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以邻苯二甲酸根及邻菲咯啉衍生物构筑的锰配位聚合物的合成、晶体结构及磁性

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摘要:采用水热法合成了一个配位聚合物 $\{[Mn(Pht)(Medpq)(H_2O)]\cdot 0.25nH_2O\}_n$(Pht=phthalate,Medpq=2-methyldipyrido[3,2-f:2′,3′-h]quinoxaline) **1**,并对其进行了元素分析、红外光谱、热重表征、磁性表征和 X 射线单晶衍射测定。配位聚合物 **1** 属于单斜晶系,空间群为 $P2_1/c$。晶胞参数为:a=1.598 0(3) nm,b=2.092 5(4) nm,c=0.659 67(13) nm,β=93.06(3)°,V=2.202 7(8) nm^3。在晶体中,锰原子与 4 个氧原子和 2 个氮原子形成六配位的畸变的八面体构型。整个晶体由 Pht-Mn-Medpq 单元组成一维双链结构。

关键词:配位聚合物;邻苯二甲酸;晶体结构;水热合成
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Synthesis, Crystal Structure and Magnetic Susceptibility Measurements of a Manganese Coordination Polymer with Phthalate and Phenanthroline Derivatives

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Abstract: A coordination polymer $\{[Mn(Pht)(Medpq)(H_2O)]\cdot 0.25nH_2O\}_n$ (Pht=phthalate, Medpq=2-methyldipyrido[3,2-f:2′,3′-h]quinoxaline) **1** has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectrum, TG, magnetic susceptibility measurements and single-crystal X-ray diffraction. Polymer **1** crystallizes in the monoclinic system, space group $P2_1/c$, with a=1.598 0(3), b=2.092 5(4), c=0.659 67(13) nm, β=93.06(3)°, V=2.202 7(8) nm^3. In the crystal structure, the manganese atom is six-coordinated with four oxygen atoms and two nitrogen atoms, showing a slightly distorted octahedral geometry. Furthermore, it exhibits a one-dimensional dual chains structure with Pht-Mn-Medpq as building units. CCDC: 867320.

Key words: coordination polymer; phthalate; crystal structure; hydrothermal synthesis

In the recent years, the design and synthesis of metal organic frameworks (MOFs) have attracted much more attention not only for their fascinating networks but also for the fact that they may be designed with specific functionalities[1-2]. The crystal engineering of supramolecular self-assembly based on noncovalent bonding interactions (hydrogen bonding, metal coordination, hydrophobic forces, van der waals forces, π-π interactions and electrostatic effects) of molecules is of great interest[3-5].

There has been considerable interest in the design and synthesis of manganese(Ⅱ) coordination polymers

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with carboxylic acid ligands owing to their potential applications, in the field of nanomagnetic materials, some large high-spin manganese carboxylate clusters display magnetic properties previously only associated with nano-sized particles of magnetic metal oxides, that is, they can be magnetised and as such have been termed single-molecule magnets (SMMs)[6]. Selection of the appropriate multidentate ligand to link metal ions is a powerful way for the building of polyfunctional coordination polymers. As a multidentate ligand, phthalic acid and its dianion have been used in synthetic systems, not only because they can act as short bridges via one carboxylic group or long bridges via the benzene ring, leading to abundant varieties of multi-dimensional coordination polymers with various kinds of topology, but also phthalic acid, as an example of a benzenedicarboxylic acid, has a rigid aromatic unit as a spacer, it can give rise to very special systems that can have interesting electronic and magnetic interactions between the metal ions in the network through possible conjugative interactions[7]. On the other hand, many coordination polymers with *N*-donor ligands, such as 1,10-phenanthroline and its derivatives, were found to display diverse structure types and broad spectrum uses[8-9]. 2-Methyldipyrido [3,2-f:2′,3′-h] quinoxaline (Medpq) as a derivative of 1,10-phenanthroline and possessing an extended aromatic system, is a planar rigid bidentate chelating reagent which can not only act as a terminal ligand but also potentially provide supramolecular interactions such as aromatic stacking to construct intriguing structures. For the past several years, our group has worked on the synthesis of Medpq ligand complexes[10-12]. However, the investigation for Medpq ligands is not enough, especially Medpq ligand and manganese(Ⅱ) constructed polymers have not been reported. Based on the above reasons, we designed and synthesized of the polymer **1**, namely {[Mn(Pht)(Medpq)(H_2O)]·0.25nH_2O}$_n$, and the research results indicated that polymer **1** is a kind of magnetic material.

