研究简报

配位聚合物$[Mn(2,4,6\text{-}TMBA)_2(H_2O)_3]_n\cdot 2nH_2O$的水热合成和晶体结构

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关键词:2,4,6-三甲基苯甲酸;锰;配位聚合物
中图分类号:O614.7+11 **文献标识码**:A **文章编号**:1001-4861(2007)01-0145-04

Hydrothermal Synthesis and Crystal Structure of Coordination Polymer $[Mn(2,4,6\text{-}TMBA)_2(H_2O)_3]_n\cdot 2nH_2O$

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Abstract: The title compound, $[Mn(2,4,6\text{-}TMBA)_2(H_2O)_3]_n\cdot 2nH_2O$ (**1**), where 2,4,6-TMBA=2,4,6-trimethylbenzoic acid, was synthesized and its crystal structure was determined by X-ray diffraction analysis. The crystal is of monoclinic, space group *C*2/*c* with *a*=2.929 9(6) nm, *b*=1.036 4(2) nm, *c*=8.222 04(17) nm, *V*=2.494 7(9) nm^3, *Z*=4, *M*=471.40, D_c=1.255 g·cm^{-3}, μ=0.571 mm^{-1}, *F*(000)=996, R_{int}=0.029 4, *R*=0.037 6 and *wR*=0.094 9. The Mn atoms are octahedrally coordinated by two O atoms of two ligands and four O atoms of water. The carboxyl group coordinates to Mn(Ⅱ) in the mode of monodentate, while the O atoms of water molecules coordinates in bridging mode. The complex shows a one-dimensional chain structure bridged by water molecules. CCDC: 297750.

Key words: 2,4,6-trimethylbenzoic acid; manganese; coordination polymer

In recent years, coordination polymeric frameworks have attracted great attention not only due to their potential applications in the areas of magnetism, nonlinear optics, electronics, catalysis, and molecular recognition and sorption but also to their intriguing structure topologies [1~5]. The coordination polymers can be specially designed by careful selection of the metal ions with definite coordination geometry, the structure of the connecting ligands, the nature of counteranions, and the reaction conditions. Moreover sterically hindered ligands are commonly used to control the coordination environment of metal ions, and hence their properties, through favouring lower coordination numbers and by preventing the unwanted formation of polynuclear species that often arise through ligand bridging[6]. With sterically hindered carboxylate ligands the challenge is not primarily to limit coordination numbers, but rather to inhibit the strong natural

收稿日期:2006-06-13。收修改稿日期:2006-10-31。
湖南省基础研究项目(No.03JZY3036)和衡阳师范学院科学基金青年项目资助(No.2006A15)。
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tendency of the carboxylate group to bridge between two or more metal ions which results in the undesired formation of polymeric or highly polynuclear species[7].

In order to continue our studies on the manganese complexes[8~10], we have chosen 2,4,6-trimethylbenzoic acid as ligand and investigated its reaction with $Mn(ClO_4)_2 \cdot 6H_2O$. We report herein the synthesis and X-ray crystal structure of the novel manganese(Ⅱ) coordination polymer, $[Mn(2,4,6\text{-}TMBA)_2(H_2O)_3]_n \cdot 2nH_2O$ (**1**). The complex has a one-dimensional chain structure bridged by water molecules.

1 Experimental

1.1 Materials and instruments

All the regents and solvents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on Shimadzu FTIR-8700 spectrophotometer using KBr discs. TG curves was recorded on a Perkin-Elmer Pyris Diamond thermoanalyser in flow of N_2, in the temperature range from 20 ℃ to 800 ℃, with a heating rate of 10 ℃·min^{-1}.

1.2 Synthesis of the title compound

The compound was hydrothermal synthesized under autogenous pressure. A mixture of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol), 2,4,6-trimethylbenzoic acid (0.165 g, 1 mmol), NaOH (0.041 g, 1 mmol), and H_2O (10 mL, 0.55mmol) was heated in a 25 mL capacity Teflon-lined reaction vessel at 160 ℃ for 4 days, the reaction mixture was cooled to room temperature over a period of 40 h. The product was collected by filtration, washed with H_2O and air-dried, Yields based on Mn: 36%. Molecular formula is $C_{20}H_{32}MnO_9$. Elemental analysis (%) C, 50.91; H, 6.78; O, 30.54. Found: C, 50.77; H, 6.71; O, 30.58. Main IR bands (cm^{-1}): 3 631m, 3408m, 3 246w, 1 612s, 1 529s, 1 446m, 1 402m, 1 182w, 1 114w, 856vw, 817m, 611w, 571w.

