# Alkoxo-Bridged Trinuclear Manganese(III) Complex with an Isosceles Triangle Core

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An alkoxo-bridged trinuclear manganese(III) complex with an isosceles triangle core, $[Mn_3(L)_2(CH_3O)_2(CH_3OH)(C_2H_5OH)](ClO_4)\cdot CH_3OH$ ($H_3L$= bis(benzoylacetone)-1,3-diiminopropan-2-ol), has been prepared and characterized by X-ray structure analyses, electronic spectra and magnetic susceptibilities (80—300 K).

The chemistry of polynuclear manganese complexes has been the subject of extensive study over the past decade since the structure of the oxygen evolving center (OEC) in photosystem II of green plants and the mechanism of water oxidation are unknown.[1-4] Recent biological results for the OEC show that the four manganese atoms are necessary for the activity and in close proximity to one another. Several tetranuclear manganese complexes with a variety of structures have been reported as model compounds of the OEC.[1-4] However, trinuclear systems are still fascinating as a possible model, because a trinuclear unit close to a mononuclear site has been proposed for manganese atoms of the OEC.[5,6] By far the most intensely studied trinuclear manganese systems are μ-oxo $Mn^{III}_3$ and mixed-valence $Mn^{II}Mn^{III}_2$ complexes of the general formula $[Mn_3O(O_2CR)_6L_3]X$.[7] As part of continuing project on manganese complexes, we have reported preparation and characterization of several manganese complexes with the Schiff base ligand, 1,5-bis(salicylideneamino)pentan-3-ol or 1,3-bis(salicylideneamino)propan-2-ol.[8,9] These dinucleating ligands afford interesting dinuclear manganese(III) complexes. In extending these works, we have introduced a dinucleating ligand, bis(benzoylacetone)-1,3-diiminopropan-2-ol ($H_3L$), aiming at giving O-donor-rich environments to manganese atoms. In the course of this activity, we have isolated a novel trinuclear manganese complex with an isosceles triangle core. We herein report the preparation, X-ray crystal structure, electronic spectra, and magnetic properties of the trinuclear manganese(III) complex, $[Mn_3(L)_2(CH_3O)_2(CH_3OH)(C_2H_5OH)]$-$(ClO_4)\cdot CH_3OH$ (1).

The trinuclear complex 1 was isolated as follows. Bis(benzoylacetone)-1,3-diimino-propan-2-ol (20 mg, 0.05 mmol) and manganese-(II) acetate tetrahydrate (27 mg, 0.11 mmol), and sodium perchlorate (27 mg, 0.22 mmol) were dissolved in a methanol—ethanol (1:1) solution.
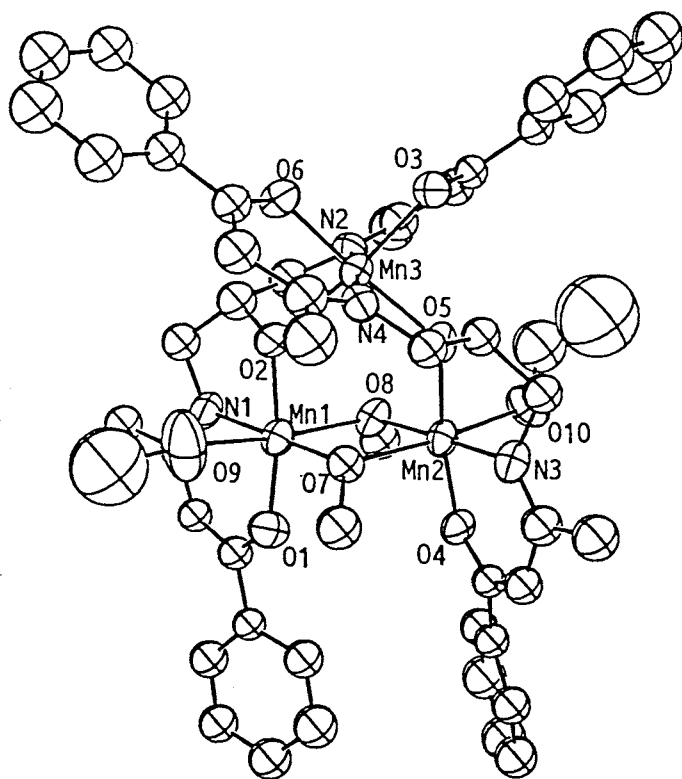


