  Bull. Chem. Soc. Jpn., 65, 2624—2637 (1992)

Synthesis, Properties, and Crystal Structures of a Series of Dinuclear Manganese(III) Complexes with 1,5-Bis(salicylideneamino)-3-pentanol and Various Anions: Formation of a Tetranuclear Manganese(III) Complex

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(Received May 27, 1992)

μ-Alkoxo-bridged dinuclear and tetranuclear manganese(III) complexes with 1,5-bis(salicylideneamino)-3-pentanol (H_3L), $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**), $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]X$(X=Br (**2**), I (**3**)), $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)Y]$(Y=NCS (**4**), N_3 (**5**), ClO_4 (**6**)), $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**), and $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**) have been prepared and characterized by infrared and electronic spectra, magnetic susceptibilities, and cyclic voltammetry. The molecular structures of **1**—**5**, **7**, and **8** were determined by the single-crystal X-ray structure analyses. All the complexes except for **8** have a similar structure, where Cl^-, CH_3COO^-, N_3^-, NCS^-, CH_3OH, or H_2O is incorporated into the fifth or sixth coordination site on the $Mn_2(L)(CH_3O)$ plane. The structure of **8**, is a tetramer consisting of two $Mn_2(L)(O)(CH_3COO)$ dimeric units held together through the oxo ions and the phenoxo-oxygen atoms of L. The spectral and magnetic properties were discussed in relation to the crystal structures.

The coordination chemistry of manganese has achieved a remarkable progress in the last decade due to the increased recognition of this metal's role in biological systems.[1-8] Dinuclear and tetranuclear manganese complexes are of current interest, since 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 necesssary for the activity, the Mn···Mn separations are of two types (2.7 and 3.3 Å), the metals are bridged by oxo (or hydroxo) ions, and the coordination environment is predominantly O donor in character.[4,6,7] Interestingly chloride ions are known to be required for the water oxidation activity and other small anions such as Br^-, I^-, and NO_3^- can substitute for the chloride ions with varying efficiencies.[2-4,7] It has been suggested that the chloride ions may be serving as a ligand to manganese although no chloride coordination was found within 2.2 Å of the manganese atom in the EXAFS spectra. At present, the nature of their interaction with the OEC is not known. In this regard, it is of interest to examine the effect of small anions on the structures and properties of dinuclear manganese center. However, there has been no such a study from the standpoint of coordination chemistry, probably due to lack of appropriate manganese complexes. Therefore, we have initiated a systematic study on dinuclear manganese complexes containing a variety of anions. In this study, our attention has been focused on manganese complexes with 1,5-bis(salicylideneamino)-3-pentanol (abbreviated as H_3L) as a dinuclear manganese center, since 1,5-bis(salicylideneamino)-3-pentanol is O-donor-rich and good dinucleating ligand.[9-13] By using this ligand, we have isolated a series of dinuclear manganese(III) complexes containing various anions and a novel tetranuclear manganese(III) complex. Here we present full details of the synthesis and characterization of these complexes.[14-17]

Experimental

Ligand Synthesis. 1,5-Diamino-3-pentanol dihydrochloride was synthesized according to the method reported by Murase et al.[18] The free 1,5-diamino-3-pentanol was obtained by the method described elsewhere.[13] 1,5-Bis(salicylideneamino)-3-pentanol was prepraed by the condensation of salicylaldehyde and 1,5-diamino-3-pentanol.[13]

Preparation of Complexes. $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (1). Manganese(II) chloride tetrahydrate (99 mg, 0.50 mmol) and 1,5-bis(salicylideneamino)-3-pentanol (82 mg, 0.25 mmol) were dissolved in absolute methanol, then triethylamine (ca. 200 mg) was added. The mixture was refluxed for 15 min and filtered. Diethyl ether (ca. 2 ml) was layered onto the filtrate and the mixture placed in a refrigerator overnight. The dark green crystals were deposited and collected by filtration (yield 12 mg). The crystals were efflorescent in air, so microanalytical determination was not possible. IR (Nujol mull, cm^{-1}) ν(OH) 3206; ν(C=N) 1617. Λ_M (methanol, S $mol^{-1}cm^2$) 132.

$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (2). Manganese(III) acetate dihydrate (134 mg, 0.50 mmol) and 1,5-bis(salicylideneamino)-3-pentanol (82 mg, 0.25 mmol) were dissolved in absolute methanol (3.5 ml) and filtered. To the filtrate was added a methanol solution of sodium bromide (103 mg, 1.0 mmol). From the dark green solution, black crystals were deposited upon cooling. The crystals were filtered, washed with methanol, and dried over P_2O_5 in vacuo (yield 91 mg). Anal. Calcd for $C_{24}H_{33}BrMn_2N_2O_8$: C, 43.20; H, 4.98; N, 4.20%. Found: C, 42.79; H, 4.97; N, 4.18%. IR (Nujol mull, cm^{-1}) ν(OH) 3206; ν(C=N) 1614; $\nu(COO^-)$ 1536, 1409. Λ_M (methanol, S $mol^{-1}cm^2$) 94.

Table 1. Crystal Data and Data Collection Details

Complexes	$[Mn_2(L)(CH_3O)(CH_3OH)_2Cl_2]$ (1)	$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (2)	$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]I$ (3)	$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(NCS)]$ (4)
Formula	$Mn_2Cl_2O_6N_2C_{22}H_{30}$	$Mn_2BrO_8N_2C_{24}H_{33}$	$Mn_2IO_8N_2C_{24}H_{33}$	$Mn_2SO_7N_3C_{24}H_{29}$
F.W.	599.3	667.3	714.3	613.4
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	$P2_12_12_1$	$P2_12_12_1$	*Pbca*
a/Å	15.932(3)	17.087(4)	17.374(4)	19.405(3)
b/Å	23.496(4)	19.626(5)	19.813(5)	30.957(6)
c/Å	14.053(2)	8.413(3)	8.433(3)	8.970(2)
β/°				
V/Å^3	5260.8	2821.3	2902.8	5388.4
Z	8	4	4	8
D_c/g cm^{-3}	1.52	1.57	1.63	1.51
D_m/g cm^{-3}	1.56	1.57	1.63	1.52
$F(000)$	2464	1360	1432	2528
μ(Mo $K\alpha$)/cm^{-1}	11.69	23.08	19.33	10.20
Crystal dimensions/mm	0.10×0.60×0.61	0.25×0.48×0.50	0.15×0.36×0.40	0.18×0.29×0.72
2θ range/°	2.0—48.0	2.0—58.0	2.0—58.0	2.0—54.0
Total no. of observed reflections	4421	4237	4348	4900
No. of unique reflections with $I>3\sigma(I)$	2057	2222	2374	1782
Final no. of variables	307	334	334	334
Final residuals				
R	0.049	0.068	0.054	0.065
R_w	0.054	0.079	0.059	0.074

