

New Dinuclear Methoxo-Bridged Manganese(III) complex: Synthesis, Characterization and Usage as New Precursor for Synthesis of Mn₂O₃ Particles

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Abstract

New dinuclear methoxo-bridged manganese(III) complex [Mn₂((MeO-bph)en)₂Cl₂(μ-CH₃O)₂] (**1**) was synthesized by template reaction of 2-hydroxy-4-methoxybenzophenone, 1,2-ethanediamine and MnCl₂·6H₂O with molar ratio (1:1:1) in methanol as solvent. The title compound **1** was characterized by elemental analyses (CHN), Fourier Transform infrared spectroscopy (FT-IR) and single crystal X-ray diffraction. X-ray result reveal that **1** is dimeric with methoxo bridges between two symmetry equivalent manganese ions. The Mn ions are surrounded in a distorted octahedral geometry influenced by Jahn-Teller effect. The tridentate Schiff base ligand MeO-bp-en and one of the methoxo-bridges bind in the equatorial mode, whereas in the axial positions, other methoxo-bridge and Cl atom bind to the Mn ions. Thermogravimetric analysis of **1** was studied and display the title compound **1** decompose in three stages. Finally, by calcination of **1** at 500 °C for 3 h, we prepared Mn₂O₃ particles and characterized by FT-IR, XRD and SEM.

Keywords: Dinuclear; Manganese(III); Schiff base; Crystal structure; Mn₂O₃ particles.

Introduction

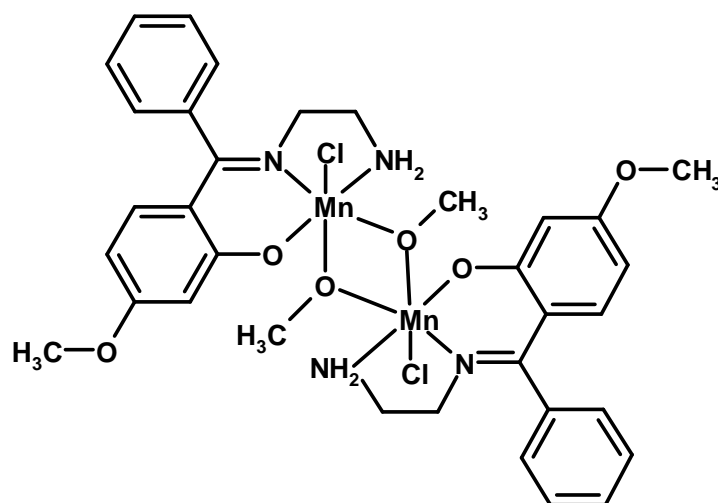
Schiff base compounds, as chelating ligands, played an important role in the development of coordination chemistry [1-6]. They were coordinated to the transition metal ions to form Schiff base complexes with interesting structural features, suitable properties and industrial applications [1-6]. There are many interesting for the preparation of multinuclear Mn(III) Schiff bases due to application in single-molecule magnets (SMM) based on the existence of paramagnetic Mn(III) ions [7-9]. Their magnetic properties depend on the nature of

the bridging ligand, such as azide and thiocyanate, and also on the whole structure geometry around the Mn(III) ions [7-9]. In this work, new dinuclear methoxo-bridged manganese(III) complex [Mn₂(MeO-bp-en)₂Cl₂(μ-CH₃O)₂] (**1**) (Scheme 1) was prepared and characterized. Also, Mn₂O₃ particles were prepared by calcination of **1** at 500 °C for 3 h and characterized.

Materials and Methods

All reagents and solvents were purchased from Merck and Aldrich company and used as received

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Scheme 1. The chemical structure of $[\text{Mn}_2(\text{MeO-bp-en})_2\text{Cl}_2(\mu\text{-CH}_3\text{O})_2]$ (**1**)

without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR Perkin-Elmer spectrophotometer as a KBr disk. The TG/DTA were performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in argon atmosphere with a heating rate of 20 °C/min in the temperature span of 50–800 °C. The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-K radiation with nickel beta filter in the range $2\theta = 10^\circ\text{--}80^\circ$.