$H_3L$
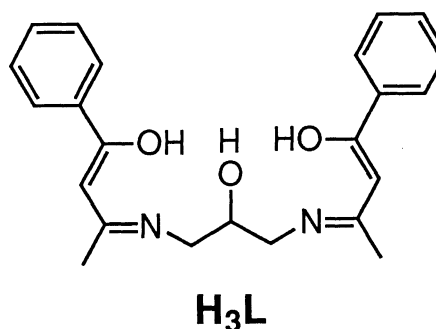
Fig. 1. A perspective view of 1.

To the solution was added triethyl-amine (30 mg, 0.30 mmol) to give a dark brown solution. The solution was filtered and allowed to stand for several days at room temperature. Black crystals deposited were collected by filtration (yield 26 mg).

The molecular structure of **1** was determined by X-ray crystallography.[10] A perspective view of **1** is shown in Fig. 1. The three Mn atoms occupy the corners of an isosceles triangle: Mn1-Mn2 3.141(3) Å, Mn1-Mn3 3.686(4) Å, and Mn2-Mn3 3.686(3) Å. The Mn1 and Mn3 atoms are bridged by an alkoxo oxygen atom (O2) of a dinucleating ligand and the Mn2 and Mn3 atoms are bridged by an alkoxo oxygen atom (O5) of the other dinucleating ligand. On the other hand, the Mn1 and Mn2 atoms are bridged by two methoxo oxygen
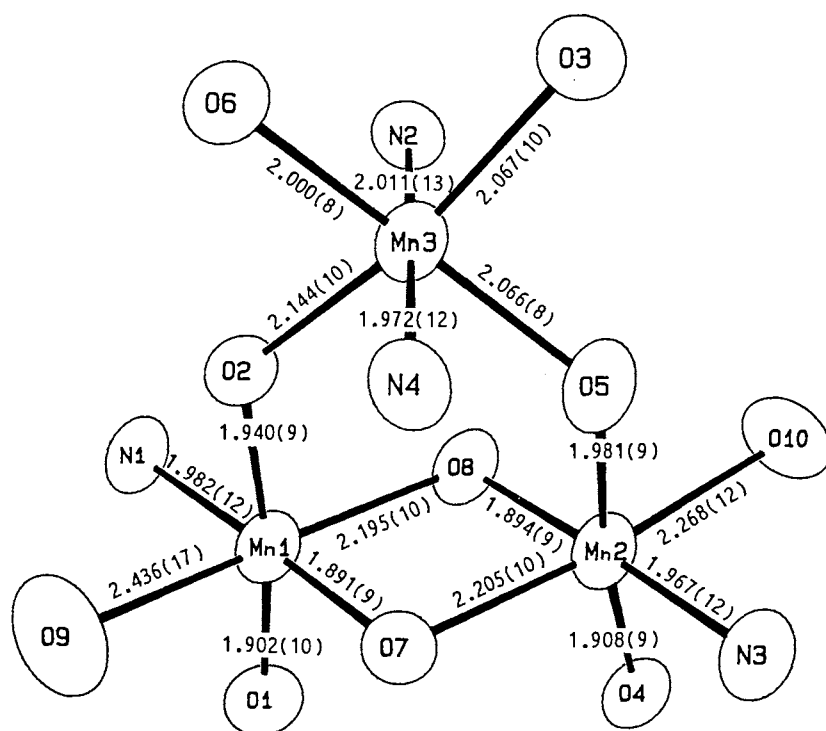


| | |
|---|---|
| Mn1-Mn2 | 3.141(3)Å |
| Mn1-Mn3 | 3.686(4) |
| Mn2-Mn3 | 3.686(3) |

| | |
|---|---|
| Mn1-O2-Mn3 | 128.9(4)° |
| Mn2-O5-Mn3 | 131.2(5) |
| Mn1-O7-Mn2 | 99.9(4) |
| Mn1-O8-Mn2 | 100.1(4) |
| Mn1-Mn3-Mn2 | 50.4(1) |
| Mn2-Mn1-Mn3 | 64.8(1) |
| Mn1-Mn2-Mn3 | 64.8(1) |

