

## 甲酸桥联四核锰配合物 $[\text{Mn}_4(\text{O}_2\text{CH})_4(\text{phen})_8](\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$ 的水热合成和晶体结构

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### Hydrothermal Synthesis and Crystal Structure of a Tetranuclear Manganese(II) Complex Bridged by Formate $[\text{Mn}_4(\text{O}_2\text{CH})_4(\text{phen})_8](\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$

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Abstract: The title compound,  $[\text{Mn}_4(\text{O}_2\text{CH})_4(\text{phen})_8](\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$  (1), where phen=1,10-phenanthroline, was synthesized and its crystal structure was determined by X-ray diffraction structure analysis. The crystal is of monoclinic, space group P2/c with  $a=1.928\ 0(16)$  nm,  $b=1.297\ 0(11)$  nm,  $c=2.126\ 4(18)$  nm,  $V=5.242\ 2(8)$  nm<sup>3</sup>,  $Z=2$ ,  $M_r=2\ 347.36$ ,  $D_c=1.487$  g·cm<sup>-3</sup>,  $\mu=0.659$  mm<sup>-1</sup>,  $F(000)=2\ 400$ ,  $R_{\text{int}}=0.043\ 7$ ,  $R=0.052\ 3$ ,  $wR=0.118\ 6$ . The Mn atoms are octahedrally coordinated by two O atoms of two ligands and four N atoms of two 1,10-phenanthroline molecules. The carboxyl group coordinates to Mn(II) in the bridging bidentate mode. CCDC: 675520.

Key words: Mn(II) complex; crystal structure; formic acid; hydrothermal synthesis

## 0 Introduction

Many manganese carboxylate clusters have been implicated as an essential part of the active center in a variety of manganese enzymes. Various nuclearities have been observed from mononuclear atom in superoxide dismutase to the tetranuclear atom in oxygen-evolving complex (OEC) of photosystem (PS ) in green plants, where the light-driven oxidation of

water oxygen gas happens. The syntheses and structures of manganese model complexes have provided a wealth of data for comparison and contrast for the Mn<sub>4</sub> water oxidation complex (WOC)<sup>[1-6]</sup>. So the complexes containing N,O-donor ligands have been studied extensively as simple active-site model of PS in recent years.

In order to continue our studies on the manganese complexes<sup>[7-10]</sup>, we have chosen formic acid and phen as ligands and investigated its reaction with Mn (ClO<sub>4</sub>)<sub>2</sub>·

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6H<sub>2</sub>O. We report herein the synthesis and crystal structure of the tetranuclear manganese (II) complex, [Mn<sub>4</sub>(O<sub>2</sub>CH)<sub>4</sub>(phen)<sub>8</sub>](ClO<sub>4</sub>)<sub>4</sub>·6H<sub>2</sub>O (1).

## 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 Shimadzu FTIR-8700 spectrophotometer using KBr discs. TG curves was recorded on a Perkin-Elmer Pyris Diamond thermoanalyser in flow of N<sub>2</sub>, in the temperature range from 20 to 800 °C, with a heating rate of 10 °C·min<sup>-1</sup>.

### 1.2 Synthesis of the title compound

The compound was hydrothermal synthesized under autogenous pressure. A mixture of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.181 g, 0.5 mmol), formic acid (0.065 g, 1 mmol), NaOH (0.041 g, 1 mmol), phen (0.100 g, 0.5 mmol) and H<sub>2</sub>O (10 mL, 0.55 mmol) was heated in a 25 mL capacity Teflon-lined reaction vessel at 170 °C 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<sub>2</sub>O and air-dried. Yields based on Mn: 34%. Molecular formula is C<sub>100</sub>H<sub>80</sub>Cl<sub>4</sub>Mn<sub>4</sub>N<sub>16</sub>O<sub>30</sub>. Elemental analysis (%) C, 51.12; H, 3.41; N, 9.54. Found (%) C, 51.47; H, 3.25; N, 10.28. Main IR bands (cm<sup>-1</sup>): 3 433s, 1 637s, 1 608s, 1 454ms, 1 114s, 1 087s, 846ms, 725m, 624w.

### 1.3 X-ray crystallography

A yellow block crystal with dimensions of 0.31 mm × 0.23 mm × 0.12 mm was selected for the measurement. The diffraction data were collected at 291(2) K on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromatized Mo K radiation (λ = 0.071 073 nm). A total of 41 087 reflections were collected in the range of 2.49 ° to 26.00 ° by using an ω-scan mode, of which 10 300 were unique and used in the succeeding structure calculations. The structure was solved by direct method and difference Fourier synthesis. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced geometrically. All calculations were performed with SHELXTL-2000 package. Crystal data and structure refinement parameters are listed in Table 1.

CCDC: 675520.

