdc and water. The broad absorption band near 3 500 $cm^{-1}$ corresponds to $\nu$(O-H) of the coordinate and lattice water molecules. The peaks at 1 597, 1 543, 1 471, 1 440 $cm^{-1}$ indicate existence of salicylaldoxime. No absorption peak around 1 690~1 730 $cm^{-1}$ indicates that the 2,3,5,6-tetrafluoroterephthalic acid is deprotonated. The strong peaks at 1622 and 1374 $cm^{-1}$ are assigned the asymmetric stretching vibration $\nu_{as}$ ($COO^-$) and the symmetric stretching vibration $\nu_s$ ($COO^-$) of $tfbdc^{2-}$. The 248 $cm^{-1}$ difference between $\nu_{as}$ ($COO^-$) and $\nu_s$ ($COO^-$) indicates that the $tfbdc^{2-}$ ligand adopts monodentate coordination[44], as proved by X-ray crystal structural analysis. In addition, the strong peak at 917 $cm^{-1}$ is the

$\delta(COO^-)$ bent vibration of tfbdc$^{2-}$[45].

### 2.3 Thermogravimetric analysis

Thermal stability of complex **1** has been investigated by TG technique and the thermogravimetric curve is shown in Fig.4. TG analysis shows that the lattice water and ethanol molecules are eliminated in the temperature range of 60~70 ℃ (Calcd. 9.94% ; Found: 10.06% ). The following weight-loss occured from 70 to 190 ℃ is attributed to the loss of four coordinated water molecules (Calcd. 7.06% ; Found: 7.07% ). Then 2,3,5,6-tetrafluoroterephthalate ligand is eliminated when heating from 190 to 270 ℃ (Calcd. 23.18%; Found: 23.23%). The decomposition of salicylaldoximes begins at 270 ℃ , without stopping until 800 ℃.

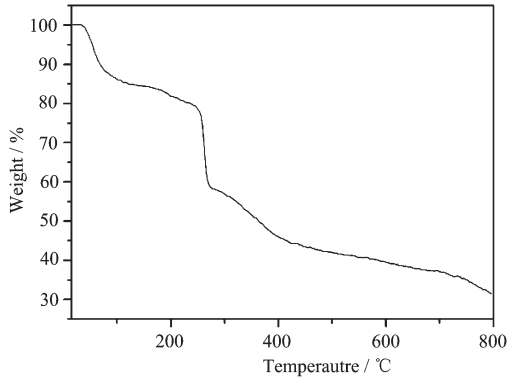



Fig.4 Thermogravimetric curve of complex **1**

### 2.4 Magnetic Properties

Magnetic susceptibility measurements of crystalline sample of **1** were carried out using a Quantum Design MPMS-XL7 SQUID magnetometer in an applied magnetic field of 2 kOe in the temperature range of 1.8~300 K. The results are shown in the form of $\chi_M T$ versus T (Fig.5). The $\chi_M T$ value of **1** is 8.76 emu·K·mol$^{-1}$ at room temperature, lower than the spin-only value of 9.0 emu·K·mol$^{-1}$ expected for three high-spin non-interacting $Mn^{Ⅲ}$ ions ($S$=2 and $g$=2). When the temperature is lowered, $\chi_M T$ smoothly decreases above 130 K. Below 130 K, $\chi_M T$ shows a sharp drop to a value of 1.79 emu·K·mol$^{-1}$ at 1.8 K, which is typical for antiferromagnetic interactions[46-47]. In order to further investigate the magnetic interaction between the $Mn^{Ⅲ}$ ions in the triangular-shaped $[Mn_3O]$ cluster, the magnetic data are simulated by the isotropic spin

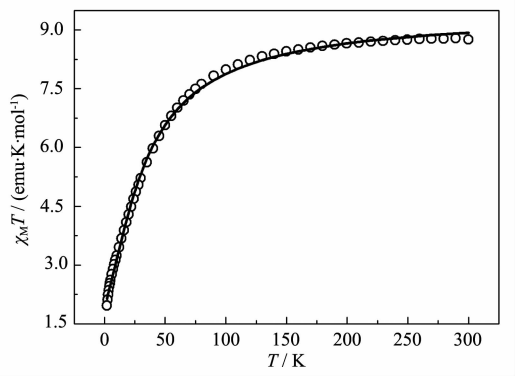



Fig.5 Temperature dependence of magnetic susceptibili ties of **1** in an applied eld of 2000 Oe

Hamiltonian $H = -2J_1 (S_{Mn1}S_{Mn2} + S_{Mn1}S_{Mn3}) - 2J_2 S_{Mn2}S_{Mn3}$, allowed us to satisfactorily simulate the data with the parameters $J_1$=−1.06 cm$^{-1}$, $J_2$=−2.81 cm$^{-1}$, $g$=2.05. The agreement factor R, defined here as $R = \sum [(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2 / \sum (\chi_M T)_{obs}^2$, is equal to $7.31 \times 10^{-3}$. Normally, interaction through the oximato bridges is antiferromagnetic couple in such complexes due to the low Mn-N-O-Mn torsion angles, which is in good agreement with the magneto-structural correlations found in oxide-centered triangle $[Mn^{Ⅲ}_3]$ cluster[48].

