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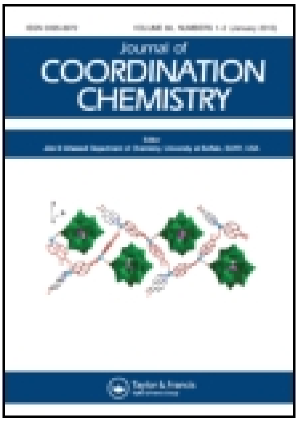

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Synthesis, crystal structure, and spectral analysis of a 1-D Mn(II) coordination polymer

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Synthesis, crystal structure, and spectral analysis of a 1-D Mn(II) coordination polymer

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A manganese(II) coordination polymer $[Mn(TMB)_2 \cdot H_2O]_n$ (**1**) (HTMB = 3,4,5-trimethoxybenzoic acid) has been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction, elemental analysis, powder X-ray diffraction analysis, spectroscopic (IR, solid state UV-Vis), and thermal methods. The crystal belongs to orthorhombic system, space group $P2_12_12_1$, with cell parameters $a = 7.3001(8)$, $b = 11.4146(13)$, $c = 27.053(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2254.3(4)$ Å^3, $Z = 4$. In **1**, TMB in two different coordination modes bridges six-coordinate manganese(II) centers forming a 1-D infinite chain coordination framework. The spectral and thermal properties of the complexes have also been studied.

Keywords: Manganese complex; Crystal structure; Spectral analysis

1. Introduction

The chemistry of transition metal carboxylates attracts attention because of their unusual structures and as functional models. Different type, shape, and conformation of carboxylate ligands can produce many unique properties, such as luminescence [1], magnetism [2], gas storage [3], etc. Coordination modes of carboxylates induce a variety of complexes with different dimensional structures, ranging from zero- to 3-D [4].

In this article, we report a manganese(II) complex with 3,4,5-trimethoxybenzoic acid as ligand and obtained an infinite 1-D chain coordination framework $[Mn(TMB)_2 \cdot H_2O]_n$.

Two different coordination modes of carboxylates in **1** are the same with the trinuclear manganese(II) complex which was synthesized with 3,4,5-trimethoxybenzoic acid and Phen (Phen = 1,10-phenanthroline) in our previous research [5]. Similarly, other Mn(II) carboxylate complexes, such as $[Mn(OOCCMe_3)_2(EtOH)]_n$, have the same coordination modes [6].

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2. Experimental

2.1. *Materials and methods*

$MnCl_2 \cdot 4H_2O$ and NaOH were obtained from Tian Jin Dong Li Tianjin University Chemical Corporation. HTMB and phenothiazine were from Shang Hai Aladdin Chemical Corporation. All reagents were reagent grade and obtained commercially without purification. Solvents were dried according to standard methods and freshly distilled prior to use. Elemental analyses (for carbon and hydrogen) were performed on a VarioElcube elemental analyzer. Infrared (IR) spectra were collected from 4000 to 400 cm^{-1} on a Nicolet 6700 spectrometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were recorded on a X'Pert PRO diffractometer with monochromated Cu-Kα ($\lambda = 1.5406$ Å) radiation at room temperature. UV-Vis spectrum was measured by UV-2550 instrument (Shimadzu Corporation, Japan). The thermal decomposition of **1** was measured on a HCT-1 thermal analyzer (Henven Corporation, China) with a heating rate of 10°C min^{-1} from 20°C to 800°C under air.

2.2. *Synthesis of 1*

Compound **1** was synthesized by mixing a solution of $MnCl_2 \cdot 4H_2O$ (0.196 g, 1 mmol), HTMB (0.423 g, 2 mmol), and phenothiazine (0.197 g, 1 mmol) in an H_2O/EtOH (2 : 1, *v* : *v*, 15 mL) mixture with stirring at room temperature; the pH value of the mixed solvent was adjusted to about 6.5 by adding sodium hydroxide. Then the mixture was placed in a 23 mL Teflon-lined autoclave and heated at 150°C for 24 h. The autoclave was cooled over a period of 13 h at a rate of 10°C h^{-1}. Purple block crystals were obtained by filtration, washed with water, and dried in air. Crystals were selected under a microscope for X-ray diffraction studies and subsequent spectroscopic measurements. Yield: 0.18 g (36.7% based on Mn). Anal. Calcd for $C_{20}H_{24}MnO_{11}$ (%): C, 48.28; H, 5.27. Found: C, 48.02; H, 4.67. IR spectrum (KBr pellet, cm^{-1}): 3480 (νOH), 3410 (νOH), 1558 (ν_{as}COO), 1399 (ν_sCOO).