Complexes	$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (5)	$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)]$ (7)	$[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (8)
Formula	$Mn_2O_7N_5C_{23}H_{29}$	$Mn_2O_8N_4C_{22}H_{26}$	$Mn_4O_{18}N_4C_{44}H_{60}$
F.W.	597.4	584.3	1152.7
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pca2_1$	$P2_1/c$	$P2_1/n$
a/Å	19.905(4)	13.917(18)	17.380(7)
b/Å	15.760(2)	10.513(4)	11.338(4)
c/Å	8.200(2)	18.138(15)	12.439(5)
β/°		110.92(4)	95.93(2)
V/Å^3	2572.3	2478.9	2438.0
Z	4	4	2
D_c/g cm^{-3}	1.54	1.57	1.57
D_m/g cm^{-3}	1.53	1.55	1.54
$F(000)$	1232	1200	1192
μ(Mo $K\alpha$)/cm^{-1}	9.92	10.30	10.46
Crystal dimensions/mm	0.10×0.25×0.55	0.08×0.21×0.31	0.25×0.34×0.49
2θ range/°	2.0—56.0	2.0—46.0	2.0—48.0
Total no. of observed reflections	3548	3834	4243
No. of unique reflections with $I>3\sigma(I)$	1414	1260	2213
Final no. of variables	333	215	316
Final residuals			
R	0.066	0.059	0.046
R_w	0.074	0.065	0.049

[Mn_2(L)(CH_3O)(CH_3COO)($CH_3OH)_2$]I (3). This complex was prepared in the same way as that for [Mn_2(L)(CH_3O)(CH_3COO)($CH_3OH)_2$]Br except for using potassium iodide instead of sodium bromide. Anal. Calcd for $C_{24}H_{33}IMn_2N_2O_8$: C, 40.36; H, 4.66; N, 3.92%. Found: C, 40.15; H, 4.64; N, 3.93%. IR (Nujol mull, cm^{-1}) ν(OH) 3270; ν(C=N) 1613; $\nu(COO^-)$ 1536, 1408. Λ_M (methanol, S $mol^{-1}cm^2$) 98.

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)NCS] (4). Manganese(III) acetate dihydrate (134 mg, 0.50 mmol) and 1,5-bis(salicylideneamino)-3-pentanol (82 mg, 0.25 mmol) were dissolved in absolute methanol (3.5 ml) and filtered. To the filtrate was added a methanol solution of sodium thiocyanate (41 mg, 0.50 mmol) to give dark green crystals. The crystals were filtered, washed with methanol, and dried over P_2O_5 in vacuo (yield 81 mg). Anal. Calcd for $C_{24}H_{29}Mn_2N_3O_7S$: C, 46.99; H, 4.76; N, 6.85%. Found: C, 46.91; H, 4.80; N, 6.81%. IR (Nujol mull, cm^{-1}) ν(OH) 3482; ν(NCS) 2060; ν(C=N) 1613; $\nu(COO^-)$ 1539, 1414. Λ_M (methanol, S $mol^{-1}cm^2$) 98.

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)N_3] (5). This complex was prepared in the same way as that for [Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)NCS] except for using sodium azide instead of sodium thiocyanate. The crystals were efflorescent, so microanalytical determination was not possible. IR (Nujol mull, cm^{-1}) ν(OH) 3330; $\nu(N_3)$ 2030; ν(C=N) 1616; $\nu(COO^-)$ 1542, 1407. Λ_M (methanol, S $mol^{-1}cm^2$) 85.

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)ClO_4] (6). This complex was prepared in the same way as that for [Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)NCS] except for using sodium perchlorate instead of sodium thiocyanate. Anal. Calcd for $C_{23}H_{29}ClMn_2N_2O_{11}$: C, 42.19; H, 4.46; N, 4.28%. Found: C, 42.11; H, 4.47; N, 4.39%. IR (Nujol mull, cm^{-1}) ν(OH) 3404; ν(C=N) 1615; $\nu(COO^-)$ 1536, 1420; $\nu(ClO_4)$ 1120sh, 1105, 1065, 1050. Λ_M (methanol, S $mol^{-1}cm^2$) 106.

[(Mn_2(L)(CH_3O)($NCO)_2$($H_2O)_2$] (7) and [Mn_4(L)$_2$($O)_2$($CH_3COO)_2$]·$4H_2O$·$2CH_3OH$ (8). Manganese(III) acetate dihydrate (134 mg, 0.50 mmol) and 1,5-bis(salicylideneamino)-3-pentanol (82 mg, 0.25 mmol) were dissolved in 3.5 ml of absolute methanol and filtered. To the filtrate was added a methanol–water (1 : 1) solution of sodium cyanate (73 mg, 1.0 mmol) to give a small amount of dark green crystals of **7**. The crystals were collected by filtration (yield 9 mg). Anal. Calcd for $C_{22}H_{26}Mn_2N_4O_8$: C, 45.22; H, 4.48; N, 9.59%. Found: C, 45.25; H, 4.51; N, 9.53%. IR (Nujol mull, cm^{-1}) ν(OH) 3426, 3286; ν(NCO) 2172; ν(C=N) 1615. Λ_M (methanol, S $mol^{-1}cm^2$) 79. Upon standing the filtrate for several weeks, black crystals **8** were deposited (yield 40 mg). Anal. Calcd for $C_{44}H_{60}Mn_4N_4O_{18}$: C, 45.85; H, 5.25; N, 4.86%. Found: C, 45.16; H, 5.04; N, 5.00%. IR (Nujol mull, cm^{-1}) ν(OH) 3374; ν(C=N) 1619; $\nu(COO^-)$ 1545, 1407. Λ_M (methanol, S $mol^{-1}cm^2$) 131. The complex **8** can also be prepared as follows. Manganese(III) acetate dihydrate (134 mg, 0.50 mmol) and 1,5-bis(salicylideneamino)-3-pentanol (82 mg, 0.25 mmol) were dissolved in methanol (3.5 ml) and filtered. To the filtrate was added 2.0 ml of water and triethylamine (51 mg, 0.50 mmol). From the dark green solution, black crystals were deposited (yield 44 mg).