Table 1 Crystal data and structure parameters for the title complex

|  |  |   |   |
|--|--|---|---|
| Empirical formula                      | C <sub>100</sub> H <sub>80</sub> Cl <sub>4</sub> Mn <sub>4</sub> N <sub>16</sub> O <sub>30</sub> | Z   | 2   |
| Formula weight                         | 2 347.36   | Absorption coefficient / mm <sup>-1</sup>           | 0.659   |
| Temperature / K                        | 291(2)   | F(000)  | 2 400   |
| Crystal system                         | Monoclinic   | Crystal size / mm                                   | 0.31 × 0.23 × 0.12                                |
| Space group                            | P2/c   | θ / (°)   | 2.49 to 26.00                                     |
| a / nm                                 | 1.928 0(16)  | Limiting indices                                    | -22 h 23, -15 k 15, -25 l 25                      |
| b / nm                                 | 1.297 0(11)  | Reflections collected / unique (R <sub>int</sub> )  | 41 087 (0.043 7)                                  |
| c / nm                                 | 2.126 4(18)  | Data / restraints / parameters                      | 10 300 / 0 / 750                                  |
| β / (°)                                | 99.654(10)   | Goodness of fit on F <sup>2</sup>                   | 1.063   |
| V / nm <sup>3</sup>                    | 5.242 2(8)   | final R indices [I > 2σ(I)]                         | R <sub>1</sub> =0.052 3, wR <sub>2</sub> =0.118 6 |
| D <sub>c</sub> / (g·cm <sup>-3</sup> ) | 1.487  | Largest diff. peak and hole / (e·nm <sup>-3</sup> ) | 202 and -277                                      |

## 2 Results and discussion

### 2.1 Crystal structure of the title complex

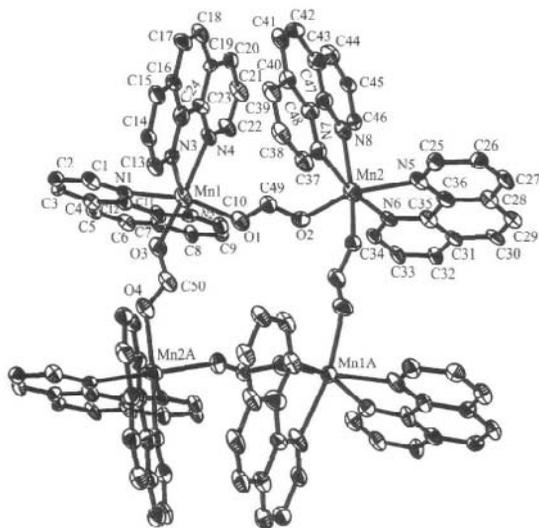
The molecular structure of the title complex is shown in Fig.1, and the selected bond lengths and bond angle are given in Table 2.

The single-crystal structure reveals that, in 1, the Mn(II) ions are bridged by μ<sub>2</sub>-O<sub>2</sub>CH molecules forming a

tetranuclear structure. Each Mn is coordinated with a slightly distorted octahedron formed with two O atoms, which come from two bidentate bridged HCOO<sup>-</sup> units (O1, O3), four terminal N atoms from two bidentate coordinated phen molecules (N1, N2, N3, N4). Around each Mn center together with two perchlorate ions and six solvate water molecules. We can presume that the equatorial plane is composed of O1, N1, N2, and N3, the

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

|                 |            |                   |            |                   |            |
|-----------------|------------|-------------------|------------|-------------------|------------|
| Mn(1)-O(1)      | 0.212 9(3) | Mn(1)-N(3)        | 0.227 2(2) | Mn(2)-N(5)        | 0.226 0(2) |
| Mn(1)-O(3)      | 0.212 2(2) | Mn(1)-N(4)        | 0.229 7(3) | Mn(2)-N(6)        | 0.2265(2)  |
| Mn(1)-N(1)      | 0.223 5(3) | Mn(2)-O(4)#1      | 0.212 9(2) | Mn(2)-N(8)        | 0.227 6(3) |
| Mn(1)-N(2)      | 0.226 8(2) | Mn(2)-O(2)        | 0.213 9(2) | Mn(2)-N(7)        | 0.228 5(2) |
| O(3)-Mn(1)-O(1) | 89.04(9)   | N(1)-Mn(1)-N(3)   | 98.35(9)   | O(2)-Mn(2)-N(6)   | 87.46(8)   |
| O(3)-Mn(1)-N(1) | 85.55(10)  | N(2)-Mn(1)-N(3)   | 159.37(10) | N(5)-Mn(2)-N(6)   | 73.54(8)   |
| O(1)-Mn(1)-N(1) | 159.17(8)  | O(3)-Mn(1)-N(4)   | 161.21(9)  | O(4)#1-Mn(2)-N(8) | 163.53(9)  |
| O(3)-Mn(1)-N(2) | 108.18(9)  | O(1)-Mn(1)-N(4)   | 90.88(10)  | O(2)-Mn(2)-N(8)   | 93.73(9)   |
| O(1)-Mn(1)-N(2) | 89.37(9)   | O(4)#1-Mn(2)-O(2) | 89.10(9)   | N(5)-Mn(2)-N(8)   | 94.97(9)   |
| N(1)-Mn(1)-N(2) | 73.34(9)   | O(4)#1-Mn(2)-N(5) | 87.73(8)   | N(6)-Mn(2)-N(8)   | 95.17(9)   |
| O(3)-Mn(1)-N(3) | 89.54(9)   | O(2)-Mn(2)-N(5)   | 159.71(9)  | O(4)#1-Mn(2)-N(7) | 90.30(9)   |
| O(1)-Mn(1)-N(3) | 101.72(9)  | O(4)#1-Mn(2)-N(6) | 101.17(9)  | O(2)-Mn(2)-N(7)   | 98.14(8)   |

