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Synthesis and Characterization of Novel Tetranuclear and Binuclear Manganese(III) Complexes with 1,5-Bis(salicylideneamino)-3-pentanol

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Tetranuclear and binuclear manganese(III) complexes with 1,5-bis(salicylideneamino)-3-pentanol (H_3L), $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot4H_2O\cdot2CH_3OH$ and $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$, have been prepared and characterized by X-ray structure analysis and magnetic susceptibilities (80—300 K).

Tetranuclear manganese complexes are of current interest because such systems are known to exist in the oxygen evolution center (OEC) of the photosystem II of green plants. The current data available for the OEC indicate that the four manganese atoms are necessary for the activity, the Mn···Mn separations are of two types (2.7 Å and 3.3 Å), the metals are bridged by oxo (or hydroxo) ions, and the coordination environment is predominantly O donor in character.1) Several tetranuclear manganese complexes with adamantane,2) cubane,3) butterfly,4) and linear5) structures have been reported as model compounds of the OEC recently.

During the course of our studies on manganese complexes with a binucleating ligand, 1,5-bis(salicylideneamino)-3-pentanol (H_3L),6,7) we have found that reaction with cyanate ion in the presence of water leads to formation of a binuclear manganese(III) complex, $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**1**) and a new type of tetranuclear manganese(III) complex $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot4H_2O\cdot2CH_3OH$ (**2**). Herein we report the synthesis, X-ray crystal structures, and magnetic properties of these complexes.

The complexes were prepared as follows. Manganese(III) acetate dihydrate (134 mg) and H_3L (82 mg)6,7) were dissolved in 3.5 ml of methanol and the mixture was stirred. To the resulting dark green solution was added a methanol-water (1:1) solution of sodium cyanate (73 mg) to give a small amount of dark green crystals **1**.8) The crystals **1** were removed by filtration. Upon standing the filtrate for several weeks, black crystals **2**8) were deposited.

The structures of **1** and **2** were determined by X-ray crystallography.9) The molecular structure of **1** is illustrated in Fig. 1. The Mn···Mn separation is 2.980(3) Å. The coordination geometries are elongated octahedrons for both manganese ions. The square plane around each manganese ion is formed by NO_3 donor atoms of L and the bridging-methoxo-oxygen atom. The elongated octahedral coordination is achieved by the weak coordinations of cyanate ion and water molecule at the apical positions. The elongation may result from expected Jahn-Teller distortions for a high-spin d^4 ion. The structure of **1** is similar to that found for $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$.7)

Contrary to the binuclear structure of **1**, the X-ray structure determination of **2** revealed a novel tetranuclear structure shown in Fig. 2. The tetranuclear molecule is located at the crystallographic inversion center. In the binuclear half, the two manganese atoms (Mn1 and Mn2) are bridged by the alkoxo-oxygen atom (O2) of L, the oxo ion (Ox), and the acetate ion. The two binuclear halves are held together through the oxo ions (Ox and Ox') and the phenoxo-oxygen atoms (O3 and O3') of L.

Both the Mn1 and Mn2 atoms have elongated-octahedral MnO_5N geometries. However, the axes of Jahn-Teller distortions are different from each other; the elongated axes are O4-Mn1-O3' and O2-Mn2-O3, respectively. The square plane of Mn1 is formed by NO_2 donor atoms of L and the bridging-oxo ion, whereas that of Mn2 is formed by N atom of L, two bridging-oxo ions, and one oxygen atom of the acetate ion. These in-plane-bond distances (Mn-O 1.888(5)—2.002(5) Å, Mn-N 2.021(5), 2.067(6) Å) are comparable to those reported for manganese(III) complexes.6,7,10,11) Short Mn···Mn separations are 2.875(1) Å for Mn2···Mn2',

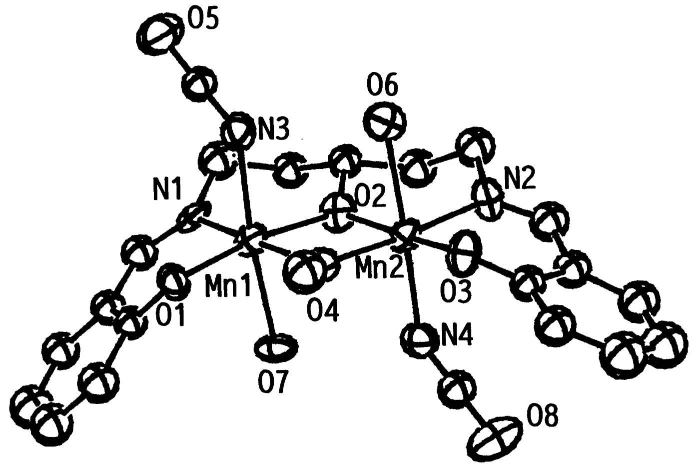

Fig. 1. Perspective view of $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn1-Mn2 2.980(3), Mn1-O1 1.863(8), Mn1-O2 1.963(9), Mn1-O4 1.935(9), Mn1-N1 2.029(11), Mn1-N3 2.221(13), Mn1-O7 2.327(10), Mn2-O3 1.867(11), Mn2-O2 1.942(10), Mn2-O4 1.926(9), Mn2-N2 2.020(11), Mn2-N4 2.221(13), Mn2-O6 2.302(10); Mn1-O2-Mn2 99.5(5), Mn1-O4-Mn2 101.0(5).