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the region 4000—400 cm^{-1} on a Nujol mull. Electric conductivities were measured on a Horiba conductivity meter DS-14 in ca. 10^{-3} $mol\,dm^{-3}$ methanol solutions of the complexes. Electronic spectra were measured with a Shimadzu UV-Vis-NIR Recording Spectrophotometer Model UV-3100. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80—300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[19] Effective magnetic moments were calculated from the equation, $\mu_{eff}=2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility. Cyclic voltammetric measurements were carried out on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HB-104 function generator and a Yokogawa 3086 X-Y recorder. A three-electrode cell comprised of a glassy carbon electrode, a platinum-wire counter electrode, and a Ag/AgCl electrode was used.

X-Ray Crystal Structure Analysis. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. Crystal data and details of the data collection are given in Table 1. Lattice constants were determined by least-squares refinement based on 25 reflections with $20\leq 2\theta\leq 30°$. The intensity data were corrected for Lorentz-polarization effects, but not for absorption. The structures were solved by the direct methods. Refinements were carried out by the full-matrix least-squares methods. Hydrogen atoms of methanol, water, and acetate ion were located from the difference Fourier maps and the Schiff-base's hydrogens were included at calculated positions. All the hydrogen atoms were fixed at their positions. The final discrepancy factors, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are listed in Table 1. The weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. All the calculations were

