

一维链状锰配位聚合物[Mn(3,5-Me₂PhCO₂)₂(phen)]_n 的合成与晶体结构

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Synthesis and Crystal Structure of a 1D Manganese Coordination Polymer Constructed by 3,5-dimethylbenzoic Acid with 1,10-phenanthroline

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Abstract: A manganese coordination polymer [Mn(3,5-Me₂PhCO₂)₂(phen)]_n (phen=1,10-phenanthroline) has been synthesized by hydrothermal methods. The crystal structure was determined by single-crystal X-ray diffraction. The crystal is of triclinic, space group $P\bar{1}$ with $a=0.770\ 3(4)$ nm, $b=1.145\ 2(6)$ nm, $c=1.537\ 0(9)$ nm, $\alpha=78.182(9)^\circ$, $\beta=77.170(9)^\circ$, $\gamma=89.784(9)^\circ$, $V=1.292\ 8(12)$ nm³, $Z=2$, $M_r=533.47$, $D_c=1.370$ g·cm⁻³, $\mu=0.549$ mm⁻¹, $F(000)=554$, $R_{int}=0.043\ 4$, $R=0.060\ 8$, $wR=0.148\ 4$. In the crystal the manganese atom is six-coordinated by two nitrogen atoms from phen and four oxygen atoms from four 3,5-dimethylbenzoate molecules, completing an octahedral geometry. And the title complex forms one-dimensional chain structure through bridging 3,5-dimethylbenzoate molecules. CCDC: 642920.

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

0 Introduction

Manganese complexes containing carboxylato ligands attract considerable interest due to the efficient Mn catalase mimics^[1,2]. The designing of coordination polymers is highly influenced by richness in structural chemistry and potential applications in catalysis^[3-8], for example, some highly several factors such as the metal

coordination preference, the structural characteristics of the polydentate organic ligand, the metal-ligand ratio, the solvent system and the counterion. Among these factors, the chemical structure of organic ligand plays an extremely important role in dictating polymer topologie.

In order to continue our studies on the manganese complexes^[9-12], we have chosen 3,5-dimethyl

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benzoic acid as ligand and investigated its reaction with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 1,10-phenanthroline. We report herein the synthesis and X-ray crystal structure of the novel manganese (II) coordination polymer, $[\text{Mn}(\text{3,5-Me}_2\text{PhCO}_2)_2(\text{phen})]_n$ (**1**). The complex has a one-dimensional chain structure bridged by 3,5-dimethylbenzoate molecules.

1 Experimental

1.1 Materials and instruments

All the reagents 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 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 °C to 800 °C, with a heating rate of 10 °C·min⁻¹.

1.2 Synthesis of the title compound

A mixture of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.112 g, 0.5 mmol), phen (0.098 g, 0.5 mmol), 3,5-dimethylbenzoic acid (0.118 g, 1 mmol), and H_2O (10 mL, 0.55 mmol) was heated in a 25 mL capacity Teflon-lined reaction vessel at 150 °C for 5 d, 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, Yield: 67% (based on phen). Anal. Calcd. for $\text{C}_{30}\text{H}_{26}\text{MnN}_2\text{O}_4$ (%): C, 67.30; H, 4.89; N, 5.49; found (%): C, 67.48; H, 4.87; N, 5.25; IR (KBr, cm⁻¹): 3 416(vs), 3 152(vs), 1 603(s), 1 582(s), 1 473(s), 1 444(s), 1 424(s), 1 224(m), 1 163(w), 1 072(w), 823(m), 632(m).

1.3 Crystal structure determination

A yellow crystal with dimensions of 0.22 mm × 0.20 mm × 0.16 mm was selected for the measurement. The diffraction data were collected at 294 K on a Bruker Smart 1 000 CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$).

A total of 6 450 reflections were collected in the range of $1.39^\circ \leq \theta \leq 25.01^\circ$ with $R_{\text{int}} = 0.043\,4$, of which 4 520 reflections with $I > 2\sigma(I)$ were used in the structure determination and refinement. The final $R = 0.060\,8$ and $wR = 0.148\,4$ ($w = 1/[\sigma^2(F_o^2)(0.101\,8P)^2 + 0.000\,0P]$, where $P = (F_o^2 + 2F_c^2)/3$). 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.

