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LETTER

A binuclear manganese(III) complex with 1,5-bis(salicylideneamino)-3-pentanol which contains chloride ions

Masahiro Mikuriya*, **Yo Yamato**
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662 (Japan)

and **Tadashi Tokii**
Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840 (Japan)

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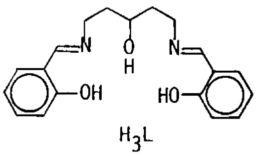
Binuclear manganese complexes have attracted much attention because of their possibility as models for the oxygen-evolving center (OEC) of photosystem II [1]. The active site is believed to contain a multinuclear manganese center composed of two or four Mn atoms. Chloride ions are known to be required for the system to function [2], however, the nature of their interaction with the OEC is not known. In order to examine the effect of chloride ion on the structures and properties of binuclear manganese centers, we have initiated synthetic studies on manganese complexes containing chloride ions. In this study we have isolated one such complex by using a binucleating ligand 1,5-bis(salicylideneamino)-3-pentanol (H_3L). The complex has been characterized on the basis of X-ray crystal structure, electronic spectra, magnetic susceptibilities (80–300 K), and electrochemical properties.



H_3L

The ligand H_3L was prepared by the condensation of salicylaldehyde and 1,5-diamino-3-pentanol [3]. The complex was prepared as follows. The ligand H_3L (82 mg) and manganese(II) chloride tetrahydrate (99 mg) were dissolved in absolute methanol, then triethylamine (*c*. 200 mg) was added. The mixture was refluxed for 15 min and filtered. Diethyl ether was layered onto the filtrate and the mixture placed in a refrigerator overnight. The dark green crystals that deposited were collected by filtration. The complex is air-sensitive, so microanalytical determination was not possible. The structure of the complex was determined by an X-ray structure analysis. Crystal data are: $C_{22}H_{30}Cl_2Mn_2N_2O_6 = [Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$, $M = 599.3$, orthorhombic, space group *Pbca*, $a = 15.932(3)$, $b = 23.496(4)$, $c = 14.053(2)$ Å, $V = 5260.8$ Å^3, $Z = 8$, $D_m = 1.56$, $D_c = 1.52$ g cm^{-3}, μ(Mo Kα) = 11.69 cm^{-1}. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiations. Of the 4421 reflections ($1 \leqslant 2\theta \leqslant 48°$) measured, the unique 2057 reflections with $I \geqslant 3\sigma(I)$ were considered as observed. The structure was solved by the direct methods and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from the difference Fourier map and fixed at their positions. This enabled us to assign O4 as methoxide and O5, O6 as methanol. The final residual values were $R = 0.049$ and $R_w = 0.054$.

The molecular structure of the complex is illustrated in Fig. 1. The two manganese ions are bridged by the alkoxide oxygen atom of L and the methoxide oxygen atom. The Mn–Mn separation is 3.006(2) Å and the Mn–O–Mn angles are 101.6(2) and 101.4(2)°. The coordination geometries are elongated octahedrons for both manganese ions. The square plane around the manganese ion is formed by NO_3 donor atoms of L and the bridging methoxide oxygen atom. The in-plane-bond distances (Mn–O 1.844(6)–1.945(5) Å, Mn–N 2.000(6)–2.002(7) Å) are com-

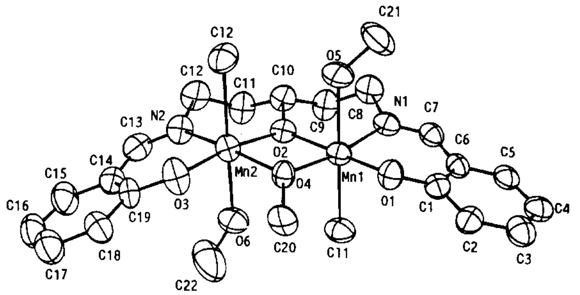


Fig. 1. Perspective view of $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$. Hydrogen atoms are not shown for clarity. Selected bond distances (l/Å) and angles (ϕ/°): Mn1–Mn2 3.006(2), Mn1–O1 1.855(6), Mn1–O2 1.941(5), Mn1–O4 1.945(5), Mn1–N1 2.002(7), Mn1–O5 2.280(6), Mn1–Cl1 2.540(3), Mn2–O2 1.939(5), Mn2–O3 1.844(6), Mn2–O4 1.939(5), Mn2–O6 2.372(6), Mn2–N2 2.000(6), Mn2–Cl2 2.532(3), Cl2–O5 3.026(7), Cl1–O6 3.055(7); Mn1–O2–Mn2 101.6(2), Mn1–O4–Mn2 101.4(2).

