



2,6-二氯苯甲酸桥联的双核锰配合物的水热合成与晶体结构

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Hydrothermal Synthesis and Crystal Structure of a Manganese(II) Compound Bridged by 2,6-dichlorobenzoic Acid

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Abstract: A dinuclear manganese(II) complex, $[\text{Mn}_2(\text{L}^1)_2(\text{phen})_4] \cdot (\text{ClO}_4)_2$ (**1**), has been synthesized and structurally characterized (HL¹=2,6-dichlorobenzoic acid, phen=1,10-phenanthroline). It crystallizes in triclinic system, space group $P\bar{1}$ with $a=1.112\ 3(4)$ nm, $b=1.378\ 2(4)$ nm, $c=2.085\ 7(3)$ nm, $\alpha=93.768(2)^\circ$, $\beta=90.606(10)^\circ$, $\gamma=95.606(3)^\circ$, $V=3.174\ 8(15)$ nm³, $Z=2$, $\text{C}_{62}\text{H}_{38}\text{Cl}_6\text{Mn}_2\text{N}_8\text{O}_{12}$, $M_r=1\ 409.58$, $D_c=1.475$ g·cm⁻³, $\mu=0.718$ mm⁻¹, $F(000)=1\ 428$, $R=0.064\ 3$, $wR=0.138\ 3$. In the crystal the manganese atom is six-coordinated by two oxygen atoms from two different 2,6-dichlorobenzolate molecules and four nitrogen atoms from two 1,10-phenanthroline molecules, completing an octahedral geometry. CCDC: 692296.

Key words: manganese complex; crystal structure; 2,6-dichlorobenzoic acid; hydrothermal synthesis

In recent years, manganese cluster has become an attractive research field because of the involvement of manganese in several biological redoxactive systems, especially in the oxygen-evolving complex (OEC) of photosystem II (PS II) in green plants. It was thought that the coordination environment of Mn in OEC contains O and N donors, and the binding of aqua to the Mn site may be important to the oxidation of aqua for the evolution of dioxygen^[1-6]. 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^[7,8]. In order to continue our studies on the manganese complexes^[9-12], we have chosen 2,6-dichlorobenzoic acid and phen as ligands and investigated their reaction with $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. We report herein the synthesis and crystal structures of the manganese(II) compound, $[\text{Mn}_2(\text{L}^1)_2(\text{phen})_4] \cdot (\text{ClO}_4)_2$ (**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

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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 $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol), 2,6-dichlorobenzoic acid (0.192 g, 1 mmol), NaOH (0.041 g, 1 mmol), phen (0.101 g, 0.5 mmol) and H_2O (10 mL, 0.55mmol) was heated in a 25 mL capacity Teflon-lined reaction vessel at 160 °C for 6 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, Yield: 0.15 g (54%). Anal. Calcd. for $C_{62}H_{38}Cl_6Mn_2N_8O_{12}$ (%): C 52.78; H 3.62; N 7.95; Found (%): C 53.22; H 3.31; N 8.12. Main IR bands (cm⁻¹): 3 435(vw,br), 1 610(s), 1 517(s), 1 454(s), 1 425(m,br), 1 199(w), 1 145(w), 1 088(s), 847(w), 810 (vw), 777(w), 725(w), 624(w), 448(w).

1.3 Crystal structure determination

A suitable yellow block crystal with dimensions of

0.24 mm × 0.26 mm × 0.30 mm was selected for structure determination and the data were collected on a Bruker Smart 1000 CCD diffractometer with a Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) at 291(2) K by using an ω scan mode in the range of $2.50^\circ < \theta < 26.00^\circ$. A total of 24 249 reflections were collected and corrected by SADABS, of which 12 265 were unique with $R_{int}=0.003\ 2$, 8 319 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. The final $R=0.061\ 6$, $wR=0.126\ 1$ ($w=1/[\sigma^2(F_o^2)+(0.05P)^2+1.22P]$, where $P=(F_o^2+2F_c^2)/3$), $S=1.038$, $(\Delta/\sigma)_{max}=0.001$. The highest and lowest residual peaks in the final difference Fourier map are 266 and 315 e·nm⁻³, respectively. All calculations were performed by the SHELXTL program^[13]. Crystal data and structure refinement parameters are listed in Table 1 and the selected bond lengths and bond angles are listed in Table 2.