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^{2} [a]	Atom	x	y	z	B_{eq}/Å^{2} [a]
[Mn_2(L)(CH_3O)Cl_2($CH_3OH)_2$] (**1**)					[Mn_2(L)(CH_3O)(CH_3COO)($CH_3OH)_2$]Br (**2**)				
Mn1	0.97461(8)	0.20690(5)	0.66776(8)	3.39(2)	Br	0.8937(1)	0.15190(8)	0.9913(3)	5.38(3)
Mn2	0.96143(7)	0.08235(5)	0.71442(8)	3.23(2)	Mn1	0.1508(1)	0.33085(9)	0.3209(2)	2.60(3)
Cl1	1.0996(2)	0.22491(9)	0.7749(2)	4.99(5)	Mn2	0.2473(1)	0.20982(9)	0.3857(2)	2.71(3)
Cl2	0.8496(1)	0.0597(1)	0.5912(2)	5.06(5)	O1	0.0555(5)	0.3427(4)	0.222(1)	3.7(2)
O1	0.9138(4)	0.2696(2)	0.7060(4)	4.7(1)	O2	0.2563(5)	0.3092(4)	0.392(1)	2.9(2)
O2	1.0198(3)	0.1339(2)	0.6291(3)	3.3(1)	O3	0.2303(5)	0.1167(4)	0.357(1)	3.7(2)
O3	0.9053(3)	0.0424(2)	0.8088(4)	4.0(1)	O4	0.1567(5)	0.2351(4)	0.259(1)	2.9(2)
O4	0.9135(3)	0.1554(2)	0.7500(4)	3.4(1)	O5	0.1028(6)	0.3026(4)	0.546(1)	4.2(2)
O5	0.8728(4)	0.1864(3)	0.5498(4)	5.5(2)	O6	0.1774(6)	0.2136(5)	0.601(1)	4.0(2)
O6	1.0697(4)	0.1003(3)	0.8159(4)	5.3(1)	O7	0.2124(6)	0.3702(5)	0.095(1)	4.4(2)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} [a)]	Atom	x	y	z	B_{eq}/Å^{2} [a)]
N1	1.0307(4)	0.2512(3)	0.5641(4)	3.8(1)	O8	0.3169(5)	0.2076(5)	0.146(1)	3.9(2)
N2	1.0277(4)	0.0130(3)	0.6793(4)	3.6(1)	N1	0.1541(7)	0.4283(5)	0.394(1)	3.2(2)
C1	0.8943(5)	0.3163(3)	0.6568(6)	3.7(2)	N2	0.3499(6)	0.1943(5)	0.495(1)	3.4(2)
C2	0.8307(6)	0.3516(4)	0.6916(6)	4.7(2)	C1	0.0212(7)	0.3995(6)	0.174(2)	2.9(2)
C3	0.8071(6)	0.3996(4)	0.6441(7)	5.4(2)	C2	−0.0403(8)	0.3942(7)	0.066(2)	4.1(3)
C4	0.8464(6)	0.4150(4)	0.5603(7)	5.7(2)	C3	−0.0803(8)	0.4536(8)	0.012(2)	5.0(4)
C5	0.9087(7)	0.3812(4)	0.5243(6)	5.6(2)	C4	−0.0596(9)	0.5164(7)	0.075(2)	5.0(4)
C6	0.9335(5)	0.3306(3)	0.5701(6)	3.9(2)	C5	0.0005(8)	0.5219(6)	0.184(2)	3.9(3)
C7	1.0028(5)	0.2987(4)	0.5333(5)	4.6(2)	C6	0.0437(7)	0.4645(6)	0.235(2)	3.0(3)
C8	1.1078(5)	0.2272(4)	0.5213(6)	4.8(2)	C7	0.1046(8)	0.4729(6)	0.346(2)	3.2(3)
C9	1.0997(6)	0.1655(4)	0.4929(6)	5.2(2)	C8	0.2095(9)	0.4473(6)	0.517(2)	4.5(3)
C10	1.0955(5)	0.1246(3)	0.5761(6)	3.9(2)	C9	0.2920(8)	0.4217(6)	0.487(2)	4.5(3)
C11	1.0989(6)	0.0630(4)	0.5443(6)	5.2(2)	C10	0.2984(8)	0.3425(7)	0.515(2)	4.0(3)
C12	1.1069(6)	0.0203(4)	0.6254(7)	5.0(2)	C11	0.3835(8)	0.3185(6)	0.517(2)	4.4(3)
C13	1.0058(5)	−0.0380(3)	0.7028(5)	3.7(2)	C12	0.3880(8)	0.2478(8)	0.594(2)	4.8(3)
C14	0.9366(5)	−0.0535(3)	0.7605(5)	3.4(2)	C13	0.3872(8)	0.1359(7)	0.488(2)	4.1(3)
C15	0.9158(5)	−0.1116(3)	0.7715(6)	4.0(2)	C14	0.3596(8)	0.0738(7)	0.414(2)	4.0(3)
C16	0.8518(6)	−0.1299(4)	0.8280(6)	4.7(2)	C15	0.412(1)	0.0187(8)	0.410(2)	6.1(4)
C17	0.8038(6)	−0.0896(4)	0.8769(6)	4.4(2)	C16	0.389(1)	−0.0434(8)	0.342(2)	6.3(4)
C18	0.8214(5)	−0.0324(3)	0.8675(6)	3.9(2)	C17	0.313(1)	−0.0487(7)	0.283(2)	5.1(4)
C19	0.8881(5)	−0.0124(3)	0.8108(5)	3.5(2)	C18	0.260(1)	0.0047(7)	0.283(2)	4.2(3)
C20	0.8308(5)	0.1637(4)	0.7860(6)	5.1(2)	C19	0.2842(8)	0.0679(6)	0.353(2)	3.4(3)
C21	0.807(1)	0.2099(6)	0.512(1)	21.3(5)	C20	0.0903(7)	0.1940(6)	0.233(2)	3.7(3)
C22	1.1137(7)	0.0675(5)	0.8829(8)	7.9(3)	C21	0.1209(8)	0.2528(7)	0.629(2)	3.6(3)
					C22	0.070(1)	0.2346(8)	0.766(2)	5.3(4)
					C23	0.183(1)	0.3761(9)	−0.056(2)	6.5(5)
					C24	0.274(1)	0.1836(8)	0.010(2)	5.0(4)
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]I$ (3)					$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(NCS)]$ (4)				
I	0.89561(5)	0.15019(4)	0.0051(1)	4.61(2)	Mn1	0.11376(4)	0.04401(8)	0.5995(2)	3.83(3)
Mn1	0.7433(1)	0.29297(9)	0.3902(2)	2.86(3)	Mn2	0.16298(4)	−0.08326(7)	0.5471(2)	3.63(3)
Mn2	0.6474(1)	0.17430(9)	0.3255(2)	2.85(3)	S	0.0689(1)	−0.1312(2)	0.1087(4)	7.18(9)
O1	0.7277(5)	0.3845(4)	0.363(1)	3.6(2)	O1	0.1258(2)	0.1366(3)	0.5680(8)	4.4(2)
O2	0.7525(4)	0.1960(4)	0.3938(9)	3.0(1)	O2	0.1040(2)	−0.0544(3)	0.5999(7)	3.6(1)
O3	0.5513(4)	0.1624(4)	0.232(1)	3.9(2)	O3	0.2184(2)	−0.1015(3)	0.4816(8)	4.6(2)
O4	0.6527(4)	0.2671(4)	0.269(1)	3.0(2)	O4	0.1651(2)	0.0131(3)	0.4957(7)	4.3(2)
O5	0.6776(5)	0.2880(4)	0.610(1)	4.1(2)	O5	0.1414(2)	0.0370(3)	0.8153(7)	4.6(2)
O6	0.6039(5)	0.1989(4)	0.554(1)	4.7(2)	O6	0.1805(2)	−0.0596(3)	0.7804(7)	4.3(2)
O7	0.8100(4)	0.2967(4)	0.150(1)	3.8(2)	O7	0.0789(2)	0.0343(4)	0.3600(8)	5.4(2)
O8	0.7025(5)	0.1375(5)	0.092(1)	5.0(2)	N1	0.0541(2)	0.0663(4)	0.6757(8)	3.6(2)
N1	0.8446(5)	0.3087(5)	0.497(1)	3.5(2)	N2	0.1541(2)	−0.1824(4)	0.6033(8)	3.9(2)
N2	0.6514(6)	0.0778(5)	0.390(1)	3.7(2)	N3	0.1329(3)	−0.1091(5)	0.3158(9)	6.3(2)
C1	0.7805(7)	0.4325(6)	0.356(2)	3.5(3)	C1	0.0979(3)	0.1871(5)	0.539(1)	4.1(2)
C2	0.7620(8)	0.4936(7)	0.285(2)	3.9(3)	C2	0.1146(3)	0.2485(5)	0.477(1)	4.3(2)
C3	0.812(1)	0.5471(7)	0.279(2)	5.3(4)	C3	0.0876(3)	0.3028(5)	0.451(1)	5.0(3)
C4	0.886(1)	0.5408(7)	0.345(2)	6.1(4)	C4	0.0436(3)	0.2989(5)	0.481(1)	5.3(3)