1 Experimental

1.1 Materials

The Medpq ligand was synthesized according to the literature method[10]. Other chemicals from commercial sources were of reagent grade and used without further purification.

1.2 Instruments and measurements

Elemental analysis was carried out with a Perkin-Elmer 240C analyzer; TG measurements were performed on a NETZSCH STA 449C analyzer. The Infrared (IR) spectrum was recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a Nicolet FTIR 170SX spectrometer.

1.3 Synthesis and measurement

Polymer **1** was prepared from a mixture of $Mn(Ac)_2$·$2H_2O$ (0.10 g), phthalic acid (0.08 g), Medpq (0.12 g) and H_2O (16 mL) obtained by stirring at room temperature. When the pH value of the mixture was adjusted with NaOH to about 6.5, the cloudy solution was put into a 30 mL Teflon-lined autoclave and heated to 165 ℃ for six days. After cooling to room temperature at a rate of 5 ℃·h^{-1}, yellow block crystals of **1** were collected by filtration and washed with distilled water in 52% yield (based on Mn). Anal. Calcd.(%) for $C_{23}H_{16.5}MnN_4O_{5.25}$(%): C, 56.56; H, 3.38; N, 11.47. Found(%): C, 56.55; H, 3.40; N, 11.49.

1.4 Crystal structure determination and physical measurements

A single crystal with dimensions of 0.20 mm×0.18 mm×0.18 mm was mounted on a Riigaku Saturn 724+ CCD X-ray diffractometer with a graphite-monochromatic Mo $K\alpha$ radiation (λ=0.071 073 nm) by using an φ-ω scan mode (5.10°≤2θ≤50.00°) at 293(2) K. A total of 9796 reflections were collected and 3 827 were independent with R_{int}=0.071 3, of which 2 603 were observed with $I>2\sigma(I)$. The correction for Lp factors was applied. The structure was solved by direct methods with SHELXS-97 program[13] and refined by SHELXL 97[14] using full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned geometrically (C-H 0.093 nm for CH or 0.096 nm for CH_3) and refined as riding mode, with U_{iso}(H) values of 1.2 U_{eq}(C). The final R=0.058 9 and wR=0.158 5 for 2 603 observed reflections with $I>2\sigma(I)$; and R=0.074 8 and wR=0.186 3 for all data. S=1.072, $(\Delta\rho)_{max}$=897 e·nm^{-3}, $(\Delta\rho)_{min}$=−476 e·nm^{-3}

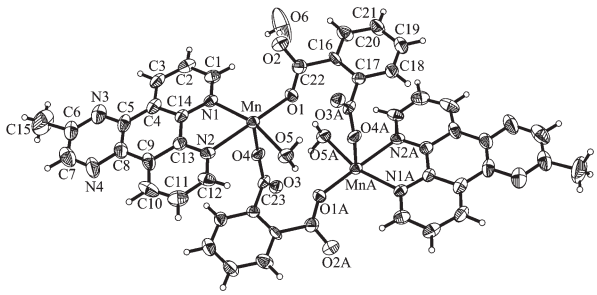
and $(\Delta/\sigma)_{max}$=0.117.

CCDC: 867320.

