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Preparation and Structural Characterization of Binuclear Manganese(III) Complexes with 1,5-Bis(salicylideneamino)-3-pentanol and Its Derivatives

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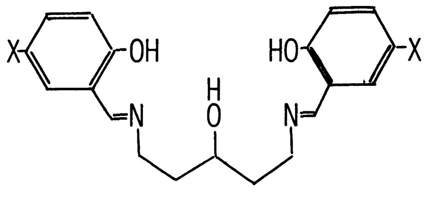
Three binuclear manganese(III) complexes with the title Schiff base ligands have been prepared and characterized. X-Ray structure analysis of $[Mn_2(L_b)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (H_3L_b = 1,5-bis(5-chlorosalicylideneamino)-3-pentanol) has revealed that the two manganese ions are bridged by the alkoxide oxygen atom of the Schiff base ligand, the methoxide oxygen atom, and the oxygen atoms of the acetate ion with the Mn---Mn separation of 2.921(2) Å.

The coordination chemistry of manganese has achieved a remarkable progress in the last half-decade due to the increased recognition of this element's role in biological systems. As a multinuclear manganese center composed of two or four Mn(III) and/or Mn(IV) atoms has been proposed as the model for the oxygen-evolving center (OEC) of photosystem II,$^{1)}$ binuclear manganese complexes have attracted a remarkable attention.$^{2-8)}$ As a part of the continuing study on binuclear manganese complexes,$^{7,8)}$ we have isolated some binuclear Mn(III) complexes using 1,5-bis(salicylideneamino)-3-pentanol and its derivatives, H_3L_a, H_3L_b, and H_3L_c. The analytical data suggested that these complexes have a complicated composition, $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (H_3L = H_3L_a, H_3L_b, or H_3L_c). Thus we have carried out X-ray structure analysis on one of these complexes and revealed the unique binuclear structure.



H_3L_a, X = H; H_3L_b, X = Cl; H_3L_c, X = Br

The ligands, H_3L_a, H_3L_b, and H_3L_c, were prepared by the condensation of the appropriate salicylaldehyde and 1,5-diamino-3-pentanol. The complexes were prepared by the reaction of $Mn(CH_3COO)_3 \cdot 2H_2O$ (1 mmol) with H_3L (0.5 mmol) in methanol followed by addition of solid $NaClO_4$ (2.5 mmol). Anal.$^{9)}$ $[Mn_2(L_a)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (1);

Found: C, 42.11; H, 4.47; N, 4.39%. Calcd for $C_{23}H_{29}ClMn_2N_2O_{11}$: C, 42.19; H, 4.46; N, 4.28%. $[Mn_2(L_b)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (2); Found: C, 38.12; H, 3.81; N, 3.92%. Calcd for $C_{23}H_{27}Cl_3Mn_2N_2O_{11}$: C, 38.17; H, 3.76; N, 3.87%. $[Mn_2(L_c)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (3); Found: C, 33.76; H, 3.72; N, 3.31%. Calcd for $C_{23}H_{27}Br_2ClMn_2N_2O_{11}$: C, 33.99; H, 3.35; N, 3.45%.

Crystals suitable for X-ray structure determination were obtained only for 2. The dark green plate with dimensions of 0.18 × 0.31 × 0.36 mm^3 was used for the X-ray work. Crystal data are: $[Mn_2(L_b)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$, F.W. = 723.71, orthorhombic, Pbca, a = 8.813(1), b = 31.275(5), c = 21.168(3) Å, V = 5834(2) $Å^3$, Z = 8, D_m = 1.65, D_c = 1.65 g cm^{-3}, μ(Mo-Kα) = 11.67 cm^{-1}. Intensity data were collected on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation and corrected for Lorentz-polarization effects and absorption. A total of 5785 reflections (1° < 2θ < 50°) were obtained, of which independent 3281 reflections ($|F_o| > 3\sigma(|F_o|)$) were considered as observed. The structure was solved by the direct methods and refined by the block-diagonal least-squares method.[10)] The final residual values were R = 0.072 and R_w = 0.071.[11)] The atomic parameters are listed in Table 1.