Fig. 2. Core structure of 1 showing Mn-O and Mn-N bond distances (*l*/Å).

atoms, O7 and O8. For Mn3, each dinucleating ligand is tridentate and acts as a meridional bis chelate with one keto oxygen, one imine nitrogen, and one alkoxo oxygen atoms in a distorted octahedron. The Mn3-O (2.000(8)—2.144(10) Å) and Mn3-N (1.972(12), 2.011(13) Å) bond lengths are in the range of those found for manganese(III) complexes.[11,12] The Mn1 and Mn2 atoms have an elongated octahedral geometry. Each square plane is formed by NOO donor atoms of L and the bridging-methoxo oxygen atom (the planes O1-N1-O2-O7 and O4-N3-O5-O8). The in-plane-bond distances (Mn1-O 1.891(9)—1.940(9) Å, Mn2-O 1.894(9)—1.981(9) Å; Mn1-N1 1.982(12) Å, Mn2-N3 1.967(12) Å) are comparable to those for the manganese(III) complexes.[11,12] The other bridging-methoxo oxygen atom occupies one site of the apical positions and the elongated octahedral coordination is achieved by the weak coordination of methanol molecule (for Mn1) or ethanol molecule (for Mn2). The elongation may result from expected Jahn-Teller distortions for a high-spin $d^4$ ion. To our knowledge 1 is the first example of trinuclear manganese(III) complex with an isosceles triangle core, although trinuclear manganese(IV) complexes with similar $Mn_3O_4$ core, $[Mn_3O_4(bpy)_4Cl_2]MnCl_4 \cdot 3DMF$ (bpy=dipyridyl, DMF=dimethylformamide) (2) and $[Mn_3O_4(bpy)_4(H_2O)_2](ClO_4)_4 \cdot 1/2[bpyH_2(NO_3)_2] \cdot 2H_2O$ (3), have been reported recently.[13,14] In 2 and 3, the isosceles triangle core is made of two mono-μ-oxo and one di-μ-oxo bridges and has a smaller size, the corresponding Mn1-Mn2, Mn1-Mn3, and Mn2-Mn3 distances being 2.681(3), 3.241(3), and 3.245(3) Å, respectively, in 2. This contraction may be due to the smaller ionic radius of $Mn^{IV}$ compared with $Mn^{III}$ and the stronger coordination of oxo ion compared with alkoxo ion.