2 Results and discussion

2.1 Description of crystal structures

Single-crystal X-ray diffraction analysis reveals that polymer $\{[Mn(Pht)(Medpq)(H_2O)]\cdot 0.25nH_2O\}_n$ crystallizes in $P2_1/c$ space group and consists of a one-dimensional dual chains structure. The structure motif consists of two Mn(Ⅱ) ions, two phthalates, two coordination of water molecules, one free water molecule and two Medpq ligands. As shown in Fig.1, the Mn(Ⅱ) atoms are bridged by two different Phthalates to form a 14-membered ring. The Mn(Ⅱ) ion is hexa-coordinated with six atoms (N(1), N(2), O(1), O(3A), O(4), O(5)) from one Medpq ligand, three different phthalates and one coordination water molecule, assuming a slightly distorted octahedral geometry. The Mn dimers are linked through the Mn-O(3) and Mn-O(4) bonds showing a one-dimensional dual chains structure. The bond lengths are 0.225 8(5) and 0.227 9(7) nm for Mn-N, 0.210 6(5)~0.219 0(5) nm for Mn-$O_{carboxylate}$, and 0.218 1(5) nm for Mn-O_{water}, respectively, comparable to those of 0.224 9(19) and 0.226 68(19) nm for Mn-N, 0.211 55(16)~0.219 43(16) nm for Mn-$O_{carboxylate}$, and 0.216 16(19) nm for Mn-O_{water} in the complex of [Mn(DPPZ)(PZDC)(H_2O)] (DPPZ=dipyrido[3,2-a:2′,3′-c]phenazine)[15]. The normal Mn-N distance is 0.226 9(8) nm and Mn-O distance is 0.215 4(17) nm, these distances are similar to the normal Mn-N and Mn-O distance of 0.224 and 0.216 nm[16]. The N(O)-Mn-O(N) angles range from 73.7(2)° to 176.37(17)°. The selected important bond parameters are given in Table 1. The interesting feature of polymer **1** is that each phthalates links two symmetry related manganese atoms into an infinite one-dimensional dual chain patterns with Mn-Mn distance of about 0.500 2 nm. Hydrogen bonding interactions are usually important in the synthesis of supramolecular architectures[17]. There are persistent strong O–H⋯O hydrogen bonding interactions between crystal molecules, coordinated water molecules, free water molecules and phthalates (Table 2), which play an important role in stabilizing the network structure. At the same time, aromatic ring of Medpq ligand and symmetry of the two adjacent equivalent of aromatic ring (symmetry codes: x, 1/2−y, −1/2 +z; 1 −x, 1 −y, 2 −z) have π-π interactions with distance between cg(2) → cg(2^{i}) ring centroids of 0.349 4(5) nm, cg(4) → cg(4^{i}) is 0.332 6(6) nm and cg(3) → cg(5^{ii}) of 0.388 5(6) nm (defined rings Cg(2): N(1) → C(9) → C(10) → C(11) → C(12) → C(13), Cg(3): N(2) → C(14) → C(18) → C(17) → C(16) → C(15), Cg(4): N(3) → C(20) → C(19) → N(4) → C(21) → C(22) and Cg(5): C(2) → C(3) → C(4) → C(5) → C(6) → C(7)) (Fig.2). Through hydrogen bonding interactions and π-π interactions between the adjacent aromatic ring of



Symmetry code: A: 1−x, 1−y, 2−z

Fig.1 ORTEP drawing of **1** showing the structure motif of polymer **1** with ellipsoids at 30% probability

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

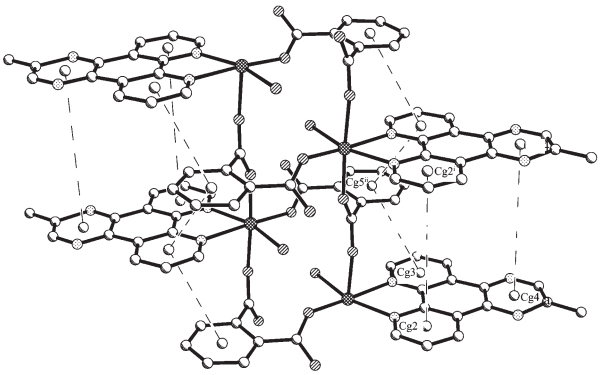
Mn(1)-N(1)	0.225 8(5)	Mn(1)-N(2)	0.227 9(7)	Mn(1)-O(1)	0.210 6(5)
Mn(1)-O(3A)	0.213 7(5)	Mn(1)-O(4)	0.219 0(5)	Mn(1)-O(5)	0.218 1(5)
O(1)-Mn(1)-O(3A)	94.6(2)	O(1)-Mn(1)-O(4)	86.7(2)	O(1)-Mn(1)-O(5)	93.7(2)
O(3A)-Mn(1)-O(4)	176.37(17)	O(3A)-Mn(1)-O(5)	95.33(19)	O(4)-Mn(1)-O(5)	87.95(18)
N(1)-Mn(1)-N(2)	73.7(2)	O(1)-Mn(1)-N(1)	101.0(2)	O(3A)-Mn(1)-N(1)	90.32(18)
O(4)-Mn(1)-N(1)	86.11(18)	O(5)-Mn(1)-N(1)	163.7(2)	O(1)-Mn(1)-N(2)	171.9(2)
O(3A)-Mn(1)-N(2)	91.6(2)	O(4)-Mn(1)-N(2)	86.8(2)	O(5)-Mn(1)-N(2)	90.9(2)