#1:  $-x+1/2, y, -z+3/2$ .Code A:  $-x+1/2, y, -z+3/2$ 

All water molecules and perchlorate ion are omitted for clarity

Fig.1 Ortep view of the complex with displacement ellipsoids (30% probability)

sum of bond angles O(1)-Mn(1)-N(2) (89.37(9) °), O(1)-Mn(1)-N(3) (101.72(9) °), N(3)-Mn(1)-N(1) (98.35(9) °) and N(1)-Mn(1)-N(2) (73.34(9) °) is 362.78 °. And the

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(13)...H(13A)...O(3) <sup>b</sup>  | 0.085       | 0.220       | 0.304 0(3)  | 170.9       |
| O(13)...H(13A)...O(4) <sup>b</sup>  | 0.085       | 0.253       | 0.316 2(3)  | 132.1       |
| O(13)...H(13B)...O(8) <sup>c</sup>  | 0.085       | 0.226       | 0.280 2(3)  | 121.9       |
| O(14)...H(14C)...O(10) <sup>a</sup> | 0.085       | 0.245       | 0.287 5(5)  | 112.1       |
| O(15)...H(15C)...O(14) <sup>d</sup> | 0.085       | 0.183       | 0.249 4(3)  | 133.2       |
| O(16)...H(16D)...O(1)               | 0.085       | 0.200       | 0.285 1(6)  | 179.7       |
| O(16)...H(16C)...O(14)              | 0.085       | 0.244       | 0.300 2(5)  | 123.8       |

Note: <sup>a</sup> 1-x, 1-y, 1-z; <sup>b</sup> x, -y+1, z+1/2; <sup>c</sup> x, y-1, z; <sup>d</sup> -x+1/2, y, -z+3/2.

bond distances of Mn1-O1 and Mn1-O3 are 0.212 9(3) and 0.212 2(2) nm, the bond distances of Mn-N is in the ranges of 0.223 5 (3)–0.229 7 (3) nm, respectively. The O3 and N4 atoms occupy the axial position with the angle of 161.21(9) °. It should be noted that the disposition mode of four Mn atoms differs from that found in several previously reported complexes where the four Mn atoms in the  $[\text{Mn}_4(\mu_3\text{-O})_2]^{8+}$  core display a folded "butterfly-like" con-formation<sup>[11-13]</sup>. The distance of Mn(1)...Mn(2) (0.607 0 nm) is much longer than that of Mn(1)...Mn(2) (0.329 3 (9) nm)<sup>[9]</sup>, so there exists no weak metal bond between Mn(1) and Mn(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 bonds thus appear to stabilize the asymmetry molecular disposition around the Mn center, as shown in Fig.2.

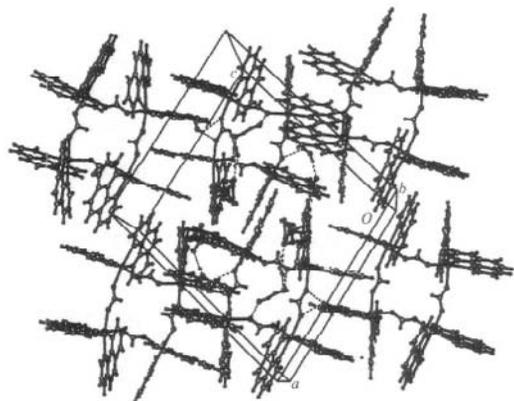


Fig.2 Unit cell and packing diagram for the complex

## 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<sup>[14]</sup>. The separation ( ) between  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  is  $146 \text{ cm}^{-1}$  for 1, indicating bidentate coordinating modes for the coordinated carboxylate groups, and the strong absorption at  $1114$  and  $1087 \text{ cm}^{-1}$  indicates the presence of perchlorate ion. These IR results are coincident with the crystallographic structural analyses. In the IR spectra, the band at  $3433 \text{ cm}^{-1}$ , due to the (O-H) absorptions of water molecules.

The results of TG-DTG illustrate that the compound decomposition takes place in two steps.

The TG curve shows that the first stage mass loss is 4.73% between  $73$  and  $150$ , which coincides with the calculated value (4.60%) of losing all the water molecules. In the second stage, The loss of all phen

molecules occurred in the temperature range of  $150 \sim 475$  (loss weight 79.98), the theoretical value being 80.57%, corresponding to the loss of all of the ligands and the formation of  $\text{MnO}_2$ .

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