

**Synthesis, Structure and Magnetochemistry of a New Hexanuclear
Manganese Oxide Complex of the Formula
[Mn₆O₂(O₂CPh)₁₀(CH₃CN)₄]**

Jin AN^{1,2}, Zhi Da CHEN^{1,2*}, Jiang BIAN^{1,2}, Shi Xi WANG^{2,3},
Guang Xian XU^{1,2}

¹ Department of Chemistry, Peking University, Beijing 100871

² State Key Laboratory of Rare Earth Materials Chemistry and Applications, Rare Earth Materials
and Bio-inorganic Chemistry Laboratory of Peking University and Hongkong University
Peking University, Beijing 100871

³ Department of Chemistry, Teachers college of Jining, Jining 272125

Abstract: The reported X-ray structure and magnetochemical properties of [Mn₆O₂(OCPh)₁₀(CH₃CN)₄], effectively derived from [NBu₄][Mn₄O₂(O₂CPh)₉(H₂O)] with equivalent of tren in CH₃CN is shown.

Keywords: Manganese complex; hexanuclear; magnetochemistry; oxide complex; crystal structure.

Manganese complexes with nuclearities up to 18 have been reported¹, which has been stimulated by a number of factors. These Mn_x show new and ingenious structures. Tetra nuclear clusters may be the models of the photosynthetic water oxidation center (WOC) in green plants and cyarobacteria². The poly-nuclear manganese clusters exhibit, indeed, highly unusual magnetic properties. They often display high spin (S) values in the ground state³ and certain complexes have been identified as being able to be magnetized below a critical temperature *i.e.*, they can be regards as “single-molecule magnets”⁴. On account of the interest in the structure and magnetic properties of poly-nuclear manganese clusters, we have been exploring synthetic routes to new examples of such species. In this paper we describe another use of an aggregation procedure triggered by solvent to obtain the hexanuclear complex with a [Mn₆O₂]¹⁰⁺ core. The variable-temperature magnetic susceptibility is also reported in here.

Preparation

The solid of [NBu₄][Mn₄O₂(O₂CPh)₉(H₂O)] (1 mmol) was dissolved in CH₃CN (200 ml), and then tren [tris (2-aminoethyl)amine] (1 mmol) was added. During stirring, the brown precipitate was formed. The precipitate was filtered off. And the filtrate was evaporate in the air. After about 1 month, well-formed, dark-red crystals were collected by filtration, washed with Et₂O, and dried in air. Yield: 35 %. Selected FT-IR ν/cm⁻¹:

1402, 1564, 1601, 717, 1447, 611, 677, 1492, 2930, 496, 429, 1157. Anal. Calcd (found) for $C_{78}H_{62}Mn_6N_4O_{22}$: C, 53.91 (53.63); H, 3.57 (3.60); N, 3.23 (3.58) %.

X-ray Crystallography⁵

Diffraction data were collected at 299 K on a Enraf Nonius CAD4 X-ray four circle diffractometer with graphite monochromatic Mo-K α radiation ($\lambda=0.71073$ Å) by using the ω -2 θ scan technique. For the title complex the cell parameters were determined by 25 reflections with 2 θ angles ranging between 19.82° and 24.28°. 7590 intensity data, of which 5309 were unique, were collected in the range 53° $\geq 2\theta \geq 0$ °. The title complex crystallizes in the orthorhombic space group Pbcn with $a=17.412$ (3) Å, $b=18.695$ (4) Å, $c=24.835$ (5) Å, $V=8084$ (4) Å³, $Z=4$, $F(000)=3536$. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms were added theoretically, refined with riding model position parameters and fixed isotropic thermal parameters. The R_1 and wR_2 were 0.083 and 0.069, respectively.

Description of the Crystal Structure

The title complex crystallizes in orthorhombic space group Pbcn (No. 60). The crystal structure of the title complex is showed in **Figure 1**. The structure of complex is visualized as an $[Mn_6O_2]^{10+}$ core having two edge-sharing tetrahedrons. The Mn atoms forming the shared edge [Mn (2)-O=1.884 (9) Å Mn (2a)-O=1.884 (6) Å] are closer to the two centered oxygen than the outer Mn atoms [Mn (1)-O (1)=2.201 Å Mn (3)-O (1a)=2.204 Å]. And charge considerations require the molecule to contain two Mn^{3+} and four Mn^{2+} ions, that is a mixed-valence $Mn^{III}_2Mn^{II}_4$ cluster. According to the fact of high-spin d^4 (Mn^{3+}) shows a pronounced Jahn-Teller elongation along the equivalent. The length of Mn (2)-O (13)= 2.262 (5) Å Mn (2)-O (19)=2.257 (6) Å are obviously longer than the other Mn (2)-O bonds length. And Mn (2), Mn (2a) shows relatively short Mn-O bond distances. The Mn (2)-O average distance 2.035 Å is shorter than the average distance of Mn (1)-O (2.1782 Å) Mn (3)-O (2.1692 Å). On the basis of the above-mentioned facts the Mn (2), Mn (2a) are assigned as Mn (III). The terminal ligands of the title complex are four acetonitrile molecules. And six μ^2 -carboxylate ligands are terminally coordinated to a Mn atom. The other four μ^3 -carboxylate ligands coordinated the Mn (II) and the pair of Mn (II) Mn (III).