C5	0.9051(9)	0.4807(7)	0.410(2)	5.5(3)	C5	0.0273(3)	0.2398(5)	0.541(1)	4.6(2)
C6	0.8551(8)	0.4252(7)	0.415(2)	4.1(3)	C6	0.0539(3)	0.1834(5)	0.573(1)	3.9(2)
C7	0.8801(6)	0.3661(6)	0.489(2)	4.1(3)	C7	0.0357(3)	0.1245(5)	0.644(1)	4.0(2)
C8	0.8820(8)	0.2532(7)	0.591(2)	4.8(3)	C8	0.0308(3)	0.0151(5)	0.767(1)	5.4(3)
C9	0.8757(6)	0.1860(6)	0.517(2)	4.2(3)	C9	0.0324(3)	−0.0577(5)	0.706(1)	5.1(3)
C10	0.7938(6)	0.1588(6)	0.515(2)	3.6(2)	C10	0.0779(3)	−0.0872(5)	0.710(1)	4.0(2)
C11	0.7879(8)	0.0832(6)	0.483(2)	5.1(3)	C11	0.0778(3)	−0.1648(5)	0.680(1)	5.1(3)
C12	0.7087(8)	0.0546(6)	0.510(2)	5.6(3)	C12	0.1210(3)	−0.1981(5)	0.719(1)	4.7(2)
C13	0.6030(8)	0.0335(6)	0.337(1)	3.7(2)	C13	0.1776(3)	−0.2315(5)	0.551(1)	3.9(2)
C14	0.5421(7)	0.0433(6)	0.228(1)	3.0(2)	C14	0.2126(3)	−0.2235(4)	0.446(1)	3.5(2)
C15	0.5024(8)	−0.0142(7)	0.177(2)	4.5(3)	C15	0.2304(3)	−0.2835(4)	0.379(1)	4.5(2)
C16	0.4420(9)	−0.0070(7)	0.068(2)	5.6(4)	C16	0.2647(3)	−0.2790(5)	0.281(1)	5.1(3)
C17	0.4203(7)	0.0551(7)	0.017(2)	5.2(3)	C17	0.2825(3)	−0.2152(5)	0.252(1)	4.9(3)
C18	0.4573(7)	0.1123(7)	0.071(2)	4.2(3)	C18	0.2675(3)	−0.1563(5)	0.319(1)	4.5(2)
C19	0.5200(6)	0.1058(6)	0.182(2)	3.2(2)	C19	0.2318(3)	−0.1591(4)	0.417(1)	3.6(2)
C20	0.5882(7)	0.3100(6)	0.244(2)	4.4(3)	C20	0.2004(3)	0.0516(5)	0.448(1)	6.1(3)
C21	0.6216(7)	0.2489(6)	0.634(2)	3.9(3)	C21	0.1664(3)	−0.0096(4)	0.858(1)	3.5(2)
C22	0.5708(9)	0.2667(9)	0.774(2)	7.0(4)	C22	0.1838(3)	−0.0058(6)	1.017(1)	5.2(3)
C23	0.7686(7)	0.3184(7)	0.013(2)	4.5(3)	C23	0.0863(4)	0.0783(6)	0.237(1)	6.4(3)
C24	0.674(1)	0.119(1)	−0.053(2)	8.3(6)	C24	0.1067(3)	−0.1180(5)	0.230(1)	4.7(2)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} [a]	Atom	x	y	z	B_{eq}/Å^{2} [a]
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (**5**)					$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**)				
Mn1	0.59202(9)	0.8248(1)	0.277	2.92(3)	Mn1	0.3107(2)	0.2649(2)	0.3258(1)	2.58(4)
Mn2	0.4700(1)	0.7217(1)	0.3308(3)	3.02(3)	Mn2	0.1970(2)	0.4346(2)	0.1913(1)	2.47(4)
O1	0.6059(4)	0.9359(6)	0.214(1)	3.8(2)	O1	0.3568(7)	0.277(1)	0.4354(5)	3.0(2)
O2	0.5675(4)	0.7065(5)	0.321(1)	3.2(2)	O2	0.2756(6)	0.278(1)	0.2112(5)	3.2(2)
O3	0.3787(4)	0.7418(5)	0.303(1)	3.7(2)	O3	0.1137(7)	0.577(1)	0.1817(5)	3.7(2)
O4	0.4970(4)	0.8239(6)	0.218(1)	3.1(2)	O4	0.2353(6)	0.4235(9)	0.3042(5)	2.8(2)
O5	0.5686(5)	0.8557(7)	0.526(1)	4.6(2)	O5	0.1168(8)	−0.049(1)	0.3370(6)	5.1(3)
O6	0.4759(5)	0.7781(7)	0.560(1)	4.1(2)	O6	0.0586(7)	0.306(1)	0.1797(6)	3.7(3)
O7	0.4690(5)	0.6547(6)	0.062(1)	4.4(2)	O7	0.4520(7)	0.3866(9)	0.3294(5)	3.1(2)
N1	0.6885(5)	0.8127(7)	0.337(2)	4.3(3)	O8	0.3808(8)	0.756(1)	0.1835(7)	5.8(3)
N2	0.4523(6)	0.6058(7)	0.411(2)	3.4(2)	N1	0.3958(8)	0.105(1)	0.3339(6)	2.7(3)
N3	0.6251(6)	0.7792(8)	0.015(2)	4.2(3)	N2	0.1595(9)	0.428(1)	0.0730(6)	3.5(3)
N4	0.6121(6)	0.7127(9)	−0.034(2)	4.8(3)	N3	0.1687(9)	0.154(1)	0.3096(7)	3.6(3)
N5	0.5971(9)	0.648(1)	−0.091(3)	8.8(5)	N4	0.3387(9)	0.542(1)	0.2019(6)	3.5(3)
C1	0.6622(6)	0.9697(8)	0.154(2)	2.9(3)	C1	0.4537(9)	0.257(1)	0.4785(7)	2.5(3)*
C2	0.6589(8)	1.045(1)	0.064(2)	4.0(3)	C2	0.499(1)	0.331(2)	0.5490(9)	3.8(4)*
C3	0.7135(8)	1.086(1)	0.005(2)	4.3(4)	C3	0.598(1)	0.310(2)	0.5979(9)	4.4(4)*
C4	0.7776(7)	1.050(1)	0.032(2)	4.8(4)	C4	0.655(1)	0.212(2)	0.5837(9)	4.7(4)*
C5	0.7826(7)	0.978(1)	0.123(2)	4.7(4)	C5	0.615(1)	0.139(2)	0.5171(8)	3.3(3)*
C6	0.7259(7)	0.9353(9)	0.181(2)	3.6(3)	C6	0.514(1)	0.157(1)	0.4650(8)	2.8(3)*
C7	0.7351(5)	0.8631(8)	0.283(2)	3.9(3)	C7	0.478(1)	0.084(2)	0.3944(8)	3.1(3)*
C8	0.7067(7)	0.743(1)	0.447(2)	5.1(4)	C8	0.364(1)	0.019(2)	0.2652(9)	3.7(3)*
C9	0.6760(7)	0.6585(9)	0.407(2)	4.4(3)	C9	0.354(1)	0.085(1)	0.1896(8)	3.2(3)*
C10	0.6016(6)	0.6553(8)	0.440(2)	3.4(3)	C10	0.266(1)	0.176(1)	0.1575(8)	2.7(3)*
C11	0.5745(8)	0.568(1)	0.436(2)	5.0(4)	C11	0.258(1)	0.233(2)	0.0771(8)	3.7(3)*
C12	0.5035(8)	0.561(1)	0.508(2)	4.9(4)	C12	0.162(1)	0.304(2)	0.0350(8)	3.8(4)*
C13	0.3985(8)	0.5620(9)	0.382(2)	3.9(3)	C13	0.136(1)	0.530(2)	0.0325(8)	3.6(3)*
C14	0.3391(7)	0.5956(9)	0.297(2)	3.4(3)	C14	0.123(1)	0.656(1)	0.0599(8)	3.3(3)*
C15	0.2859(7)	0.5398(9)	0.266(2)	4.8(4)	C15	0.120(1)	0.762(2)	0.0120(8)	4.0(3)*
C16	0.2265(7)	0.570(1)	0.204(2)	5.8(4)	C16	0.102(1)	0.880(2)	0.035(1)	5.1(4)*
C17	0.2194(8)	0.657(1)	0.180(2)	5.5(4)	C17	0.084(1)	0.895(2)	0.105(1)	5.2(4)*
C18	0.2697(6)	0.713(1)	0.212(2)	4.4(4)	C18	0.088(1)	0.797(2)	0.1558(9)	3.7(3)*
C19	0.3314(6)	0.6846(9)	0.275(2)	3.5(3)	C19	0.111(1)	0.674(1)	0.1345(8)	2.8(3)*
C20	0.4559(7)	0.8966(9)	0.202(2)	4.8(4)	C20	0.185(1)	0.476(2)	0.3531(9)	4.4(4)*
C21	0.5180(8)	0.8323(9)	0.604(2)	4.1(3)	C21	0.144(1)	0.054(1)	0.3241(7)	2.7(3)*
C22	0.5079(8)	0.872(1)	0.775(2)	4.9(4)	C22	0.360(1)	0.649(2)	0.1933(8)	3.4(3)*
C23	0.4233(9)	0.676(1)	−0.064(2)	6.1(4)					