CCDC: 692296.

Table 1 Crystal data and structure parameters for the title complex

| | | | |
|---------------------|---------------------------------|-----------------------------------------------------|--------------------------------------------------------------|
| Empirical formula | $C_{62}H_{38}Cl_6Mn_2N_8O_{12}$ | $D_c / (g \cdot cm^{-3})$ | 1.475 |
| Formula weight | 1 409.58 | Z | 2 |
| Temperature / K | 291(2) | Absorption coefficient / mm ⁻¹ | 0.718 |
| Crystal system | Triclinic | $F(000)$ | 1 428 |
| Space group | $P\bar{1}$ | Crystal size / mm | 0.24 × 0.26 × 0.30 |
| a / nm | 1.112 3(4) | $\theta / (^\circ)$ | 2.50 to 26.00 |
| b / nm | 1.378 2(4) | Limiting indices | $-13 \leq h \leq 13, -16 \leq k \leq 16, -25 \leq l \leq 25$ |
| c / nm | 2.085 7(3) | Reflections collected / unique | 24 249 ($R_{int}=0.003\ 2$) |
| $\alpha / (^\circ)$ | 93.768(2) | Data / restraints / parameters | 12 265 / 0 / 858 |
| $\beta / (^\circ)$ | 90.606(1) | Goodness of fit on F^2 | 1.088 |
| $\gamma / (^\circ)$ | 95.606(3) | Final R indices [$I > 2\sigma(I)$] | $R_1=0.064\ 3, wR_2=0.138\ 3$ |
| V / nm^3 | 3.174 8(15) | Largest diff. peak and hole / (e·nm ⁻³) | 466 and -596 |

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

| | | | | | |
|-------------------------------|------------|-------------------------------|------------|-------------------------------|------------|
| Mn(1)-O(1) | 0.215 0(3) | Mn(1)-N(3) | 0.228 3(3) | Mn(2)-N(5) | 0.230 2(3) |
| Mn(1)-O(2) ^a | 0.219 2(3) | Mn(1)-N(4) | 0.227 6(3) | Mn(2)-N(6) | 0.230 0(3) |
| Mn(1)-N(1) | 0.227 2(4) | Mn(2)-O(4) | 0.214 1(3) | Mn(2)-N(7) | 0.226 9(4) |
| Mn(1)-N(2) | 0.229 6(4) | Mn(2)-O(3) ^b | 0.217 6(3) | Mn(2)-N(8) | 0.227 4(4) |
| O(1)-Mn(1)-O(2) ^a | 93.56(9) | N(1)-Mn(1)-N(3) | 96.26(12) | N(8)-Mn(2)-N(5) | 97.43(13) |
| O(1)-Mn(1)-N(1) | 101.65(12) | N(4)-Mn(1)-N(3) | 73.42(11) | O(4)-Mn(2)-N(7) | 92.10(12) |
| O(2) ^a -Mn(1)-N(1) | 94.34(11) | O(1)-Mn(1)-N(2) | 90.72(11) | O(3) ^b -Mn(2)-N(7) | 165.91(11) |
| O(1)-Mn(1)-N(4) | 89.11(10) | O(2) ^a -Mn(1)-N(2) | 167.57(11) | N(8)-Mn(2)-N(7) | 73.27(13) |

Continued Table 2

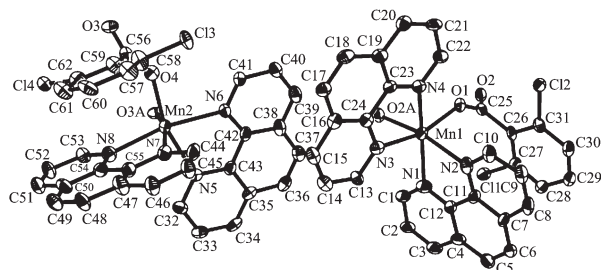
| | | | | | |
|-------------------------------|------------|-------------------------------|------------|-------------------------------|------------|
| O(2) ^a -Mn(1)-N(4) | 94.73(9) | O(4)-Mn(2)-N(8) | 99.50(12) | N(5)-Mn(2)-N(7) | 90.14(12) |
| N(1)-Mn(1)-N(4) | 165.45(13) | O(3) ^b -Mn(2)-N(8) | 93.83(12) | O(4)-Mn(2)-N(6) | 90.07(11) |
| O(1)-Mn(1)-N(3) | 162.06(10) | O(4)-Mn(2)-N(5) | 162.85(11) | O(3) ^b -Mn(2)-N(6) | 92.61(10) |
| O(2) ^a -Mn(1)-N(3) | 84.06(10) | O(3) ^b -Mn(2)-N(5) | 85.86(11) | N(8)-Mn(2)-N(6) | 167.86(13) |