Preparation of **1**

0.1 mmol of 1,2-ethanediamine dissolved in 15 mL methanol is added drop-wise to a stirring methanolic solution of 2-hydroxy-4-methoxybenzophenone (0.1 mmol). The yellow solution is refluxed for 1 h. Then, a 15 mL methanolic solution of $\text{MnCl}_2\cdot 6\text{H}_2\text{O}$ (0.1 mmol) was added drop-wise and stirred for 3 h. By slow evaporation of solvent after few days, suitable brown crystals of **1** were filtered, washed with cold methanol and dried at room temperature. *Anal. Calcd.* for $\text{C}_{34}\text{H}_{40}\text{Cl}_2\text{Mn}_2\text{N}_4\text{O}_6$: C, 50.43%; H, 4.94%; N, 6.92%. *Found*; C, 50.39%; H, 5.01%; N, 6.96%. FT-IR (KBr, cm^{-1}): 3237, 3191 (NH_2), 2873-3050 (C-H aromatic and aliphatic), 2806 ($-\text{CH}=\text{N}$), 1567 ($-\text{C}=\text{N}$).

Preparation of Mn_2O_3 particles

0.5 g of **1** was loaded into a crucible, grind for about 10 minutes, and then heated at 500 °C for 3 h in an oven with a rate of 10 °C min^{-1} . The black precipitates was

collected, washed with cold ethanol and dried at 70 °C for 1 day. Then characterized by FT-IR, XRD and SEM.

X-ray structure determination

Single crystal of **1** with the size dimensions of 0.14 mm \times 0.1 mm \times 0.03 mm, was chosen for X-ray diffraction study. Crystallographic measurements was done with a four circle CCD diffractometer SuperNova of Rigaku Oxford diffraction at 120 K, using Cu-K radiation from a micro-focus sealed tube collimated by mirrors. We used the CCD detector Atlas S2. By charge flipping with program SUPERFLIP [10], we solved the crystal structure of **1**. Refinement of **1** prepared by the Jana2006 program package [11] by full-matrix least-squares technique on F^2 . The molecular structure plot of **1** was prepared by Diamond 4.0 [12].

All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice H atoms bonded to C were kept in ideal positions with $\text{C-H} = 0.96 \text{ \AA}$ and with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. Position of hydrogen atoms on nitrogen was refined with bond restraint, using also the above mentioned constraint for $U_{\text{iso}}(\text{H})$. All non-hydrogen atoms were refined using harmonic refinement. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Results and Discussion

Description of the crystal structure of **1**

The molecular structure of **1** display in Figure 1. There are two symmetric methoxo-bridges, two Cl atoms, two tridentate Schiff base ligands and two

Table 1. Crystallographic data and structural refinement details of **1**

Formula weight	C ₃₄ H ₄₀ Cl ₂ Mn ₂ N ₄ O ₆
Formula weight	809.15
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> ,	6.7308(4)
<i>b</i> ,	8.1203(4)
<i>c</i> ,	15.8621(12)
, deg	92.504(5)
, deg	97.256(6)
, deg	99.888(5)
<i>V</i> , Å ³	845.34(9)
<i>Z</i>	1
μ , mm ⁻¹	7.96
<i>R</i> _{int}	0.040
<i>S</i>	2.02
Measured reflections	5217
Independent reflections	3322
Parameters	223
Reflections with <i>I</i> > 3 (<i>I</i>)	2733
<i>R</i> (<i>F</i> ² > 2 (<i>F</i> ²))	0.076
<i>wR</i> (<i>F</i> ²)	0.173
max	0.85
min	-0.97

manganese(III) ions in the title compound **1**. The two halves of the dinuclear complex are related by an inversion center. Selected important bond distances and angles around the Mn(III) ions are summarized in Table 2. The manganese(III) ions are located in a distorted octahedral environment. The equatorial plane is formed

by the tridentate NNO Schiff base ligand and \sim -O atom from one of the methoxo-bridges. An oxygen atom from another methoxo-bridge and Cl atom are coordinated in the axial positions. The equatorial atoms Mn1, N1, O1, N2, and O15 are nearly coplanar.