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} [a]	Atom	x	y	z	B_{eq}/Å^{2} [a]
$[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**)									
Mn1	0.36829(6)	0.08292(9)	0.39899(8)	3.42(2)	C5	0.1039(4)	0.1609(7)	0.4299(7)	4.7(2)
Mn2	0.53646(5)	0.05081(9)	0.41229(8)	3.08(2)	C6	0.1825(4)	0.1458(6)	0.4173(6)	3.8(2)
Ox	0.4596(2)	0.0922(4)	0.5026(3)	3.14(9)	C7	0.2028(4)	0.0868(7)	0.3214(6)	4.0(2)
O1	0.3134(2)	0.1710(4)	0.4950(4)	4.1(1)	C8	0.2744(5)	−0.0162(9)	0.2010(6)	6.5(2)
Ow1	0.4134(4)	0.6960(6)	0.3808(5)	8.8(2)	C9	0.3483(5)	0.0047(9)	0.1480(6)	5.5(2)
Om1	0.6276(6)	0.478(2)	0.494(1)	22.1(6)	C10	0.4194(4)	−0.0476(7)	0.2082(5)	4.4(2)
O2	0.4322(3)	−0.0054(4)	0.3151(3)	3.9(1)	C11	0.4914(4)	−0.0296(7)	0.1522(6)	4.9(2)
Ow2	0.5746(5)	0.6625(6)	0.3908(6)	10.0(2)	C12	0.5635(5)	−0.0865(8)	0.2094(6)	5.3(2)
O3	0.6433(2)	0.0947(4)	0.5053(4)	3.8(1)	C13	0.6758(4)	0.0059(7)	0.2941(6)	4.7(2)
O4	0.4050(3)	0.2454(4)	0.3220(4)	4.6(1)	C14	0.7294(4)	0.0709(6)	0.3684(6)	4.2(2)
O5	0.5328(3)	0.2083(4)	0.3391(4)	4.2(1)	C15	0.8054(4)	0.0857(8)	0.3392(7)	5.5(2)
N1	0.2703(3)	0.0534(5)	0.3004(4)	4.0(1)	C16	0.8604(4)	0.1406(8)	0.4048(8)	6.5(2)
N2	0.6026(3)	−0.0138(5)	0.2966(4)	3.8(1)	C17	0.8432(4)	0.1845(7)	0.5039(8)	6.5(2)
C1	0.2383(4)	0.1843(6)	0.4993(6)	3.6(1)	C18	0.7699(4)	0.1714(7)	0.5364(7)	5.0(2)
Cm1	0.680(1)	0.430(1)	0.432(1)	15.9(5)	C19	0.7112(4)	0.1127(6)	0.4702(6)	3.9(2)
C2	0.2128(4)	0.2376(7)	0.5911(6)	4.4(2)	C20	0.4731(4)	0.2735(6)	0.3149(6)	4.3(2)
C3	0.1354(4)	0.2499(7)	0.6017(7)	5.2(2)	C21	0.4894(5)	0.3952(7)	0.2726(7)	5.8(2)
C4	0.0813(4)	0.2109(8)	0.5210(7)	5.5(2)					