1.3 Crystal structure determination

A yellow crystal with dimensions of 0.26 mm × 0.24 mm × 0.20 mm was selected for the measurement. The diffraction data were collected at 294 K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ= 0.071 073 nm). A total of 6 869 reflections were collected in the range of $2.08° \leqslant \theta \leqslant 26.42°$ by using an ω-scan mode, of which 2 554 were unique and used in the succeeding structure calculations. The structure was solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. All calculations were performed with SHELXTL-97 package. Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 297750.

Table 1 Crystal data and structure refinement parameters for the title complex

Empirical formula	$C_{20}H_{32}MnO_9$	Z	4
Formula weight	471.40	Absorption coefficient / mm^{-1}	0.571
Temperature / K	294(2)	F(000)	996
Crystal system	Monoclinic	Crystal size / mm	0.26 × 0.24 × 0.20
Space group	$C2/c$	θ / (°)	2.08 to 26.42
a / nm	2.929 9(6)	Limiting indices	$-34 \leqslant h \leqslant 36, -12 \leqslant k \leqslant 12, -6 \leqslant l \leqslant 10$
b / nm	1.036 4(2)	Reflections collected / unique	6 869 (R_{int}=0.029 4)
c / nm	8.220 4(17)	Data / restraints / parameters	2 554 / 7 / 141
β / (°)	92.038(4)	Goodness of fit on F^2	1.027
V / nm^3	2.494 7(9)	final R indices [$I>2\sigma(I)$]	R_1=0.037 6, wR_2=0.094 9
D_c / (g·cm^{-3})	1.255	Largest diff. peak and hole / (e·nm^{-3})	295 and −236

2 Results and discussion

2.1 Crystal structure of the title complex

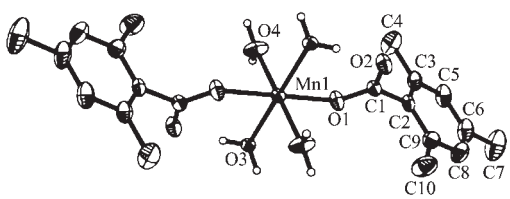
The molecular structure of the title complex is shown in Fig.1, and the 1D chain structure in Fig.2. The selected bond lengths are given in Table 2.

The crystal structure of **1** consists of an infinite 1D chain, and shows that, the Mn(Ⅱ) ions are bridged

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

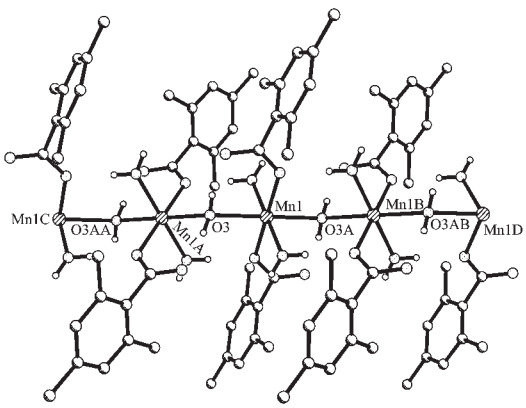
Mn(1)-O(4)#1	0.214 4(18)	Mn(1)-O(3)#1	0.227 7(19)	Mn(1)-O(1)#1	0.215 1(15)
Mn(1)-O(4)	0.214 4(18)	Mn(1)-O(3)	0.227 7(19)	Mn(1)-O(1)	0.215 1(15)
O(4)#1-Mn(1)-O(4)	180.00(7)	O(4)#1-Mn(1)-O(1)	89.77(8)	O(1)#1-Mn(1)-O(3)#1	90.28(5)
O(4)#1-Mn(1)-O(3)#1	86.64(6)	O(4)-Mn(1)-O(1)	90.23(8)	O(1)-Mn(1)-O(3)	90.28(5)
O(4)-Mn(1)-O(3)#1	93.36(6)	O(4)#1-Mn(1)-O(1)#1	90.23(8)	O(1)#1-Mn(1)-O(3)	89.72(5)
O(4)#1-Mn(1)-O(3)	93.36(6)	O(4)-Mn(1)-O(1)#1	89.77(8)	O(3)#1-Mn(1)-O(3)	180.0
O(4)-Mn(1)-O(3)	86.64(6)	O(1)-Mn(1)-O(1)#1	180.0		
O(3)#1-Mn(1)-O(3)	180.0	O(1)-Mn(1)-O(3)#1	89.72(5)		

#1: $-x+2, -y, -z$.