Magnetic Susceptibility for the Title Complex

Temperature dependent molar susceptibility measurement of powdered sample of the title complex was carried out in the temperature 5-300 K. The $\chi_m T$ decreases from 15.278 cm³mol⁻¹ K at 300 K to 1.79 cm³mol⁻¹ K at 6.6 K for the title complex. The rate of decrease of the effective magnetic moment is accelerated below 55 K. (*cf.* **Figure 2**). This indicates an antiferromagnetic coupling between manganese atoms. The detailed studies on this complex will be further reported.

Figure 1.

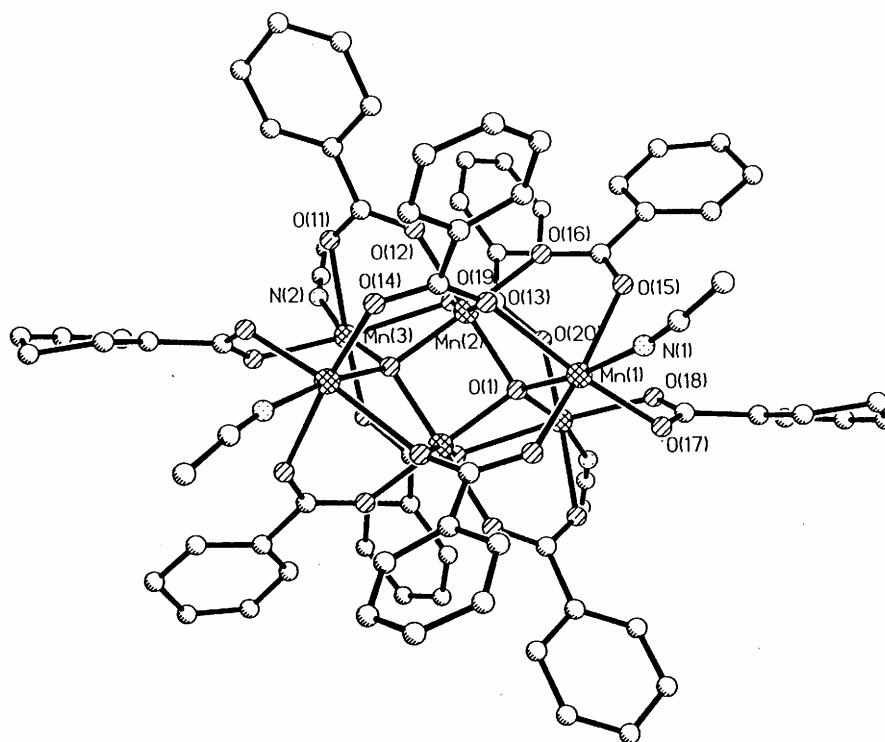
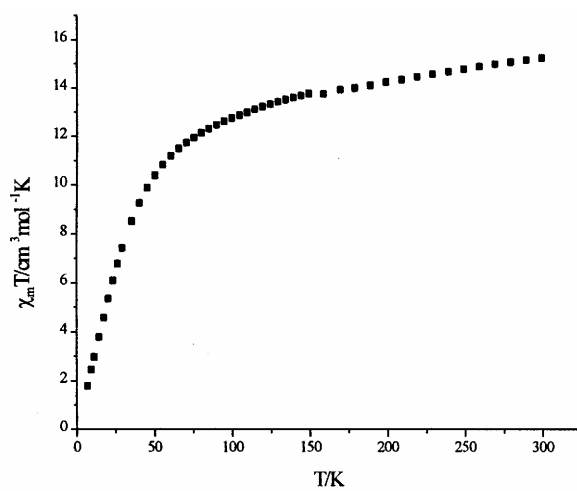


Figure 2.



Acknowledgments

This project was supported by the National Natural Science Foundation of China (29831010).

References and Notes

1. R. C. Squire, *et al.*, *Inorg. Chem.*, **1995**, *34*, 6463. and references therein.
2. M.W. Wemple, *et al.*, *J. Am. Chem. Soc.*, **1995**, *117*, 7275. and references therein.
3. S. Wang, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **1991**, *30*, 1672.
4. Z. M. Sun, *et al.*, *Inorg. Chem.*, **1998**, *37*, 4758.
5. Crystallographic parameters have been deposited in the editorial office of CCL.

Received 9 March 1999