2.933(1) Å for Mn1···Mn2, and 3.122(1) Å for Mn1···Mn2'. This is the first example of manganese complex which has a layered structure consisting of four edge-sharing pseudooctahedra (MnO_5N). The intriguing aspects of the structure of **2** are (i) the Mn···Mn distances of 2.875(1) Å and 3.122(1) Å, (ii) the oxo-ion bridges between the metal centers, and (iii) the coordination environment having O donors mainly. These features are in harmony with those observed for the natural system and suggest the complex **2** as one of potential models for the manganese site in the OEC.

Magnetic susceptibilitiy measurements on solid samples of **1** and **2** indicate magnetic moments of 4.08 and 4.32 B.M./Mn, respectively, at room temperature, decreasing to 2.47 and 3.56 B.M./Mn, respectively, at liquid nitrogen temperature. Since spin-only values of the magnetic moment for high-spin d^4 ion is 4.90 B.M./Mn, the above values are consistent with net antiferromagnetic interactions within the molecules.

Further stiudies on these manganese complexes are now under way.

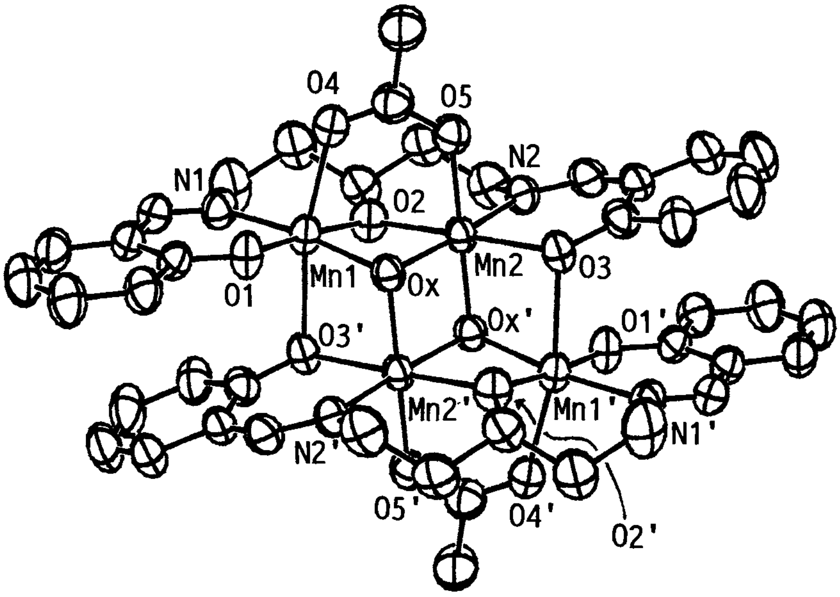

Fig. 2. Perspective view of $[Mn_4(L)_2(O)_2(CH_3COO)_2]$. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn1-Mn2 2.933(1), Mn1-Mn2' 3.122(1), Mn2-Mn2' 2.875(1), Mn1-O1 1.889(5), Mn1-O2 1.888(5), Mn1-Ox 1.941(4), Mn1-N1 2.021(5), Mn1-O4 2.201(5), Mn1-O3' 2.359(5), Mn2-O3 2.142(4), Mn2-O2 2.168(4), Mn2-Ox 1.892(4), Mn2-N2 2.067(6), Mn2-O5 2.002(5), Mn2-Ox' 1.934(4); Mn1-O2-Mn2 92.4(2), Mn1-Ox-Mn2 99.9(2), Mn1-Ox-Mn2' 107.4(2), Mn2-Ox-Mn2' 97.4(2), Mn1-O3'-Mn2' 87.7(2).

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8) A satisfactory analysis (C, H, N) has been obtained.

9) Crystal data for **1**: $Mn_2O_8N_4C_{22}H_{26}$, F.W.=584.3, monoclinic, space group $P2_1/c$, a=13.917(18), b=10.513(4), c=18.138(15) Å, β=110.92(4)°, V=2478.9(40) $Å^3$, Z=4, D_m=1.55, D_c=1.57 g cm^{-3}, μ(Mo-Kα)=10.30 cm^{-1}, R=0.059, R_w=0.065. 3834 reflections were measured in the range $1 \le 2\theta \le 46°$; 1260 with $I \ge 3\sigma(I)$ were assumed observed. For **2**: $Mn_4O_{18}N_4C_{44}H_{60}$, F.W.=1152.7, monoclinic, space group $P2_1/n$, a=17.380(7), b=11.338(4), c=12.439(5) Å, β=95.93(2)°, V=2438.0(16) $Å^3$, Z=2, D_m=1.54, D_c=1.57 g cm^{-3}, μ(Mo-Kα)=10.46 cm^{-1}, R=0.046, R_w=0.049. 4243 reflections were measured in the range $1 \le 2\theta \le 48°$; 2213 with $I \ge 3\sigma(I)$ were assumed observed. For the determination of both structures, 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.

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