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*Author to whom correspondence should be addressed.

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parable to those reported for manganese(III) complexes [3–6]. The elongated octahedral coordination is achieved by the weak coordinations of chloride ion and methanol molecule at the apical positions. This elongation may result from expected Jahn–Teller distortions for a high-spin d^4 ion. There are hydrogen bonds between the chloride ions and the methanol molecules. Contrary to the present structure, the chloride ion is incorporated as a bridging group in the case of the binuclear copper(II) complex with the same Schiff base ligand L, $[Cu_2(L)Cl]$ [7]. The different coordinating behavior of the chloride ion in the present complex is interesting. The X-ray structure analysis has shown that the complex is one of few dialkoxo-bridged binuclear manganese(III) complexes [3, 5, 6]. Recently another binuclear manganese(III) complex with two oxygen bridges, bis(μ-oxo)bis[*N*,*N*′-bis((6-methylpyrid-2-yl)methyl)ethane-1,2-diamine]dimanganese(III) perchlorate [8] has been reported concerning model compounds of the OEC. In this complex, the Mn–Mn separation is 2.676(3) Å and the Mn–O–Mn angles are 94.5(4) and 92.1(4)°, which are substantially different from those of the present complex.

Diffuse reflectance spectrum of the complex shows three absorption bands at 381, 470(sh) and 635 nm, probably being d–d transitions.

Magnetic susceptibility measurement over the temperature range 80–300 K showed an antiferromagnetic interaction between the two manganese ions. The magnetic moment (4.17 BM/Mn at 292 K) is considerably lower than the spin-only value for a high-spin d^4 ion. The magnetic susceptibility data were analyzed with the van Vleck equation based on the Heisenberg model ($\mathscr{H} = -2J\hat{S}_1 \cdot \hat{S}_2$ ($S_1 = S_2 = 2$)) and the best fitting parameters are $J = -15.5$ cm^{-1} and $g = 2.00$ (Fig. 2). The antiferromagnetic spin-exchange interaction in the complex is comparable to that of $[Mn_2(L)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)]$ ($J = -10.6$ cm^{-1}) [6].

A cyclic voltammogram of the complex (Fig. 3) shows two coupled cathodic and anodic waves at *c.* 0.20 and -0.33 V (versus Ag/AgCl) corresponding to reduction of the Mn(III)Mn(III) ion to the Mn(II)Mn(III) ion and the Mn(II)Mn(III) ion to the Mn(II)Mn(II) ion, respectively. At more positive potentials, irreversible oxidation occurred at *c.* 1.0 V. For the present complex, the formation of the Mn(III)Mn(IV) or Mn(IV)Mn(IV) species seems to be difficult. Contrary to this, two redox couples of Mn(III)Mn(III)–Mn(III)Mn(IV) and Mn(III)-Mn(IV)–Mn(IV)Mn(IV) are observed at 0.568 and 1.337 V (versus Ag/AgCl), respectively, in the bis(μ-oxo)dimanganese(III) complex [8].

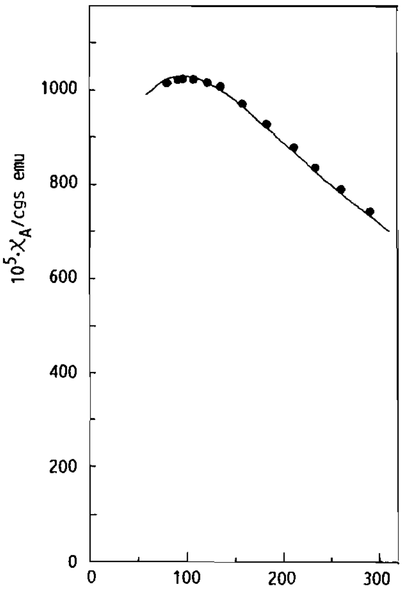

Fig. 2. Temperature dependence of the magnetic susceptibilities of $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$.

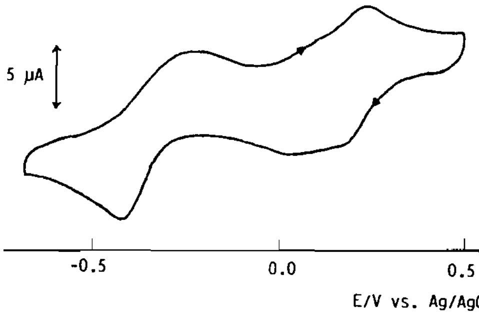

Fig. 3. Cyclic voltammogram of $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ with 0.1 M n-Bu_4NClO_4 as supporting electrolyte in methanol. The scan speed is 100 mV/s.

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