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. b) Starred atoms were refined isotropically.

carried out on the Micro-VAXII computer using the Enraf-Nonius SDP program package.[20] Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and temperature factors of hydrogen atoms, and the F_o-F_c tables are deposited as Document No. 9031 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis. Using 1,5-bis(salicylideneamino)-3-pentanol as dinucleating ligands has proved to be convenient to prepare a series of alkoxo-bridged dinuclear manganese(III) complexes. The synthesis of $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]X$ (X=Br (**2**), I (**3**)) and $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)Y]$ (Y=NCS (**4**), N_3 (**5**), ClO_4 (**6**)) was accomplished by a reaction of the dinucleating ligand and manganese(III) acetate in methanol followed by addition of an appropriate potassium salt (or sodium salt). However, we have been unable to find conditions for isolation of manganese complex containing chloride ions by this method. We could isolate such a complex, $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**), by a procedure starting from manganese(II) chloride instead of manganese(III) acetate. In the case of the cyanate complex, we used a small amount of water to dissolve sodium cyanate in the preparative process and resulted in isolation of a dinuclear complex, $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**), and a tetranuclear complex, $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**). Ligation of water molecule to the manganese atom in **7** is interesting from the viewpoint of water oxidation studies, although it is not surprising to find water rather than acetate ion bound to the manganese atom because ample water is present in the reaction system. Formation of the tetranuclear complex with oxo bridges may be due to a basic condition caused by decomposition of cyanate ion during the long standing of the filtrate. It is known that sodium cyanate decomposes to form sodium carbonate and urea.[21] Addition of 1 equiv of Et_3N facilitates the conversion of dinuclear species into the tetranuclear form **8**.

Description of the Structures. $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (1). A perspective drawing of the molecule is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 3. The two manganese ions, Mn1 and Mn2, are bridged by an alkoxo oxygen atom (O2) of the Schiff base ligand and the methoxo oxygen atom, O4. The Mn1···Mn2 separation is 3.006(2) Å, and the Mn1–O2–Mn2 and Mn1–O4–Mn2 angles are 101.6(2) and 101.6(2)°, respectively. The coordination geometry of each manganese ion is an elongated octahedron. The square plane around the manganese ion is formed by O_3N donor atoms of L and the methoxo O atom. The in-plane-bond distances

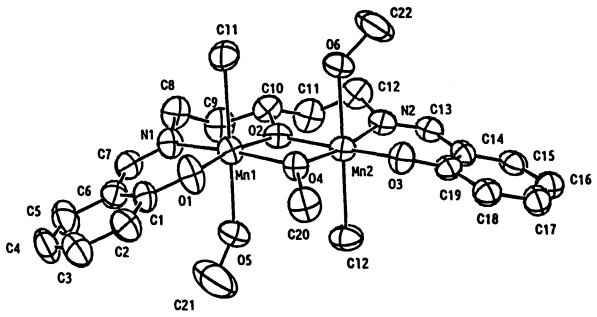

Fig. 1. A perspective view of $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**). Hydrogen atoms are not shown for clarity.

Table 3. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

$[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**)				$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (**2**)			
Mn1–Mn2	3.006(2)	Mn1–N1	2.001(6)	Mn1–Mn2	2.943(3)	Mn1–N1	2.012(10)
Mn1–O1	1.844(5)	Mn1–O2	1.938(5)	Mn1–O1	1.841(9)	Mn1–O2	1.948(9)
Mn1–O4	1.937(5)	Mn1–O5	2.369(6)	Mn1–O4	1.953(7)	Mn1–O5	2.140(10)
Mn1–Cl1	2.532(3)	Mn2–N2	2.004(6)	Mn1–O7	2.306(10)	Mn2–N2	2.002(11)
Mn2–O2	1.942(5)	Mn2–O3	1.855(5)	Mn2–O2	1.958(7)	Mn2–O3	1.866(8)
Mn2–O4	1.944(5)	Mn2–O6	2.278(6)	Mn2–O4	1.946(9)	Mn2–O6	2.173(10)
Mn2–Cl2	2.541(3)			Mn2–O8	2.339(10)		
Mn1–O2–Mn2	101.6(2)	Mn1–O4–Mn2	101.6(2)	Mn1–O2–Mn2	97.8(4)	Mn1–O4–Mn2	98.0(4)
O1–Mn1–O4	93.5(2)	O1–Mn1–N1	91.7(2)	O1–Mn1–O4	92.7(4)	O1–Mn1–N1	92.5(5)
O2–Mn1–O4	78.5(2)	O2–Mn1–N1	95.2(2)	O2–Mn1–O4	79.9(3)	O2–Mn1–N1	94.9(4)
O5–Mn1–O1	90.4(2)	O5–Mn1–O2	83.0(2)	O5–Mn1–O1	95.3(5)	O5–Mn1–O2	91.4(3)
O5–Mn1–O4	86.9(2)	O5–Mn1–N1	84.4(2)	O5–Mn1–O4	90.5(4)	O5–Mn1–N1	89.1(4)
Cl1–Mn1–O1	96.1(2)	Cl1–Mn1–O2	91.3(2)	O7–Mn1–O1	89.5(4)	O7–Mn1–O2	84.5(4)
Cl1–Mn1–O4	98.3(2)	Cl1–Mn1–N1	89.7(2)	O7–Mn1–O4	94.4(3)	O7–Mn1–N1	85.5(4)
O3–Mn2–O4	94.2(2)	O3–Mn2–N2	91.1(2)	O3–Mn2–O4	93.1(4)	O3–Mn2–N2	92.7(4)
O2–Mn2–O4	78.3(2)	O2–Mn2–N2	95.9(2)	O2–Mn2–O4	79.9(3)	O2–Mn2–N2	94.0(4)
O6–Mn2–O2	84.7(2)	O6–Mn2–O3	90.6(2)	O6–Mn2–O2	89.1(3)	O6–Mn2–O3	93.2(4)
O6–Mn2–O4	88.5(2)	O6–Mn2–N2	84.6(2)	O6–Mn2–O4	90.7(4)	O6–Mn2–N2	96.0(4)
Cl2–Mn2–O2	92.6(2)	Cl2–Mn2–O3	92.5(2)	O8–Mn2–O2	90.2(3)	O8–Mn2–O3	87.1(4)
Cl2–Mn2–O4	94.8(2)	Cl2–Mn2–N2	91.8(2)	O8–Mn2–O4	86.3(4)	O8–Mn2–N2	86.9(4)

