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一个锰的二维配位聚合物的合成及其性质

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摘要:本文用 2-咪唑乙酸 (Hiaa),2,2′-联吡啶, 氢氧化钠和六水合高氯酸锰在水和乙醇中反应合成了 1 个二维配位化合物 $\{[Mn(iaa)(2,2'\text{-bipyridine})(H_2O)](ClO_4)\}_n$ (**1**)。单晶结构表明化合物 **1** 是 1 个新颖的二维双核锰配位聚合物,锰离子的配位构型为扭曲的八面体。每一个锰离子与 3 个配体配位,而每个配体与 3 个锰离子桥连。磁性研究表明 **1** 中 Mn(Ⅱ)离子间存在弱的反铁磁偶合作用。

关键词:锰配合物;配位聚合物;磁性质;晶体结构
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Synthesis and Characterization of a Two-dimensional Manganese Coordination Polymer

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Abstract: Slow evaporation of the reaction mixture of ligand 2-(1H-imidazol-1-yl)acetic acid (Hiaa), 2,2′-bipyridine, NaOH, and $Mn(ClO_4)_2\cdot 6H_2O$ in water/ethanol affords a complex $\{[Mn(iaa)(2,2'\text{-bipyridine})(H_2O)](ClO_4)\}_n$ (**1**). Single crystal structure determination reveals that **1** is a novel two-dimensional dinuclear manganese coordination polymer. The local coordination environment around manganese ions is a distorted octahedron. Every manganese ion coordinates with three ligands, while each ligand acts as a bridge linking three Mn ions. Magnetic studies suggest a weak antiferromagnetic coupling interaction between two Mn(Ⅱ) ions. CCDC: 668269.

Key words: manganese complexes; coordination polymers; magnetic properties; crystal structures

0 Introduction

Metal-organic frameworks have attracted widespread interest because of their fascinating structures[1] and various potential applications, such as catalysis[2], magnetism[3~5], nonlinear optics[6,7] and gas storage[8]. In particular, manganese complexes have been widely studied in recent years to mimick the model compounds in some biosystems[9], such as the oxygen-evolving complex (OEC) of photosystem Ⅱ (PSⅡ). In addition, they are rich source of single-molecule magnets (SMMs)[10~12], and they could be also studied as model systems for the water-oxidizing complex (WOC)[13,14]. Dinuclear manganese complexes bridged by carboxylate group have been considered as Mn-catalase[15], models of pseudo-catalase and the active site in the ribonucleotide reductase[16], as well as useful precursors to high nuclearity clusters[17]. According to magnetic materials, fascinations of polynuclear manganese complexes with large spin multiplicities and uniaxial magnetic anisotropies are widely shown because of their unique solid-sate properties such as superparamagnetism and quantum spin tunneling[18]. Ligand Hiaa[19,20] is a good candinate to construct novel coordination polymer with possible fas-

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cinating properties, because it has both carboxylate group and nitrogen atoms as possible donors to bridge metal ions. Herein, we present the synthesis, crystal structure, TGA and magnetic property of a novel dinuclear two-dimensional manganese complex {[Mn(iaa)(2,2′-bipyridine)(H_2O)](ClO_4)}$_n$ (**1**).

1 Experimental

1.1 Reagent and apparatus

Chemicals were obtained from commercial resources and used without further purification. The magnetic susceptibility was measured using a Quantum Design MPMS-XL7 SQUID magnetometer at temperature ranging from 1.8 to 300 K and using an applied magnetic field of 2 000 Oe. Elemental analysis for C, H, and N was performed on a Perkin-Elmer 240C analyzer. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449C unit at a heating rate of 10 ℃·min^{-1} under nitrogen.