Diffuse reflectance spectrum of 1 shows weak absorption bands at 1100, 590(sh), and 480(sh) nm with an intense band at 361 nm. The former two or three bands may be reasonably assigned to the d-d transitions for $Mn^{III}$.[15,16] The magnetic susceptibility was measured on a powder sample over the temperature range
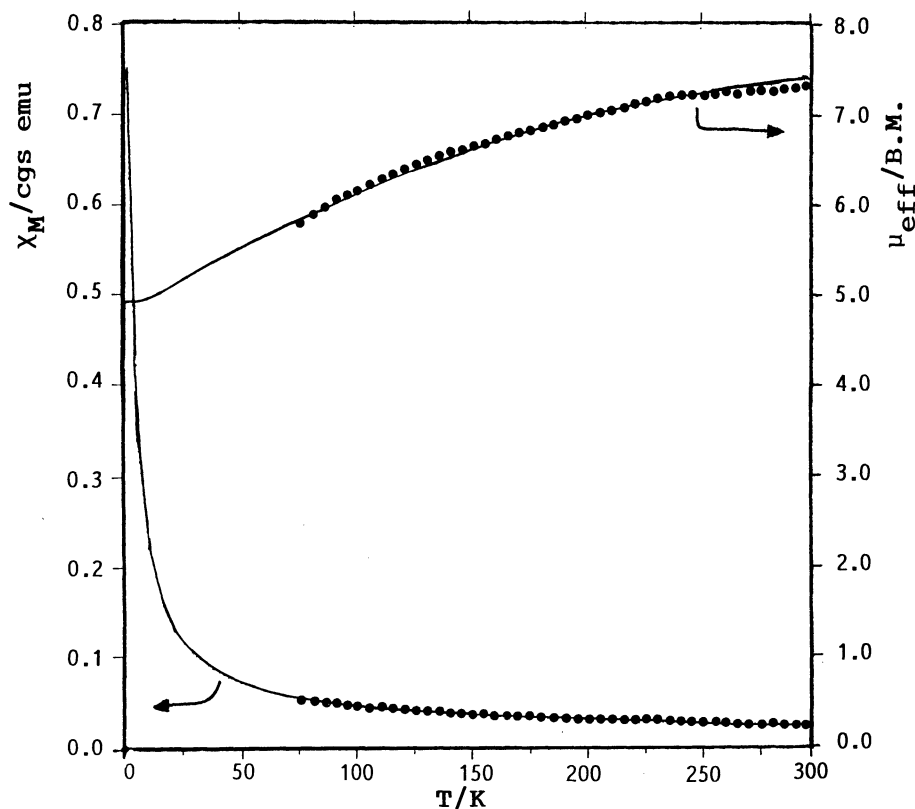


Fig. 3. Temperature dependence of the magnetic moments (above) and magnetic susceptibilities (below) of 1. The solid lines are the fittings with $J$=-19.2 cm$^{-1}$ and $J'$=0.0 cm$^{-1}$.

80—300 K. The room temperature magnetic moment (7.31 B.M./mol) is smaller than the spin-only value (8.49 B.M.) expected for three high-spin $d^4$ system. The magnetic susceptibility data were analyzed with the Van-Vleck equation based on the Heisenberg model ($\mathcal{H}$=-2$J$S$_{Mn1}$·S$_{Mn2}$ -2$J'$(S$_{Mn2}$·S$_{Mn3}$+S$_{Mn3}$·S$_{Mn1}$) (S$_{Mn1}$=S$_{Mn2}$=S$_{Mn3}$=2) and a good fit was found with $J$=-19.2 cm$^{-1}$ and $J'$=0.0 cm$^{-1}$, keeping g fixed at 2.00 (Fig. 3). Thus, a significant antiferromagnetic coupling exists between the Mn1 and Mn2 atoms. Our exchange coupling parameters are considerably smaller than those of 2 and 3 (2: $J$=-85.5 cm$^{-1}$, $J'$=-54.0 cm$^{-1}$; 3: $J$=-91 cm$^{-1}$, $J'$=-49 cm$^{-1}$).[13,14] This may be ascribed to the larger Mn-Mn separations in the isosceles triangle and the differences in the metal oxidation states and the bridging atoms.

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10) Crystal data for 1: Mn$_3$ClO$_{15}$N$_4$C$_{52}$H$_{66}$, F.W.=1187.3, monoclinic, space group $P2_1/c$, $a$=14.131(4), $b$=16.271(5), $c$=24.825(14) Å, β=106.14(3)°, $V$=5483.1(38) Å$^3$, $Z$=4, $D_m$=1.44, $D_c$=1.44 g cm$^{-3}$, μ(Mo-Kα) =7.68 cm$^{-1}$, $R$=0.068, $R_w$=0.074. 8324 reflections were measured in the range 1≤2θ≤46°; 2626 with $I$≥3σ($I$) were assumed as observed. For the determination of structure, intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods and refined by the full-matrix least-squares methods using the SDP program package. The Mn, Cl, O, and N atoms were refined with anisotropic thermal parameters.

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15) The absorption spectrum of 1 in DMF shows shoulders at 1160 (ε=115 mol$^{-1}$dm$^3$cm$^{-1}$) and 475 nm (ε=2180 mol$^{-1}$dm$^3$cm$^{-1}$) , and an intense band at 378 nm (ε=30000 mol$^{-1}$dm$^3$cm$^{-1}$).

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