The TG curve of the title compound **1** under argon

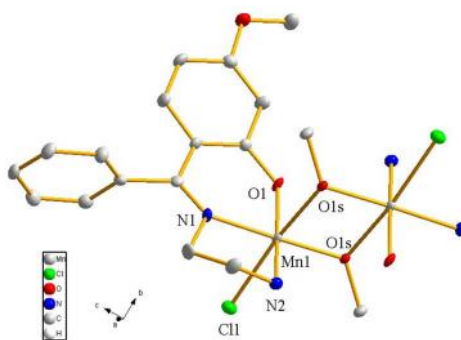


Figure 1. ORTEP view of the dimer in **1**. The right part of the molecule is related to the left one by the inversion center (symmetry operation 1-x, 2-y, -z)

Table 2. Selected bond distances (in Å) and angles (in °) of **1**

Mn1 O1	1.907(4)	Mn1 O1s	1.890(3)
Mn1 N1	2.014(4)	Mn1 N2	2.037(5)
Mn1 O1sA	2.252(4)	Mn1 Cl1	2.517(4)
O1 Mn1 O1s	91.51(15)	O1 Mn1 N1	91.12(16)
O1 Mn1 N2	168.32(14)	O1s Mn1 N1	174.80(16)
O1s Mn1 N2	92.97(16)	N1 Mn1 N2	83.62(17)
Cl1 Mn1 N2	89.93(11)	Cl1 Mn1 N1	86.24(11)
Cl1 Mn1 O1s	97.73(8)	Cl1 Mn1 O1sa	171.07(11)

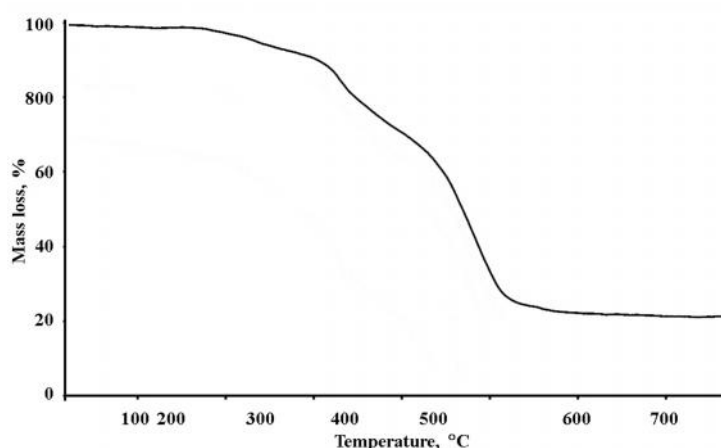


Figure 2. TG curve of the title compound 1

atmosphere is given in Figure 2. There is no detectable change in the TG curve up to 200 °C, then during further heating the complex undergoes decomposition in two stages (200 – 370 °C (25%) and 370 – 520 °C (50%)).

Characterization of Mn_2O_3 particles

The FT-IR spectrum of the Mn_2O_3 particles is shown in Figure 3. The peaks at about 3390 and 1605 cm^{-1} can be assigned to O-H vibration of H_2O molecules

adsorbed on the surface of Mn_2O_3 [13-15]. The two peaks appear at 576 and 475 cm^{-1} are assigned to the Mn-O-Mn asymmetric stretching and bending vibration mode, respectively [13-15]. Figure 4 shows the XRD patterns of Cubic structure of Mn_2O_3 particles (JCPDS card No. 24-0508) [13-15] without any impurities. The morphology of the obtained Mn_2O_3 particles was further investigated by SEM. Figure 5 show the SEM image of the obtained particles.