Free water molecules are omitted for clarity

Fig.1　Molecular structure of the title complex



Code: A $-x+2,-y,-z$; B $-x+2, y, -y+1/2$

Fig.2　1D chain structure for the complex

by μ_2-OH_2 molecules forming one-dimensional linear chains (Fig.2). Each Mn1 is a slightly distorted octahedron with six O atoms, which come from two terminal monodentate coordinated C_9H_2COO units (O1, O1A), two terminal monodentate coordinated H_2O molecules (O4, O4A), and two bridging μ_2-OH_2 molecules (O3, O3A). We can presume that the equatorial plane is composed of O1, O1A, O4, and O4A, which form a perfect plane. The O1-Mn1-O1A and O4-Mn1-O4A bond angles are both 180°, and the bond distances of Mn1-O1 and Mn1-O4 are 0.215 1(15) and 0.214 4(18) nm, respectively. The O3 and O3A atoms occupy the axial position. Because it takes part in bridging, the Mn1-O3 [0.227 7(9) nm] distance is longer than those of Mn1-O1 and Mn1-O4 in the equatorial position, and the axial angle O3-Mn1-O3A is 180°. Compared with some reported di-Mn(Ⅱ) complexes containing (μ_2-aqua)(μ_2-carboxylato) bridges, the Mn-O(μ_2-OH_2) distance in (I) is a slightly longer than the corresponding Mn-O distances of $[Mn_2(\mu_2\text{-}OH_2)(\mu_2\text{-}OAc)_2(Im)_4(OAc)_2]$ (Im=imidazole) [0.224 6(2) nm] and $[Mn_2(\mu_2\text{-}OH_2)(\mu_2\text{-}OAc)_2(Bzim)_4(OAc)_2]$ (Bzim=benzimidazole) [0.222 7(2) nm][11], but it is significantly shorter than the $\{[Mn(OOCH_4C_6Fc)_2(\mu_2\text{-}OH_2)(H_2O)_2](H_2O)\}_n$ [0.231 1(3) nm][6]. Except for the angles mentioned above, all other angles around Mn1 are in the range of 86.64 (6)°~93.36 (6) °, which are very close to right angles. All of the Mn atoms are connected by the bridging H_2O molecules forming one-dimensional chain with the 2,4,6-trimethyl-benzoic acid ligands hanging on the two sides of these chains (Fig.2).

An interesting feature of this structure is the presence of intrachain hydrogen bonds which are observed between the water O-H groups and carboxylate oxygen atoms, as given in Table 3. These hydrogen

Table 3　Parameters of hydrogen bonds for the complex

D···H···A	*d*(D-H) / nm	*d*(H-O) / nm	*d*(D-O) / nm	∠D-H-A / (°)
O(3)···H(3A)···O(2)[a]	0.085 1	0.178 6	0.262 9	169.88
O(4)···H(4D)···O(5)[b]	0.086 5	0.187 2	0.273 3	173.08
O(4)···H(4E)···O(1)[c]	0.084 6	0.185 8	0.270 4	178.83
O(5)···H(5A)···O(2)	0.085 7	0.197 8	0.278 3	155.89

[a] $-x, -y, -z+1$; [b] $-x, y, -z+3/2$; [c] $-x, y, -z+1/2$.

bonds thus appear to stabilize the asymmetry molecular disposition around the Mn center.

2.2 Spectra characteristics

The infrared spectra of the title complex has been recorded and some important assignments are shown above. One feature of the IR data is the separation between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, which have often been used to diagnose the coordination modes in the carboxylate ligands. The separation for monodentate carboxylate groups is >200 cm^{-1}, whereas it is <200 cm^{-1} in bidentate groups[12]. The separation (Δ) between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is 210 cm^{-1} for **1**, indicating monodentate coordinating modes for the coordinated carboxylate groups. These IR results are coincident with the crystallographic structural analyses. In the IR spectra, the band at 3 408 cm^{-1}, due to the ν(O-H) absorptions of water molecules.

The results of TG-DTG illustrate that the compound decomposition takes place in two steps. The TGA curve of **1** reveals two distinct weight loss regions centered around 272 ℃ and 425 ℃. The first weight loss of 20.45% occurred at 25~272 ℃, corresponding to the removal of five water molecules per subunits (19.09% calculated). The loss of two 2,4,6-trimethylbenzoic acid molecules occurred in the temperature range of 272~425 ℃. Beyond this temperature, decomposition of the network was apparent.

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