^a $-x+1, -y, -z$; ^b $-x+2, -y, -z+1$.

2 Results and discussion

2.1 Crystal structure of the title complex

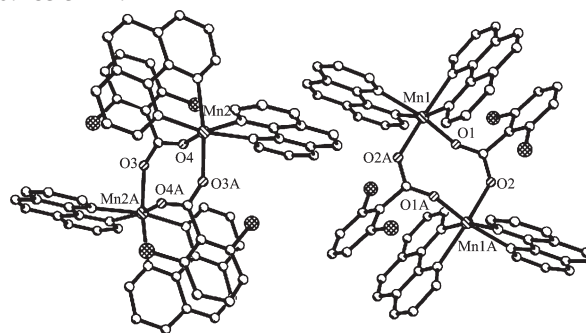
The selected bond lengths and bond angles are listed in Table 1. The coordination structure of the title compound is shown in Fig.1, and the molecular structure consists of two completely uniform dimanganese molecules (Fig.2). In every unit, the Mn^{II} ion in each cation is in a distorted octahedral coordination environment, coordinated by a pair of chelating phen ligands and two oxygen atoms from two different 2,6-dichlorobenzoic acid. The phen groups exhibit their usual acute N···N distances (0.272 8~0.273 4 nm) and N-Mn-N angles (73.27(13)°~73.42(11)°), very close to those found in Mn(phen)₂Cl₂, and Mn(phen)₂(N₃)₂^[14,15], which the pairs of phen ligands are also cis-related. The Mn atoms are six-coordinate but the geometry is a distorted octahedron with N(2) and O(2)^b at the apical positions, principally due to the “bite” of the phen ligands. The Mn-N bonds range from 0.227 2(7) to 0.230 0(7) nm, while the Mn-O bonds from 0.213 4(5) to 0.218 1(3) nm. The sum of bond angles O(1)-Mn(1)-N(1) 101.65(12)°, N(1)-Mn(1)-N(3) 96.26(12)°, N(3)-Mn(1)-N(4) 73.42(11)° and N(4)-Mn(1)-O(1) 89.11(10)° is 360.44°, showing the O(1), N(1), N(3) and N(4) atoms are coplanar. These data indicate that the Mn(1) atom of the complex has a slightly distorted octahedral coordination configuration. The other Mn (2) atom is



Code: A: $-x+1, -y, -z$; All perchlorate ion are omitted for clarity

Fig.1 Asymmetric unit in compound **1** (thermal ellipsoids at 30% probability level)

similar to the Mn (1), which is in distorted octahedral configuration. In **1**, each ligand adopts an *O,O*-bidentate bridging mode using a carboxylate group. Two Mn^{II} centers are doubly bridged by the L¹ ligands, forming a dinuclear structure, with a Mn-Mn distance of 0.485 3 nm.



Code: A: $-x+1, -y, -z$

Fig.2 Dinuclear structure of the title 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 $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$, 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 $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ is 156 cm^{-1} for **1**, indicating bi dentate coordinating modes for the coordinated carboxylate groups, and the strong absorption at 1 145 and 1 088 cm^{-1} indicates the presence of perchlorate ion. These IR results are coincident with the crystallographic structural analyses.

The results of TG-DTG illustrate that the compound decomposition takes place in two steps. The TG curve shows that one 2,6-dichlorobenzoate released up to 297 °C with the estimated weight loss of 14.45wt% (calcd.: 13.48wt%). On further heating, the compound loses 35.28wt% of weight continuously during the

second step from 307 to 702 °C, corresponding to the removal of one L and two phen molecules (calcd.: 32.21wt%), and another two phen ligands is broken above 705 °C.

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