Symmetry code: A: 1−x, 1−y, 2−z.

Table 2　Hydrogen bond lengths and angles for 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D–H···A / (°)
O6–H6B···O2^{ii}	0.085	0.221	0.276(2)	122.5
O6–H6B···O6^{i}	0.085	0.257	0.332 4(6)	148.9
O6–H6C···O2^{i}	0.085	0.265	0.334(2)	139.0

Symmetry codes: ^{i} *x*, *y*, *z*−1; ^{ii} *x*, 1/2−*y*, *z*−1/2.



Symmetry codes: ^{i} *x*, 1/2−*y*, 1/2+*z*; ^{ii} −*x*, 1−*y*, 2−*z*

Fig.2　View of one-dimensional dual chains structure in **1** and π-π interactions

Medpq and Pht ligands, polymer **1** turned into two-dimensional layer structure.

2.2　Thermal analysis

The stability of polymer **1** was investigated by thermogravimetric analysis (Fig.3). The first weight loss of 8.81% for **1** are in the range from 112.6 to 154.8 ℃ corresponding to the removal of H_2O (calcd. 5.49%). Upon further heating, an obvious weight loss (53.61%) occurs in the temperature range of 154.8 ~ 494.3 ℃, corresponding to the release of Medpq ligand (calcd. 50.30%). Obvious weight loss (22.93%) occurs in the temperature range of 494.3 ~786.9 ℃, corresponds to the release of Phthalate (calcd. 29.81%). After 786.9 ℃ no weight loss is observed, indicating the complete decomposition of **1**. The residual weight 14.65% (calcd. 14.40%) corresponds to MnO.

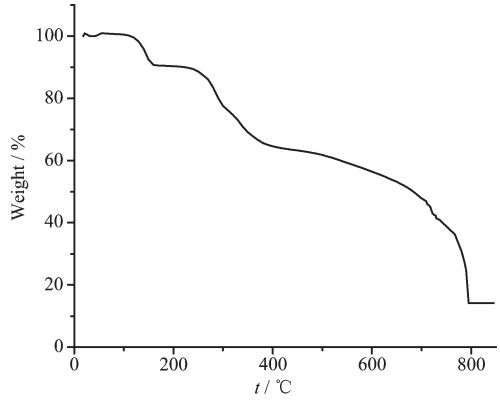


Fig.3　TG of the polymer **1**

2.3　Magnetic susceptibility measurements

Magnetic measurements for the polymer {[Mn(Pht)(Medpq)(H_2O)]·0.25*n*H_2O}$_n$ were performed on a quantum design SQUID magnetometer. Variable temperature magnetic susceptibility data were collected for the the polymer **1**. The $\chi_m T$ and $1/\chi_m$ versus *T* plots are shown in Fig.4 and Fig.5. The parameters *C* and θ values were obtained from the slope and intercept of the Curie-Weiss plot ($1/\chi_m$ versus *T*) over the entire temperature range, i.e. *C*=8.75 cm^3·K·mol^{-1}, θ=−7.24 K. The negative value of the Weiss constant θ indicates that there are antiferromagnetic exchange interactions