2.3. *X-ray crystallography*

The diffraction data of crystals were collected at 298(2) K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex CCD diffractometer. The structure was solved by direct methods [7] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXS-97 [8] and SHELXL-97 [9], respectively. Non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The crystallographic data for the structure and experimental refinement parameters are listed in table 1. Selected bond lengths and angles are given in table 2. Hydrogen bonding data are listed in table 3.

3. Results and discussion

3.1. *Crystal structure of 1*

The molecular structure of **1**, presented in figure 1, exhibits the manganese(II) as six coordinate with a distorted octahedral $[MnO_6]$ *via* five oxygen atoms from four TMB

Table 1. The crystallographic data for **1**.

Empirical formula	$C_{20}H_{24}MnO_{11}$
Formula weight (g mol^{-1})	495.33
Temperature (K)	298(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å, °)	
a	7.3001(8)
b	11.4146(13)
c	27.053(3)
α	90
β	90
γ	90
Volume ($Å^3$), Z	2254.3(4), 4
Calculated density (g cm^{-3})	1.563
Absorption coefficient (mm^{-1})	0.154
$F(000)$	752
Crystal size (mm^3)	0.23 × 0.10 × 0.10
θ range for data collection (°)	1.81 − 26.00
Limiting indices	$-9 \leq h \leq 9$; $-12 \leq k \leq 15$; $-32 \leq l \leq 36$
Reflections collected	10,511
Independent reflection	5988 [$R(\text{int}) = 0.0466$]
Number of reflections with $I > 2\sigma(I)$	3857
Max. and min. transmission	0.9848 and 0.9699
Data/restraints/parameters	5988/0/457
Goodness-of-fit on F^2	0.956
R-factor [$I > 2\sigma(I)$]	$R_1 = 0.0562$, $wR_2 = 0.0964$
R-factor (all data)	$R_1 = 0.0913$, $wR_2 = 0.1291$
Largest difference peak and hole (e $Å^{-3}$)	0.250 and −0.246

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Mn1–O6	2.093(2)	O6–Mn1–O2#2	94.13(9)
Mn1–O7#1	2.119(2)	O7#1–Mn1–O2#2	93.35(10)
Mn1–O11	2.158(3)	O11–Mn1–O2#2	153.63(11)
Mn1–O1	2.166(2)	O1–Mn1–O2#2	99.78(9)
Mn1–O2#2	2.259(2)	O6–Mn1–O1#2	84.39(9)
Mn1–O1#2	2.384(2)	O7#1–Mn1–O1#2	95.05(9)
O1–Mn1#1	2.384(2)	O11–Mn1–O1#2	97.54(11)
O2–Mn1#1	2.259(2)	O1–Mn1–O1#2	154.36(4)
O6–Mn1–O7#1	170.57(11)	C7–O1–Mn1	129.2(2)
O7#1–Mn1–O11	86.69(10)	Mn1–O1–Mn1#1	112.84(9)
O6–Mn1–O1	89.26(10)	C7–O2–Mn1#1	94.7(2)
O7#1–Mn1–O1	95.12(10)	C20–O6–Mn1	141.8(2)
O11–Mn1–O1	106.49(11)		

Symmetry transformations used to generate equivalent atoms: #1: $-0.5 + x$, $0.5 - y$, $2 - z$; #2: $0.5 + x$, $0.5 - y$, $2 - z$.

ligands and another from water. Phenothiazine was not involved in **1**. However, without it, the reaction of $MnCl_2 \cdot 4H_2O$ and HTMB in the same conditions did not afford **1**; the role of phenothiazine is not understood at present. In the crystal structure, the coordination modes of carboxylates are different (figure 2); one is bidentate and the other is chelating-bridging. Similar coordination modes have been reported in $\{(H_3O)_2[Mn_4(4\text{-Haba})_2(4\text{-aba})_6(SCN)_4(H_2O)_2]\}$ [10]. The bond lengths of Mn–O are 2.093(2)–2.384(2) Å, falling in the normal range of related Mn complexes [11, 12].

Table 3. Hydrogen bond distances (Å) and angles (°).

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(D–H···A)
O11–H11A–O10#1	0.817(17)	2.16(3)	2.898(4)	151.(4)
O11–H11A–O9#1	0.817(17)	2.54(3)	3.177(4)	135.(4)
O11–H11B–O2#2	0.814(18)	1.98(2)	2.762(4)	163.(4)

Symmetry transformations used to generate equivalent atoms: #1: x, $1+y$, z; #2: $1+x$, y, z.