## References:

[1] Cheetham A K, Férey G, Loiseau T. *Angew. Chem. Int. Ed.*, **1999**,**38**:3268-3292

[2] Rao C N R, Natarajan S, Vaidhyanathan R. *Angew. Chem. Int. Ed.*, **2004**,**43**:1466-1496

[3] Kitagawa S, Kitaura R, Noro S. *Angew. Chem. Int. Ed.*, **2004**,**43**:2334-2375

[4] Pan L, Olson D H, Ciemnolonski L R, et al. *Angew. Chem. Int. Ed.*, **2006**,**45**:616-619

[5] Mueller U, Schubert M, Teich F, et al. *J. Mater. Chem.*, **2006**,**16**:626-636

[6] Rosseinsky M J. *Microporous Mesoporous Mater.*, **2004**,**73**: 15-30

[7] Maspoch D, Ruiz-Molina D, Veciana J. *J. Mater. Chem.*, **2004**,**14**:2713-2723

[8] Collins D J, Zhou H C. *J. Mater. Chem.*, **2007**,**17**:3154-3160

[9] Morris R E, Wheatley P S. *Angew. Chem. Int. Ed.*, **2008**,**47**: 4966-4981

[10]Ma S, Zhou H C. *Chem. Commun.*, **2010**,**46**:44-53

[11]Braun M E, Steffek C D, Kim J, et al. *Chem. Commun.*, **2001**:2532-2533

[12]Chen S C, Zhang Z H, Huang K L, et al. *Cryst. Growth Des*., **2008**,**8**:3437-3445

[13]Li C P, Tian Y L, Guo Y M. *Inorg. Chem. Commun.*, **2008**,**11**:1405-1408

[14]Vela J, Smith J M, Yu Y, et al. *J. Am. Chem. Soc*., **2005**, **127**:7857-7870

[15]Ohashi M, Kambara T, Hatanaka T, et al. *J. Am. Chem. Soc*., **2011**,**133**:3256-3259

[16]Chan P W Y, Yakunin A F, Edwards E A, et al. *J. Am. Chem. Soc*., **2011**,**133**:7461-7468

[17]Ge C, Zhang X, Yin J, et al. *Chin. J. Chem.*, **2010**,**28**:2083-2088

[18]Jana A, Roesky H W, Schulzke C, et al. *Organometallics*, **2010**,**29**:4837-4841

[19]Beltrán T F, Feliz M, Llusar R, et al. *Organometallics*, **2011**,**30**:290-297

[20]Lemal D M. *J. Org. Chem*., **2004**,**69**:1-11

[21]Sandford G. *Tetrahedron*, **2003**,**59**:437-454

[22]Zhang L, Wang Q, Liu Y C. *J. Phys. Chem. B*, **2007**,**111**: 4291-4295

[23]Hübner O, Glöss A, Fichtner M, et al. *J. Phys. Chem. A*, **2004**,**108**:3019-3023

[24]Yang C, Wang X, Omary M A. *J. Am. Chem. Soc*., **2007**, **129**:15454-15455

[25]Cotton F A, Lin C, Murillo C A. *J. Chem. Soc*., *Dalton Trans*., **1998**:3151-3154

[26]Chisholm M H, Wilson P J, Woodward P M. *Chem. Commun*., **2002**:566-567

[27]Rau S, Böttcher L, Schebesta S, et al. *Eur. J. Inorg. Chem.*, **2002**:2800-2809

[28]Kitaura R, Iwahori F, Matsuda R, et al. *Inorg. Chem*., **2004**,**43**:6522-6524

[29]Ito M, Onaka S. *Inorg. Chim. Acta*, **2004**,**357**:1039-1046

[30]Chun H, Dybtsev D N, Kim H, et al. *Chem. Eur. J.*, **2005**,**11**:3521-3529

[31]Chen B, Yang Y, Zapata F, et al. *Inorg. Chem.*, **2006**,**45**: 8882-8886

[32]Yoon J H, Choi S B, Oh Y J, et al. *Catal. Today*, **2007**,**120**: 324-329

[33]ZHU En-Jing(朱恩静), LIU Qi(刘琦), CHEN Qun(陈群), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2008**, **24**(9):1428-1433

[34]YU Li-Li(于丽丽), LIU Qi(刘琦), XI Hai-Tao(席海涛), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2010**,**26**(4): 621-626

[35]Hulvey Z, Falcao E H L, Eckert J, et al. *J. Mater. Chem*., **2009**,**19**:4307-4309

[36]Hulvey Z, Ayala E, Furman J D, et al. *Cryst. Growth Des*., **2009**,**9**:4759-4765

[37]Hulvey Z, Ayala E, Cheetham A K. *Z. Anorg. Allg. Chem.*, **2009**,**635**:1753-1757

[38]Bruker 2000, *SMART* (Version 5.0), *SAINT-plus* (Version 6), *SHELXTL* (Version 6.1)

[39]Miyasaka H, Takayama K, Saitoh A, et al. *Chem. Eur. J*., **2010**,**16**:3656-3662

[40]Geng J P, Wang Z X, He X, et al. *Inorg. Chem. Commun.*, **2011**,**14**:997-1000

[41]Biswas B, Khanra S, Weyhermüller T, et al. *Chem. Commun*., **2007**:1059-1061

[42]Hulvey Z, Furman J D, Turner S A, et al. *Cryst. Growth Des*., **2010**,**10**:2041-2043

[43]Wang Z, Kravtsov V C, Walsh R B, et al. *Cryst. Growth Des*., **2007**,**7**:1154-1162

[44]Deacon G B, Phillips R J. *Coord. Chem. Rev*., **1980**,**33**:227-250

[45]Wu Y, Yu L, Cheng M, et al. *Chin. J. Chem*. **2012**,**30**:1045-1051

[46]Wang X Y, Sevov S C. *Chem. Mater*., **2007**,**19**:3763-3766

[47]Coronado E, Galán-Mascarós J R, Marti-Gastaldo C, et al. *Inorg. Chem.*, **2008**,**47**:6829-6839

[48]Milios C J, Inglis R, Vinslava A, et al. *J. Am. Chem. Soc*., **2007**,**129**:12505-12511