1.2 Synthesis of {[Mn(iaa)(2,2′-bipyridine)(H_2O)](ClO_4)}$_n$ (1)

The ligand 2-(1H-imidazol-1-yl)acetic acid (Hiaa) (12.61 mg, 0.1 mmol) in water (2 mL) was mixed with 2 mL of NaOH solution (2 mol·L^{-1}) to get a solution of A. 2,2′-bipyridine (15.62 mg, 0.1 mmol) and $Mn(ClO_4)_2\cdot 6H_2O$ (18.10 mg, 0.05 mmol) were dissolved in 2 mL of ethanol (solution B). Solution A and solution B were mixed together. After filtering, the filtrate was allowed to stand at room temperature for several days till light yellow crystals of **1** were formed. Yield: 31.7 mg (70%) on the basis of the ligand. Anal. Found (Calc. for $C_{15}H_{15}ClMnN_4O_7$)(%): C 39.85(39.71), H 3.41(3.33), N 12.21(12.35).

1.3 Crystal structure determination

A single crystal of **1** was mounted with epoxy on a Pyrex fiber affixed to a brass pin and transferred to a Siemens SMART CCD area detector diffractometer equipped with Mo $K\alpha$ radiation (λ=0.071 073 nm) using ω-scan mode. The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0°, 88° and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Crystal decay was monitored by repeating thirty initial frames at the end of data collection and analyzing the duplicate reflections and was found to be negligible. The unit cell parameters were determined using SMART[21] and refined using SAINT[22]. The three sets of data collected were reduced using SAINT. Empirical absorption correction was performed using SADABS[23]. The structure was solved with direct methods and refined using the program SHELXTL[24]. All the non-hydorgen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be almost featureless. Crystallographic data and bond lengths and angles are summarized in Tables 1 and 2.

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Table 1　Crystal data and structure refinement for complex 1

Formula	$C_{15}H_{15}ClMnN_4O_7$	D_c / (g·cm^{-3})	1.64
Formula weight	453.7	Absorption coefficient / mm	0.911
Temperature / K	293(2)	F(000)	924
Crystal system	Monoclinic	θ range / (°)	1.6~26.0
Space group	$P2_1/c$	Limiting indices	$-15 \leqslant h \leqslant 15, -17 \leqslant k \leqslant 17, -12 \leqslant l \leqslant 12$
a / nm	1.235 9(2)	Reflections collected	8 288
b / nm	1.418 8(3)	Independent reflections (R_{int})	3 545 (0.037)
c / nm	1.050 11(12)	Reflections observed [$I>2\sigma(I)$]	2 682
β / (°)	93.476 (13)	Data / restraints / parameters	3 545 / 0 / 253
Z	4	Goodness-of-fit on F^2	1.07
V / nm^3	1.838 0(5)	Final R indices [$I>2\sigma(I)$]	R_1=0.055 0, wR_2=0.118 2

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

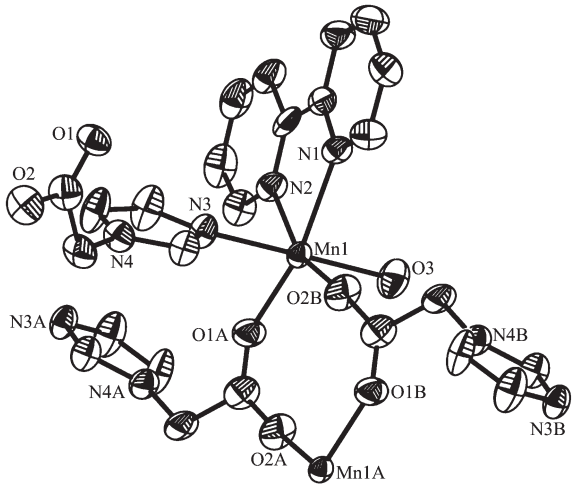
Mn1-O1#1	0.212 6(3)	Mn1-O2#2	0.210 0(3)	Mn1-N3	0.222 0(3)
Mn1-O3	0.223 9(3)	Mn1-N1	0.228 8(3)	Mn1-N2	0.230 0(3)
O1#1-Mn1-O2#2	109.05(11)	O1#1-Mn1-N3	93.43(12)	O2#2-Mn1-N1	91.69(11)
O1#1-Mn1-O3	90.27(11)	O2#2-Mn1-O3	89.22(12)	N3-Mn1-O3	177.15(12)
O1#1-Mn1-N2	87.81(11)	O2#2-Mn1-N2	162.79(11)	N1-Mn1-N2	71.56(11)
O3-Mn1-N1	90.98(12)	O1#1-Mn1-N1	159.24(11)	O2#2-Mn1-N3	93.43(12)
N1-Mn1-N3	90.02(12)	O3-Mn1-N2	87.21(12)	N2-Mn1-N3	90.57(12)