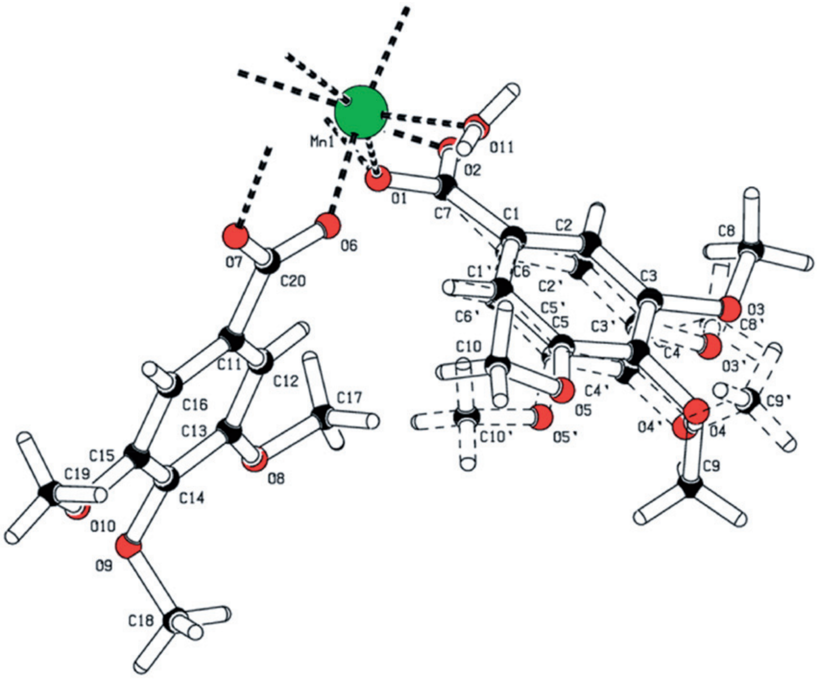

Figure 1. The crystal structure of **1**.

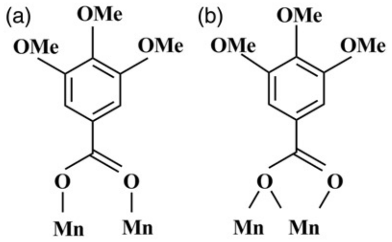

Figure 2. Two different coordination modes in **1**.

The Mn–Mn separation is 3.793 Å, slightly larger than that observed in $[Mn_3(HCOO)_6]$ and $Mn_3(C_{12}H_8N_2)_2(C_{10}H_{11}O_5)_6$, where the Mn–Mn separations are 3.616–3.650 Å [13] and 3.518 Å, respectively. The TMB ligands link manganese(II) ions to generate an infinite 1-D chain coordination framework $[Mn(TMB)_2 \cdot H_2O]_n$ with typical zigzag topology containing corner-sharing polyhedra (figure 3).

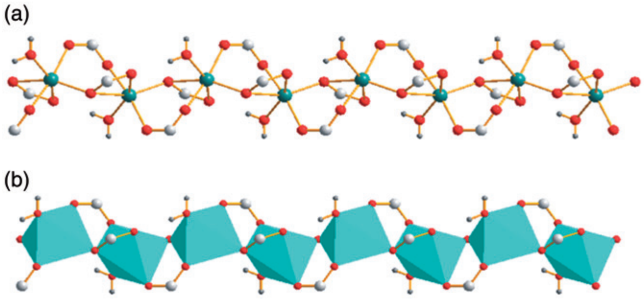

Figure 3. (a) Ball-and-stick of **1** with a 1-D coordination polymer. (b) Coordination polyhedron of **1** in 1-D coordination structure.

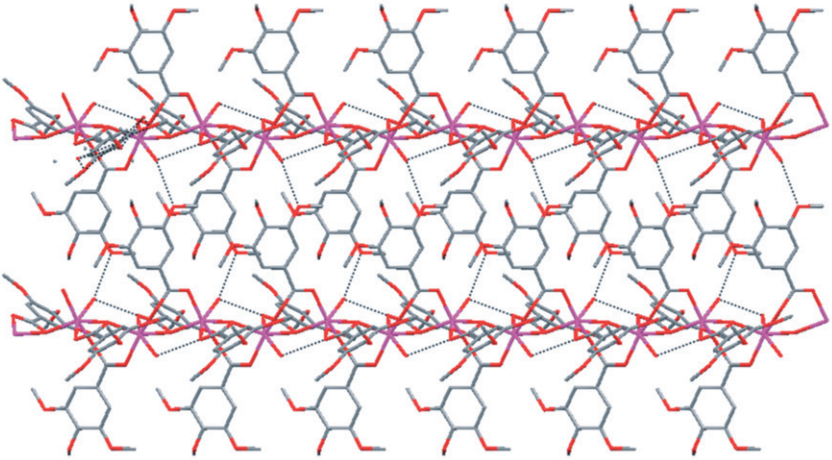

Figure 4. Crystal packing diagram of **1** viewed along the *c*-axis. Hydrogen atoms have been omitted for clarity.

