Dinuclear Manganese(III) Complex with Cyclam-based Dodecadentate Ligand Bearing Schiff-base Pendants (Cyclam = 1,4,8,11-Tetraazacyclotetradecane)

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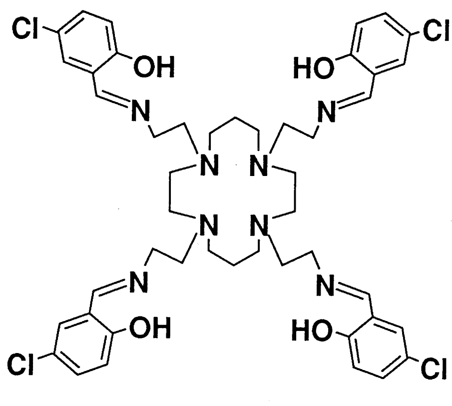
Novel dinuclear manganese(III) complex with a new dodecadentate ligand, 1,4,8,11-tetrakis(2-5-chlorosalicylideneaminoethyl)-1,4,8,11-tetraazacyclotetradecane (H_4L), $[Mn_2(L)(CH_3COO)_2]\cdot 2CHCl_3$ has been synthesized and characterized by X-ray crystallography.

There is considerable current interest in the synthesis of dinuclear, trinuclear, and tetranuclear manganese complexes, since these molecules might be useful as model compounds for understanding the properties of the oxygen evolving center of the photosystem II of green plants.[1] In order to achieve syntheses of such multinuclear manganese complexes, we have pursued a method using dinucleating ligands. Until now, we have isolated dinuclear,[2] trinuclear,[3] and tetranuclear[4] manganese complexes by using some dinucleating ligands. Here, we report another method using a macrocyclic ligand having pendant groups in order to get a multinuclear manganese system. In the family of polyaza macrocycles with pendant arms, cyclam-based octadentate ligand (cyclam = 1,4,8,11-tetraazacyclotetradecane),



H_4L

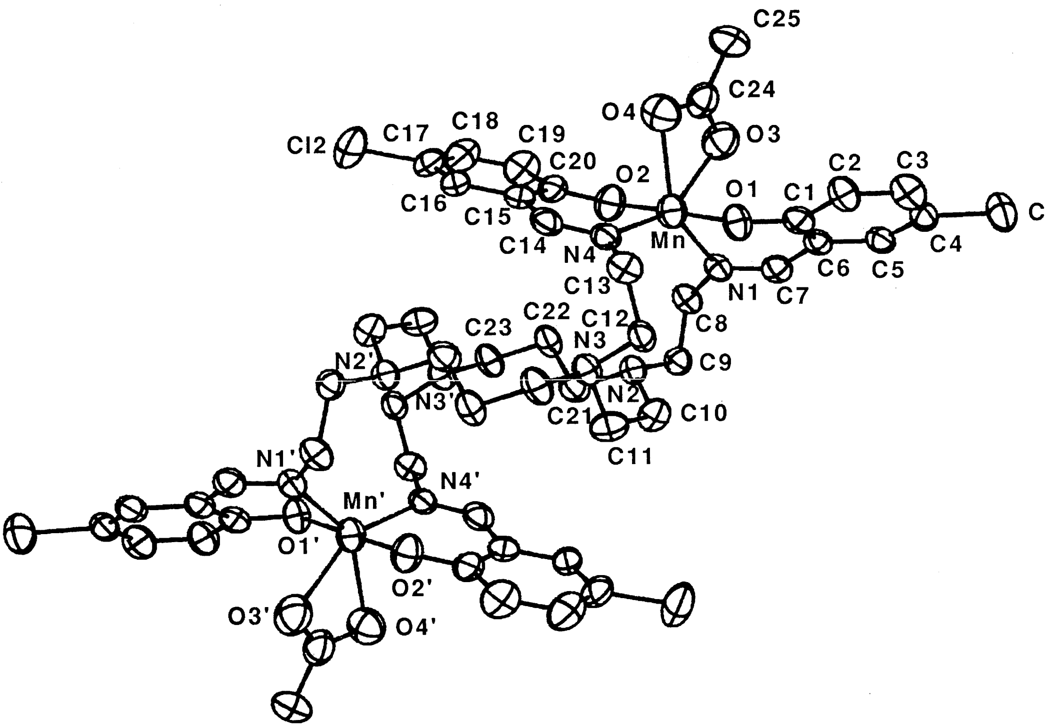


Figure 1. Structure of the complex $[Mn_2(L)(CH_3COO)_2]$. Selected interatomic distances (Å) and angles (°): Mn-O1 1.862(5), Mn-O2 1.843(5), Mn-O3 2.167(6), Mn-O4 2.318(6), Mn-N1 2.118(6), Mn-N4 2.112(6), O1-Mn-O2 178.4(2), O1-Mn-O3 90.1(2), O1-Mn-O4 90.4(2); O1-Mn-N1 86.7(2), O1-Mn-N4 89.6(2), O2-Mn-O3 90.9(2), O2-Mn-O4 91.2(2), O2-Mn-N1 92.1(2), O2-Mn-N4 90.3(2), O3-Mn-O4 57.6(2), O3-Mn-N1 88.3(2), O3-Mn-N4 145.9(2), O4-Mn-N1 145.8(2), O4-Mn-N4 88.3(2), N1-Mn-N4 125.7(2).