Symmetry transformations used to generate equivalent atoms: #1: 2−*x*, −1/2+*y*, 1/2−*z*; #2: *x*, 3/2−*y*, −1/2+*z*.

2 Results and discussion

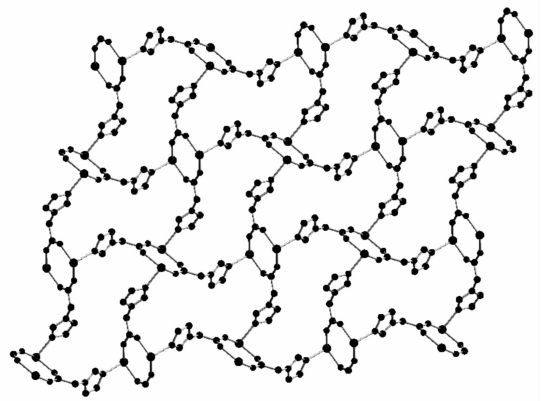
2.1 Synthesis and crystal structure

The polymeric structure of compound **1** is determined by X-ray diffraction single-crystal structure analysis. In **1**, the local coordination around manganese ion can be best described as a distorted octahedron surrounded by three oxygen atoms and three nitrogen atoms (as shown in Fig.1). Two oxygen atoms are from two bidentate coordinated carboxylic acid groups and the third oxygen atom is from the water molecule. One nitrogen atom is from the ligand iaa and the other two nitrogen atoms are from the 2,2′-bipyridine molecule. Each iaa ligand links three manganese atoms, and every six-coordinated manganese ion coordinates with three different ligands, resulting in the formation of a 2D framework, as shown in Fig.2. The distance between the dinuclear Mn⋯Mn is 0.461 3(2) nm. Among all the Mn-O bonds, the distance of Mn1-O3 0.223 9(3) nm is the longest among the bond distances. The other two Mn-O distances are 0.210 0(3) and 0.212 6(3) nm, while the Mn-N distances range from 0.222 0(3) to 0.230 0(3) nm. The adjacent layers in the network are stacked in an AA sequence and the ClO_4^- apprents between the two layers as depicted in Fig.3.



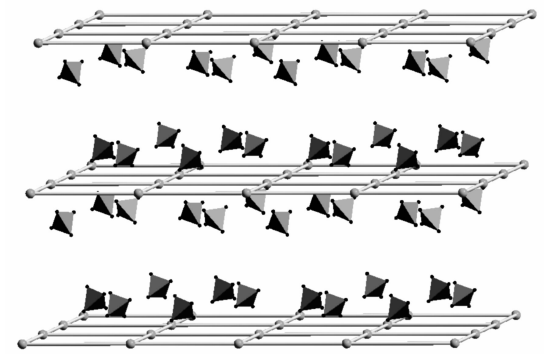
Thermal ellipsoids are drawn at the 50% probability levels; H atoms are omitted for clarity

Fig.1 An asymmetric structure unit of **1**



2,2′-bipyridine, perchlorate and water molecules and hydrogen atoms are omitted for clarity

Fig.2 Perspective view of complex **1** showing the 2D framework



Bigger balls represent for the dinuclear Mn units, while the grey tetrahedrons represent ClO_4^- anions and the straight lines represent ligand