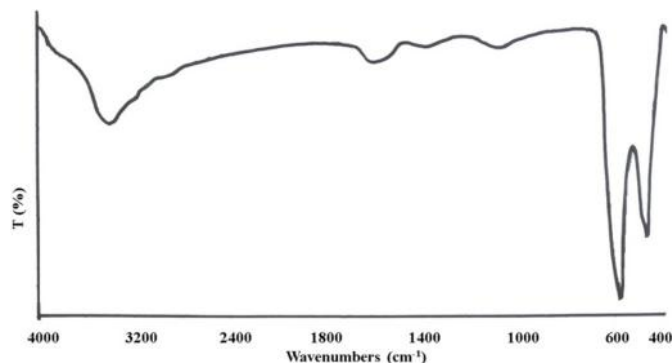


Figure 3. FT-IR spectra of the as-prepared Mn_2O_3 particles

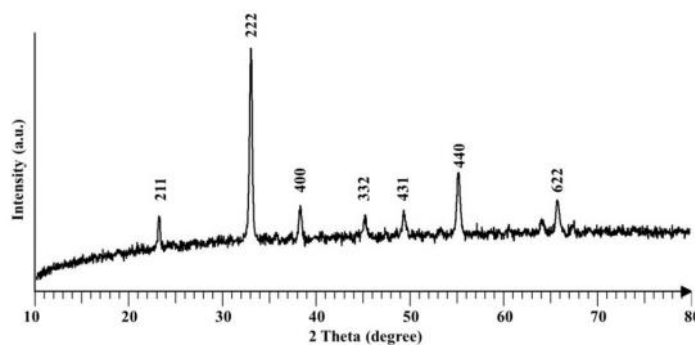


Figure 4. XRD pattern of the as-prepared Mn_2O_3 particles

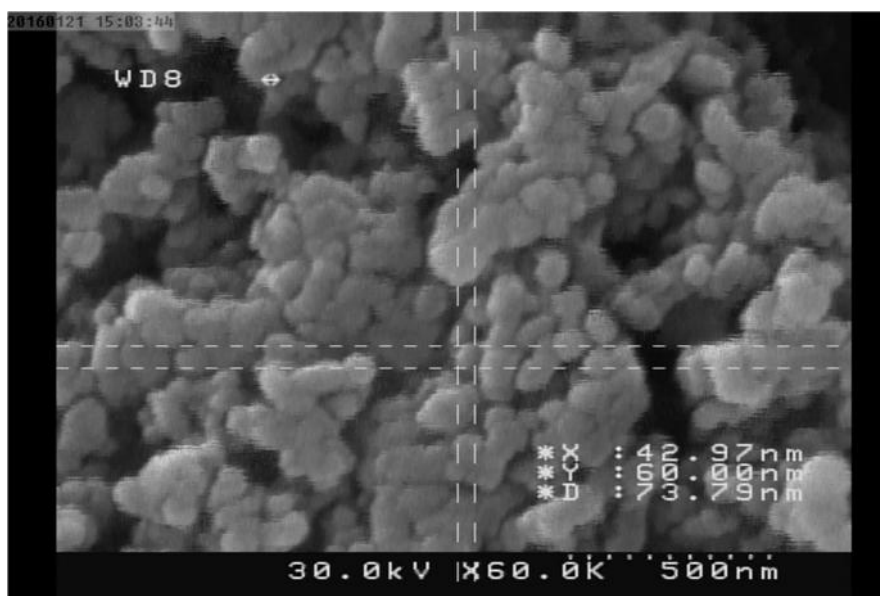


Figure 5. SEM images of the as-prepared Mn_2O_3

Conclusions

In conclusion, we synthesized the dinuclear complex $[Mn_2((MeO-bphen)_2Cl_2(\mu-CH_3O)_2)]$ (**1**) in simple procedure and characterized by the elemental analysis and FT-IR spectroscopy. Single crystal X-ray results showed that the Mn center had a distorted octahedral geometry. In addition, by decomposition of **1** at $600^\circ C$ black precipitates were prepared. Analyzing of the XRD pattern of the obtained solid, showed the formation of the Mn_2O_3 particles.

Acknowledgments

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Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 1914398 (1). Copies of the data can be obtained free of charge on deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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