Disorder of one group in a crystal structure is a normal phenomenon [14]. In **1**, the phenyl (C_6H_5) and three methoxy groups of a TMB are disordered while C7, O1, and O2 are in order. Hydrogen-bonding interactions play important roles in the self-assembly of $[Mn(TMB)_2 \cdot H_2O]_n$ (figure 4).

The experimental PXRD pattern, recorded in the range of 3−65° (2θ), is consistent with the simulated one based on single-crystal structure analysis (figure 5). The purity of **1** was confirmed by investigation of PXRD in which the as-synthesized positions of diffraction peaks are in good agreement with the simulated ones. The differences in intensity may be due to preferred orientation of the powder samples [15].

3.2. *IR characterization*

IR spectra of **1** are shown in Supplementary Material. Compared with free ligand, the spectra of **1** indicate that $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ shift to $1558\,cm^{-1}$ and $1399\,cm^{-1}$

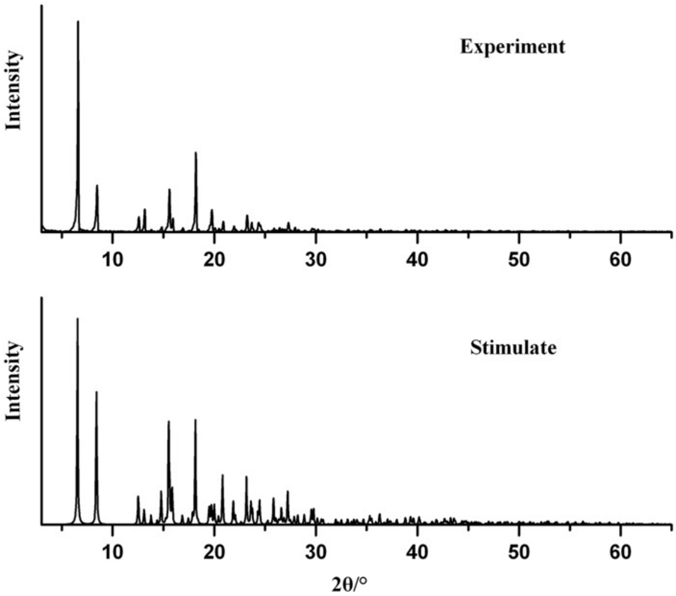

Figure 5. PXRD patterns from experiment and simulated.

due to carboxylate groups of the bridging TMB. The calculated Δ(OCO) value {ν(OCO)asym − ν(OCO)sym} of 159 cm^{-1} is consistent with the presence of a bidentate bridging coordination [16]. In addition, peaks at 3480 cm^{-1} and 3410 cm^{-1} are assigned to O−H absorptions of coordinated water. These spectra are consistent with the crystal structure data, supporting the results of X-ray diffraction.

3.3. *UV-Vis characterization*

UV-Vis spectrum shows two strong absorptions from 200 to 600 nm in **1** and pure ligand (Supplementary material). The intensities of absorptions of complex are obviously weaker than that of pure ligand. The maximum absorption remains at 264 nm after reaction, which can be regarded as the π–π* transition of TMB, whereas the peak of high wavelength shifts to 300 nm. The results indicate oxygen atoms from TMB ligands coordinated with metal centers.

3.4. *Thermogravimetric analysis*

Thermogravimetric analysis of **1** was performed in air from room temperature to 800°C (Supplementary material). The first weight loss of 3.78% (Calcd 3.61%) was observed as dehydration in the range 144.6–177.2°C, corresponding to loss of one coordinated water. On further heating, the second decomposition process occurs with weight loss of 74.41% (Calcd 74.86%), due to loss of two TMB ligands. Finally, only the MnO_2 residue (observed 21.81%, Calcd 21.53%) remained above 370°C.

4. Conclusions

We obtained and characterized a new manganese(II) coordination polymer $[Mn(TMB)_2 \cdot H_2O]_n$. The experimental data show two different coordination modes of TMB, which leads to an infinite 1-D chain coordination framework.

Supplementary material

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication CCDC No. 798858. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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