Fig.3 Simple frameworks of compound **1** show the AA stacking

2.2 Magnetic property

Magnetic susceptibility measurements of **1** at 1.8~300 K under a magnetic field of 2 kOe reveals a gradual decrease in $\chi_M T$ from 4.28 emu·K·mol^{-1} at 300 K to 4.05 emu·K·mol^{-1} at 75 K, followed by a rapid decrease to 0.40 emu·K·mol^{-1} at 1.8 K (Fig.4). The value of χ_M first increases from 0.014 emu·mol^{-1} at 300 K to a maximum value 0.25 emu·mol^{-1} at 5 K, then decreases rapidly to 0.22 emu·mol^{-1} at 1.8 K. The $\chi_M T$ value of 4.28 emu·K·mol^{-1} at 300 K is slightly lower than the spin-only value of 4.38 emu·K·mol^{-1} expected for one isolated high-spin Mn^{II} (S=5/2) with g=2 in the absence of magnetic interaction. Best-fit of the experimental data based on dinuclear Mn(Ⅱ) model with molecular field approximation (Equation **1**) gives a g value of 1.998, J and zJ' values of −0.64 and −0.051 cm^{-1} with R=5.74×10^{-6} ($R=\sum[(\chi_m T)_{obs}^2-(\chi_m T)_{calc}^2]/\sum[(\chi_m T)_{obs}^2]$), respectively, indicating a weak antiferromagnetic coupling interaction between Mn(Ⅱ) ions.

$$
\begin{aligned}
&H=-2J_1S_1S_2\\
&\chi_{di}=[Ng^2\beta^2S(S+1)/(3kT)]\times(A/B)\\
&\chi_m=\chi_{di}/\{1-[2zJ'/(Ng^2\beta^2)]\chi_{di}\} \qquad (1)\\
&A=330\exp[12.5J/(kT)]+180\exp[2.5J/(kT)]+\\
&\quad 84\exp[-5.5J/(kT)]+30\exp[-11.5J/(kT)]+\\
&\quad 6\exp[-15.5J/(kT)]\\
&B=11\exp[12.5J/(kT)]+9\exp[2.5J/(kT)]+\\
&\quad 7\exp[-5.5J/(kT)]+5\exp[-11.5J/(kT)]+\\
&\quad 3\exp[-15.5J/(kT)]+\exp[-17.5J/(kT)]
\end{aligned}
$$

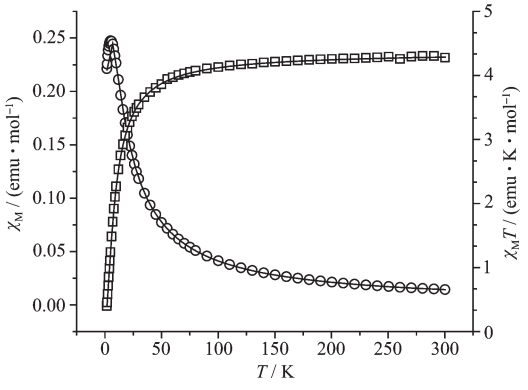


Fig.4　Plot of χ_M and $\chi_M T$ vs T for **1**

2.3 Thermalgravimetric analysis

Compound **1** is insoluble in common solvents. To investigate the thermal stability of **1**, thermalgravimetric analysis (TGA) of the crystalline samples was carried out. The TGA curve of **1** (Fig.5) shows no weight loss until 163 ℃ indicating that compound **1** can remain stable below this temperature. There is one discrete weight loss (about 4.4%) occurring between 177.8~242.6 ℃, corresponding to the removal of coordinated water molecular (about 3.97 % of weight loss). When temperature is raised up to about 278 ℃, the weight drops rapidly with increasing temperature, indicating the decomposition of compound **1**.