The crystal structure consists of discrete binuclear molecules. The molecular structure of the complex is illustrated in Fig. 1. The two manganese ions are bridged by the alkoxide oxygen atom of L_b, the methoxide oxygen atom, and the oxygen atoms of the acetate ion. The acetate ion bridges the manganese ions in a syn-syn configuration with Mn-O distances of 2.123(6) and 2.120(5) Å. In addition, the methanol molecule is weakly bonded to Mn2 with the Mn2-O7 distance of 2.392(5) Å and the perchlorate ion is loosely bound to Mn1 with the Mn1-O8 distance of 2.536(6) Å. There is a hydrogen bond between the perchlorate ion and the methanol molecule (O9---H(O7) 2.033 Å). Both Mn1 and Mn2 possess elongated-octahedral MnO_5N

Table 1. Positional parameters (× 10^4) and equivalent isotropic temperature factors ($Å^2$)

Atom	x	y	z	B_{eq}		x	y	z	B_{eq}
MN1	391 (1)	1643 (1)	4215 (1)	3.5	C4	-2343 (9)	2699 (2)	2480 (4)	3.9
MN2	927 (1)	1133 (1)	5349 (1)	3.7	C5	-1467 (9)	2351 (2)	2414 (4)	3.8
CL1	-3121 (3)	2959 (1)	1823 (1)	5.4	C6	-836 (9)	2153 (2)	2951 (3)	3.4
CL2	-105 (3)	48 (1)	8313 (1)	6.1	C7	184 (8)	1793 (2)	2855 (3)	3.6
CL3	-3050 (2)	987 (1)	3751 (1)	4.2	C8	1943 (9)	1248 (3)	3107 (4)	4.5
O1	-516 (6)	2169 (1)	4078 (2)	4.0	C9	1712 (9)	816 (2)	3395 (4)	4.1
O2	905 (5)	1060 (1)	4444 (2)	3.3	C10	2016 (8)	801 (2)	4096 (4)	3.6
O3	672 (7)	1237 (1)	6205 (2)	4.4	C11	2011 (10)	350 (2)	4376 (4)	4.5
O4	-154 (6)	1637 (1)	5085 (2)	3.9	C12	2709 (11)	323 (2)	5027 (4)	5.0
O5	2655 (6)	1834 (2)	4408 (2)	4.8	C13	1608 (9)	351 (2)	6051 (4)	4.0
O6	3078 (6)	1431 (2)	5269 (3)	4.7	C14	880 (9)	525 (2)	6602 (4)	4.3
O7	-1497 (6)	788 (2)	5360 (3)	4.8	C15	703 (9)	246 (2)	7122 (3)	4.0
O8	-2225 (7)	1345 (2)	3980 (4)	7.3	C16	119 (9)	398 (2)	7683 (4)	4.1
O9	-3413 (9)	715 (2)	4252 (3)	8.7	C17	-304 (9)	832 (2)	7749 (4)	4.6
O10	-4401 (7)	1131 (2)	3473 (3)	7.5	C18	-118 (9)	1103 (2)	7248 (4)	4.4
O11	-2140 (7)	767 (2)	3295 (3)	7.1	C19	471 (9)	969 (2)	6676 (4)	4.2
N1	803 (7)	1571 (2)	3299 (3)	3.5	C20	-662 (12)	1988 (3)	5442 (3)	5.9
N2	1821 (7)	553 (2)	5528 (3)	4.3	C21	3476 (9)	1698 (2)	4851 (4)	4.5
C1	-1150 (9)	2325 (2)	3550 (3)	3.7	C22	5100 (9)	1867 (3)	4890 (5)	5.9
C2	-2059 (9)	2677 (2)	3603 (3)	4.0	C23	-2654 (10)	868 (3)	5801 (4)	5.8
C3	-2677 (10)	2870 (2)	3078 (4)	4.7					

geometries. The in-plane-bond distances are comparable to those reported for manganese (III) complexes.[2,7,8] The axial Mn-O distances are considerably longer than the in-plane Mn-O distances. Such tetragonal elongation is attributable to the Jahn-Teller effect of high spin d^4 ion. Diffuse reflectance spectra of the present complexes show three or four absorption bands in the visible region.[12] These bands may be due to the splitting of the ground ^5E_g and the excited $^5T_{2g}$ states of octahedral manganese(III) ion. The infrared spectrum of **2** shows the $\nu_a(COO^-)$ and $\nu_s(COO^-)$ bands at 1540 and 1420 cm^{-1}, respectively. The $\Delta\nu$ value between the $\nu_a(COO^-)$ and $\nu_s(COO^-)$ bands falls in the range of those observed for a symmetrically bridging carboxylate group.[7,8] A broad band around 3400 cm^{-1} is attributable to the ν(O-H) band of the semi-coordinated methanol. The ν(Cl-O) bands of the perchlorate ion appear at 1050–1135 cm^{-1}. Small splitting of these bands is compatible with the semi-coordination of the perchlorate ion.