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Table 1 Crystal Data and Structure Parameters for the Title Complex

Empirical formula	$\text{C}_{30}\text{H}_{26}\text{MnN}_2\text{O}_4$	Absorption coefficient / mm ⁻¹	0.549
Formula weight	533.47	$F(000)$	554
Temperature / K	294(2)	Crystal size / mm	0.22×0.20×0.16
Crystal system	Triclinic	$\theta / (^\circ)$	1.39 to 25.01
Space group	$P\bar{1}$	Limiting indices	$-8 \leq h \leq 9, -13 \leq k \leq 8, -18 \leq l \leq 18$
a / nm	0.770 3(4)	Reflections collected/unique	6450 [$R_{\text{int}} = 0.043\,4$]
b / nm	1.145 2(6)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.537 0(9)	Data/restraints/parameters	4520/0/338
V / nm^3	1.292 8(12)	Goodness of fit on F^2	1.017
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.370	Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.060\,8, wR_2 = 0.148\,4$
Z	2	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	2108 and -573

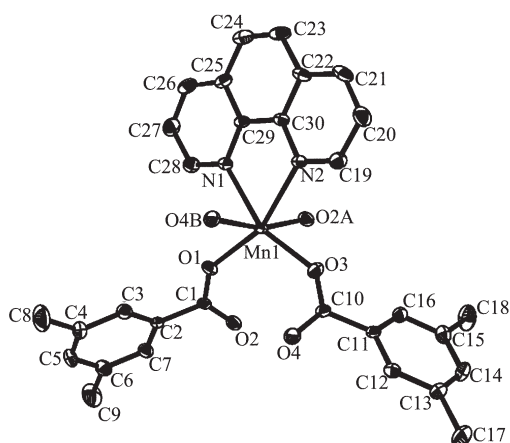
2 Results and discussion

2.1 Crystal structure of the title complex

The molecular structure of the title complex is shown in Fig.1, the 1D chain structure are located in

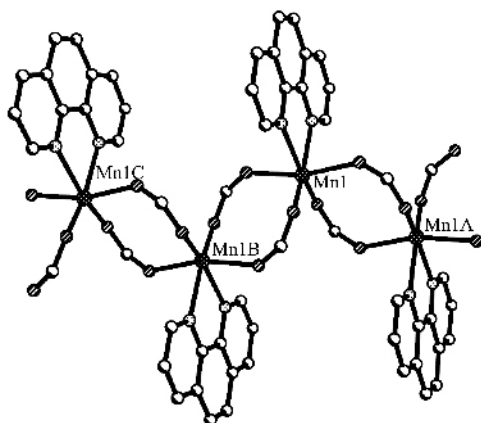
Fig.2, respectively. The selected bond lengths are given in Table 2.

X-ray analyses revealed that the structure of the complex consists of infinite 1D coordination chains $[\text{Mn}(\text{3,5-Me}_2\text{PhCO}_2)_2(\text{phen})]_n$. As shown in Fig.1, the