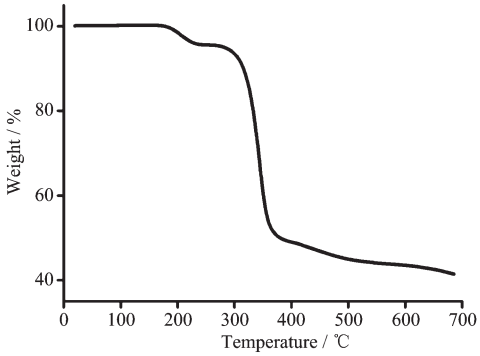


Fig.5　TGA curve of **1**

3 Conclusion

In this paper, a novel two-dimensional binuclear manganese coordination polymer is synthesized at room temperature. Magetic studies display weak antiferromagnetic interactions in compound **1**.

References:

[1] Ockwig N W, Delgado-Friedrichs O, O′Keeffe M, et al. *Acc. Chem. Res.*, **2005**,**38**:176~182

[2] Hu A, Ngo H L, Lin W. *J. Am. Chem. Soc.*, **2003**,**125**:11490~11491

[3] Tang Y Z, Wang X S, Zhou T, et al. *Cryst. Growth Des.*, **2006**, **6**:11~13

[4] Zheng Y Z, Tong M L, Zhang W X, et al. *Angew. Chem. Int. Ed.*, **2006**,**45**:6310~6314

[5] Chen C, Huang D, Zhang X, et al. *Inorg. Chem.*, **2003**,**42**: 3540~3548

[6] Evans O R, Lin W. *Acc. Chem. Res.*, **2002**,**35**:511~522

[7] Evans O R, Lin W. *Chem. Mater.*, **2001**,**13**:2705~2712

[8] Ma S, Wang X S, Manis E S, et al. *Inorg. Chem.*, **2007**,**46**: 3432~3434

[9] Yachandra V K, Sauer K, Klein M P. *Chem. Rev.*, **1996**,**96**: 2927~2950

[10]Sessoli R, Gatteschi D, Caneschi A, et al. *Nature*, **1993**,**365**: 141~143

[11]Hill S, Edwards R S, Aliaga-Alcalde N, et al. *Science*, **2003**, **302**:1015~1018

[12]Chakov N E, Zakharov L N, Rheingold A L, et al. *Inorg. Chem.*, **2005**,**44**:4555 ~4567

[13]Anderlund M F, Hoegblom J, Shi W, et al. *Eur. J. Inorg. Chem.*, **2006**:5033~5047

[14]Poulsen A K, Rompel A, McKenzie C J. *Angew. Chem. Int. Ed.*, **2005**,**44**:6916 ~ 6919

[15]Wieghardt K. *Angew. Chem., Int. Ed.*, **1989**,**28**:1153~1172

[16]Chen C, Zhu H, Huang D, et al. *Inorg. Chim. Acta*, **2001**,**320**: 159~166

[17]Glowiak T, Kozlowski H, Erre L S, et al. *Inorg. Chim. Acta*, **1995**,**236**:149~154

[18]Dismukes G C. *Chem. Rev.*, **1996**,**96**:2909~2932

[19]Wang Y T, Tang G M, Wu Y, et al. *J. Mol. Struct.*, **2007**,**831**: 61~68

[20]Wang Y T, Tang G M, Qin D W. *Aust. J. Chem.*, **2006**,**59**:647 ~652

[21]*SMART Software Reference Manual, Siemens Analytical X-ray Systems*, Inc., Madison, Wisconsin, USA, **1996**.

[22]*SAINT V*4 *Software Reference Manual, Siemens Analytical X-ray Systems*, Inc., Madison, Wisconsin, USA, **1996**.

[23]Sheldrick G M. *SADABS*, University of Göttingen, Germany **1996**.

[24]Sheldrick G M. *SHELXTL V*5.1 *Software Reference Manual, Bruker AXS*, Inc., Madison, Wisconsin, USA, **1997**.