Further studies on magnetic and electrochemical properties of these complexes are in progress.

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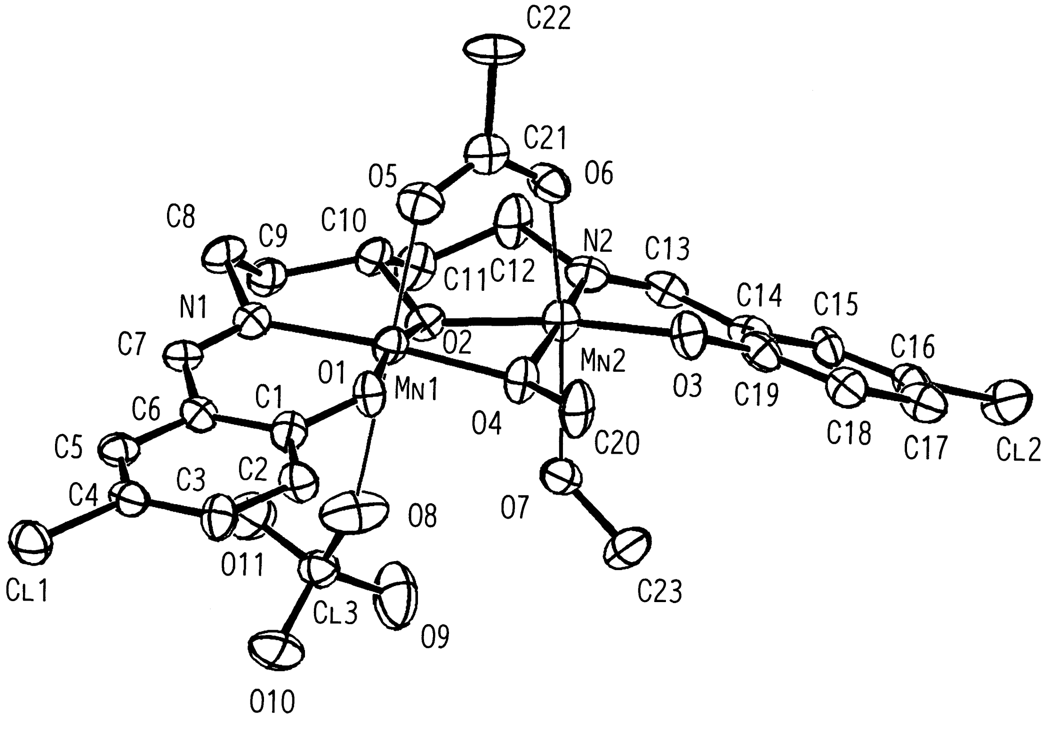

Fig. 1. Perspective view of $[Mn_2(L_b)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$. Selected bond distances (l/Å) and angles (ϕ/°): Mn1-Mn2 2.921(2), Mn1-O1 1.852(5), Mn1-O2 1.940(4), Mn1-O4 1.904(5), Mn1-N1 1.985(6), Mn1-O5 2.123(6), Mn1-O8 2.536(6), Mn2-O3 1.856(5), Mn2-O2 1.929(5), Mn2-O4 1.925(5), Mn2-N2 2.013(6), Mn2-O6 2.120(5), Mn2-O7 2.392(5); Mn1-O2-Mn2 98.0(2), Mn1-O4-Mn2 99.4(2).

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9) Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University.
10) The weighting scheme $w = [\sigma^2_{count} + (0.015|F_o|)^2]^{-1}$ was employed. Hydrogen atoms were located in the calculated positions, but those of methoxide and acetate ions, and methanol molecule were located from the difference Fourier maps. These H atoms were included in the least-squares calculation and fixed at their positions with isotropic thermal parameters of B = 6.0 Å^2.
11) All the calculations were carried out with the UNICS-III programs on the HITAC M-680H computer at the Computer Center of the Institute for Molecular Science.
12) Complex 1: 16.5, 20.9sh, 22.0sh, 26.2×10^3 cm^{-1}; 2: 16.5, 21.0sh(broad), 25.5×10^3 cm^{-1}; 3: 15.9, 20.3sh, 21.3sh, 25.2×10^3 cm^{-1}.

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