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

Fig.1 Molecular Structure of the title complex



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

Fig.2 1D infinite chain supported by carboxylate

title complex consists of one Mn(II) cation, two 3,5-dimethylbenzoate anions and two coordinated nitrogen atoms of 1,10-phenanthroline molecule, and the Mn(II) ion occupies the special position with inversion center. The deprotonated 3,5-dimethylbenzoate monoanion is bonded to the Mn(II) ion with a bidentate bridging fashion. Each Mn(II) atom possesses a distorted octahedral geometry with O(2)#2 and ON(4)#1 at the apical positions. The sum of bond angles O(3)-Mn(1)-O(1) ($112.22(12)^\circ$), O(1)-Mn(1)-N(1) ($88.80(12)^\circ$), O(3)-Mn(1)-N(2) ($88.25(12)^\circ$) and N(1)-Mn(1)-N(2) ($71.45(11)^\circ$) is 360.72° , showing the O(1), O(3), N(1) and N(2) atoms are coplanar. These data indicate that the Mn(1) atom is in a slightly distorted octahedral coordination configuration., defined by four carboxyl oxygen atoms from different 3,5-Me₂PhCO₂⁻ ligands and one coordinated phen molecules, the Mn-N distances ranging from 0.231 1(3) to 0.231 3(3) nm and the N-Mn-N angle being $71.45(11)^\circ$; the Mn-N distances are shorter than those found in [Mn₂(phen)₂(ta)₄]_n^[13]. The mean Mn-O(carboxyl) bond distance is 0.214 6(3) nm, which is slightly longer than that in [Mn(*p*-CPOA)₂(H₂O)₄]_n (0.2129(7) nm) and [Mn(phen){3,5-(NO₂)₂sal²⁻}]_n^[14-15] (0.2060(2) nm), but a little shorter than that in [Mn(phen)(tsgluO)]_n (2.170(2) nm)^[10]. These differences are probably attributed to the different coordination fashions of the ligands in the three complexes.

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$)

Mn(1)-O(4)#1	0.2193(3)	Mn(1)-O(1)	0.2097(3)	Mn(1)-N(1)	0.2311(3)
Mn(1)-O(2)#2	0.2200(3)	Mn(1)-O(3)	0.2094(3)	Mn(1)-N(2)	0.2313(3)
O(3)-Mn(1)-O(1)	112.22(12)	O(4)#1-Mn(1)-O(2)#2	165.97(10)	O(3)-Mn(1)-N(2)	88.25(12)
O(3)-Mn(1)-O(4)#1	101.33(12)	O(3)-Mn(1)-N(1)	158.37(12)	O(1)-Mn(1)-N(2)	158.85(11)
O(1)-Mn(1)-O(4)#1	86.70(12)	O(1)-Mn(1)-N(1)	88.80(12)	O(4)#1-Mn(1)-N(2)	83.95(11)
O(3)-Mn(1)-O(2)#2	86.75(12)	O(4)#1-Mn(1)-N(1)	84.29(10)	O(2)#2-Mn(1)-N(2)	84.87(11)
O(1)-Mn(1)-O(2)#2	100.97(12)	O(2)#2-Mn(1)-N(1)	84.14(11)	N(1)-Mn(1)-N(2)	71.45(11)

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

Two adjacent octahedral units are bridged together by two pairs of bi-monodentate carboxyl groups of different 3,5-Me₂PhCO₂⁻ ligands to form an eight membered ring with chair-typed configuration. Adjacent binuclear Mn₂O₁₂ motifs are further linked by carboxyl groups, giving rise to a one-dimensional

chain structure along the a-axis.(See Fig.2) The MnMn separation within the polymer is 0.466 8 nm. It is noted that the bond angle of O(2)-C(1)-O(1) ($125.9(4)^\circ$) is slightly larger than that of O(2)-C(1)-C(2) ($118.3(3)^\circ$).

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 $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, which have often been used to diagnose the coordination modes in the carboxylate ligands. The separation for monodentate carboxylate groups is $>200\text{ cm}^{-1}$, whereas it is $<200\text{ cm}^{-1}$ in bidentate groups^[16]. The separation (Δ) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ is 130 cm^{-1} for **1**, indicating bidentate coordinating modes for the coordinated carboxylate groups. These IR results are coincident with the crystallographic structural analyses. In the IR spectra, the band at $1\,582.34\text{ cm}^{-1}$ and $1\,424.66\text{ cm}^{-1}$ due to the absorptions of phen 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 277 and $428\text{ }^{\circ}\text{C}$. The first weight loss of 55.45% occurred at $277\text{ }^{\circ}\text{C}$, corresponding to the removal of one phen molecule per subunit (54.73% calculated). The loss of two 3,5-dimethylbenzoic acid molecules occurred in the temperature range of $277\sim428\text{ }^{\circ}\text{C}$. Beyond this temperature, decomposition of the chainwork complex was apparent. The final residual weight of 13.42% (calcd. 13.30%) corresponds to MnO .

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