1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclodecane (taec) is unique. This interesting ligand forms several dinuclear metal complexes, $[M_2(taec)X_2]Y_2$ and $[M_2(taec)X]Y_3$ (M = Co^{II}, Ni^{II}, Cu^{II}; X, Y = ClO_4^-, NO_3^-, Cl^-, Br^- etc.), where the two metals are chelated by the pendant groups outside the macrocyclic ring.[5] However, this ligand has only nitrogen donor atoms and is less attractive concerning the design for the manganese model compounds, since it is said that oxygen donor atoms dominate at the binding sites of the manganese center in the photosystem II.[1] So far, many manganese complexes of Schiff-base ligands have been reported as the model compounds.[2-4,6,7] The prefernce for manganese complexes may arise from the presence of oxygen donor atoms in the Schiff-bases. In order to introduce Schiff-base moiety we have synthesized a new cyclam-based dodecadentate ligand, 1,4,8,11-tetrakis(2-5-chlorosalicylideneaminoethyl)-1,4,8,11-tetraazacyclotetradecane (H_4L) and examined the complexation of this new ligand with manganese ions.

When H_4L was treated with equivalent of $Mn(CH_3COO)_2\cdot 4H_2O$ in methanol-chloroform (1:1), a novel type of dinuclear manganese(III) complex was isolated.[8] Microanalysis figures of C, H, N, and Mn agree with the formulation $[Mn_2(L)(CH_3COO)_2]\cdot 2CHCl_3$ (**1**). Its IR spectrum exhibits absorptions which confirmed the presense of coordinated C=N group and bidentate acetate group [ν(C=N) 1617s cm^{-1}, ν_{as}(COO) 1534m cm^{-1}, ν_s(COO) 1457s cm^{-1}]. The diffuse reflectance spectrum shows three absorption bands at 371, 450 (shoulder), and 708 nm. This spectral feature is characteristic of high-spin manganese(III) of Schiff-base complexes.[2-4] The complex has a magnetic moment of 4.61 B.M. per manganese atom at room temperature and obeys the Curie-Weiss law with $\theta = -7$ K in the temperature range 80–293 K. This behavior indicates that there is little antiferromagnetic coupling between the manganese ions. The molecular structure of **1** was determined by X-ray crystallography.[9] A perspective view of **1** is shown in Figure 1. The complex has the crystallographic inversion center at the center of the cyclam ring moiety of the ligand L. The cyclam ring moiety assumes the trans III form.[10] It is to be noted that the amine nitrogen atoms of the cyclam ring moiety do not take part in any coordination to the manganese ion. The ligand coordinates to each manganese(III) ion with two imine nitrogen atoms and two phenol oxygen atoms of the two pendant groups in a *cis-β* fashion and the acetate ion acts as a bidentate ligand forming a distorted octahedron. A unique aspect of this dinuclear complex is an axial compression of the Mn(III) octahedra. The axial Mn-O bond distances [Mn-O1 1.862(5), Mn-O2 1.843(6) Å] are significantly shorter than the equatorial Mn-O and Mn-N bond distances [Mn-O3 2.167(6), Mn-O4 2.318(6), Mn-N1 2.118(7), Mn-N4 2.112(6) Å]. This might be ascribed to a pseudo-Jahn-Teller distortion of a high-spin d^4 ion. Such an axial compression is quite scarce.[11] Usually manganese(III) ion adopts an axial elongated octahedron in most Mn(III) compexes.[2-4,6,7] The preference for the pseudo-Jahn-Teller distortion is probably enhanced by the donor atoms of the ligand L, since it seems likely that the phenoxy donors are better ligands to Mn(III) than the acetate oxygens.

We should like to dedicate this paper to the late Prof. Tsutomu Nakagawa of Kwansei Gakuin University who tragically died in the recent southern Hyogo Prefecture earthquake. We are also grateful to Dr. Makoto Handa (Shimane University) and Eiji Asato (Ryukyu University) for helpful discussions.

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8 The ligand H_4L was synthesized by the condensation of 5-chlorosalicylaldehyde and 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane: ν/cm^{-1} (KBr) 1632 (st, C=N); δ(^{1}H NMR, 400 MHz, $CDCl_3$) 1.42 (4H, quint), 2.40–2.45 (16H, m), 2.64 (8H, t), 3.57 (8H, t), 6.87 (4H, d), 7.18–7.23 (8H, m), 8.20 (4H, s), 13.54 (4H, br s); satisfactory microanalytical data were obtained.

9 Crystal data for $[Mn_2(L)(CH_3COO)_2]\cdot 2CHCl_3$: $C_{52}H_{60}N_8O_8Cl_{10}Mn_2$, M = 1389.5, monoclinic, space group $P2_1/n$, a = 14.712(11), b = 16.725(4), c = 14.088(12) Å, β = 118.15(3)°, V = 3056(4) Å^3, Z = 2, D_c = 1.51 gcm^{-3}, μ(Mo-Kα)=8.94 cm^{-1}, F(000) = 1424, T = 298 K. A total of 4894 reflections ($2 \le 2\theta \le 48°$) were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation; 2608 with $I \ge 3\sigma(I)$ were assumed observed. The structure was solved by the direct methods and refined by the full-matrix least-squares method. The refinement converged at R = 0.064, R_w = 0.070.

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