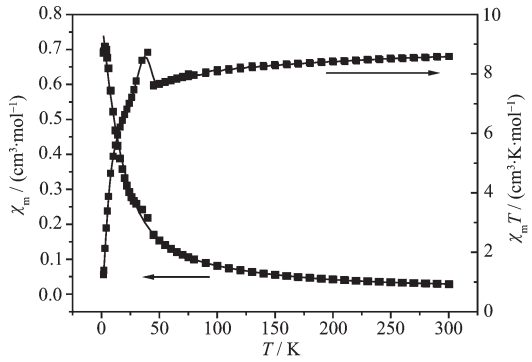


Fig.4　Temperature dependence of magnetic susceptibilities in the form of χ_m and $\chi_m T$ vs *T* for the polymer **l**

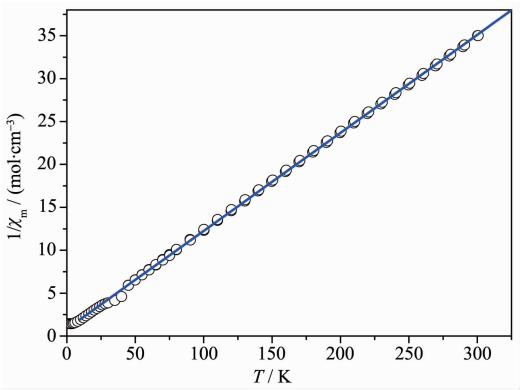


Fig.5　$1/\chi_m$ ~*T* plot for the polymer **l**

between Mn ions. This results were similar to the results reported for other manganese complex[18].

We have tried to fit the data based on the spin Hamiltonian:

$$\hat{H}=-2J\hat{S}_a\hat{S}_b$$

The quantitative information regarding g and J coupling were gotten by using the nonlinear regression. The best fit in the temperature range led to g=1.96, J=−0.53 cm^{-1}, and $R=3.5\times10^{-3}$. The negative sign of J verifies the antiferromagnetic property.

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References:

[1] Wang X L, Bi Y F, Lin H Y, et al. *J. Organomet Chem.*, **2007**, **629**:4353-4360

[2] Liu C B, Li X Y, Che G B, et al. *Chin. J. Struc. Chem.*, **2009**, **28**:11-14

[3] Sun Y G, Rong S T, Yu W, et al. *Z. Anorg. Allg. Chem.*, **2009**, **15**:2585-2591

[4] Lehn J M, Translated by SHEN Xing-Hai(沈兴海). *Supramolecular Chemistry-Concepts and Perspectives*(超分子化学–概念和展望). Beijing: Peking University Press, **2002**.

[5] Brian M, Michael J Z. *Chem. Rev.*, **2001**,**101**:1629

[6] Price D J, Batten S R, Berry K J, et al. *Polyhedron*, **2003**,**22**: 165-176

[7] Lu X M, Li P Z, Wang X T, et al. *Polyhedron*, **2008**,**27**:2402-2408

[8] Janiak C. *J. Chem. Soc.*, **2003**,**14**:2781-2804

[9] James S L. *Chem. Soc. Rev.*, **2003**,**32**:276-288

[10]Huang Y J, Ni L. *J. Inorg. Organomet. Polym.*, **2011**,**21**:97-102

[11]HUANG Yan-Ju(黄艳菊), NI Liang(倪良), WANG Lei(王蕾), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2011**, **27**:157-161

[12]HUANG Yan-Ju(黄艳菊), CUI Yun-Cheng(崔运成), DU Gang(杜刚). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2009**,**25**:1882-1884

[13]Sheldrick G M. *SHELXS* 97, *Program for the Solution of Crystal Structure*, University of Göttingen, **1997**.

[14]Sheldrick G M. *SHELXS* 97, *Program for the Refinement of Crystal Structure*, University of Göttingen, **1997**.

[15]Xu Z L, Li X Y, Che G B, et al. *Chin. J. Struc. Chem.*, **2008**, **27**:593-597

[16]Allen F H, Kennard O, Watson D G, et al. *J. Chem. Soc. Perkin Trans.*, **1987**,**2**:S1-19

[17]Krische M J, Lehn J M. *Struct. Bonding*, **2000**,**96**:3-29

[18]WANG Tian-Wei(王天维), LI Yi-Zhi(李一志). *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2009**,**25**:652-655