Table 3. (Continued)

$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]I$ (3)				$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(NCS)]$ (4)			
Mn1–Mn2	2.933(2)	Mn1–N1	2.000(9)	Mn1–Mn2	2.940(2)	Mn1–N1	2.015(6)
Mn1–O1	1.848(8)	Mn1–O2	1.928(7)	Mn1–O1	1.856(6)	Mn1–O2	1.934(6)
Mn1–O4	1.943(8)	Mn1–O5	2.179(9)	Mn1–O4	1.937(6)	Mn1–O5	2.121(6)
Mn1–O7	2.335(9)	Mn2–N2	1.987(9)	Mn1–O7	2.411(7)	Mn2–N2	2.007(7)
Mn2–O2	1.962(8)	Mn2–O3	1.861(8)	Mn2–O2	1.969(5)	Mn2–O3	1.847(6)
Mn2–O4	1.901(7)	Mn2–O6	2.128(9)	Mn2–O4	1.928(6)	Mn2–O6	2.209(6)
Mn2–O8	2.305(9)			Mn2–N3	2.329(8)		
Mn1–O2–Mn2	97.8(3)	Mn1–O4–Mn2	99.4(3)	Mn1–O2–Mn2	97.7(2)	Mn1–O4–Mn2	99.0(3)
O1–Mn1–O4	94.2(3)	O1–Mn1–N1	91.9(3)	O1–Mn1–O4	93.5(2)	O1–Mn1–N1	91.6(3)
O2–Mn1–O4	79.2(4)	O2–Mn1–N1	94.3(3)	O2–Mn1–O4	79.9(2)	O2–Mn1–N1	93.9(3)
O5–Mn1–O1	94.3(4)	O5–Mn1–O2	89.1(3)	O5–Mn1–O1	96.9(3)	O5–Mn1–O2	89.9(2)
O5–Mn1–O4	90.6(4)	O5–Mn1–N1	94.9(4)	O5–Mn1–O4	95.0(3)	O5–Mn1–N1	94.2(3)
O7–Mn1–O1	86.1(4)	O7–Mn1–O2	90.2(4)	O7–Mn1–O1	91.7(3)	O7–Mn1–O2	81.7(2)
O7–Mn1–O4	87.4(4)	O7–Mn1–N1	87.0(4)	O7–Mn1–O4	85.1(2)	O7–Mn1–N1	84.8(3)
O3–Mn2–O4	93.5(3)	O3–Mn2–N2	91.4(4)	O3–Mn2–O4	94.4(3)	O3–Mn2–N2	91.3(3)
O2–Mn2–O4	79.4(3)	O2–Mn2–N2	95.7(4)	O2–Mn2–O4	79.3(2)	O2–Mn2–N2	94.9(3)
O6–Mn2–O2	90.8(3)	O6–Mn2–O3	95.3(3)	O6–Mn2–O2	86.6(2)	O6–Mn2–O3	96.5(3)
O6–Mn2–O4	91.2(3)	O6–Mn2–N2	89.2(4)	O6–Mn2–O4	91.0(2)	O6–Mn2–N2	89.7(3)
O8–Mn2–O2	86.2(4)	O8–Mn2–O3	88.4(3)	N3–Mn2–O2	84.5(3)	N3–Mn2–O3	92.6(3)
O8–Mn2–O4	94.2(4)	O8–Mn2–N2	85.1(4)	N3–Mn2–O4	90.5(3)	N3–Mn2–N2	87.9(3)

Table 3. (Continued)

$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (5)				$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (7)			
Mn1–Mn2	2.955(3)	Mn1–N1	1.992(10)	Mn1–Mn2	2.980(3)	Mn1–N1	2.029(11)
Mn1–O1	1.847(9)	Mn1–O2	1.960(8)	Mn1–O1	1.863(8)	Mn1–O2	1.962(9)
Mn1–O4	1.952(8)	Mn1–O5	2.149(10)	Mn1–O4	1.935(9)	Mn1–O7	2.327(10)
Mn1–N3	2.358(12)	Mn2–N2	1.974(11)	Mn1–N3	2.221(12)	Mn2–N2	2.020(11)
Mn2–O2	1.957(8)	Mn2–O3	1.859(8)	Mn2–O2	1.942(10)	Mn2–O3	1.867(11)
Mn2–O4	1.934(9)	Mn2–O6	2.084(10)	Mn2–O4	1.926(9)	Mn2–O6	2.302(10)
Mn2–O7	2.446(11)			Mn2–N4	2.221(13)		
Mn1–O2–Mn2	97.9(3)	Mn1–O4–Mn2	99.0(4)	Mn1–O2–Mn2	99.5(5)	Mn1–O4–Mn2	101.0(5)
O1–Mn1–O4	94.7(4)	O1–Mn1–N1	90.9(4)	O1–Mn1–O4	96.3(4)	O1–Mn1–N1	90.7(5)
O2–Mn1–O4	78.4(3)	O2–Mn1–N1	95.9(4)	O2–Mn1–O4	79.4(4)	O2–Mn1–N1	92.9(4)
O5–Mn1–O1	94.8(4)	O5–Mn1–O2	89.2(4)	O7–Mn1–O1	88.0(4)	O7–Mn1–O2	83.2(4)
O5–Mn1–O4	91.6(4)	O5–Mn1–N1	89.7(5)	O7–Mn1–O4	85.6(4)	O7–Mn1–N1	89.3(4)
N3–Mn1–O1	89.5(4)	N3–Mn1–O2	87.0(4)	N3–Mn1–O1	97.4(4)	N3–Mn1–O2	91.3(4)
N3–Mn1–O4	92.4(4)	N3–Mn1–N1	85.8(5)	N3–Mn1–O4	91.8(5)	N3–Mn1–N1	92.6(5)
O3–Mn2–O4	94.0(4)	O3–Mn2–N2	91.4(4)	O3–Mn2–O4	94.3(4)	O3–Mn2–N2	90.6(4)
O2–Mn2–O4	78.9(3)	O2–Mn2–N2	94.5(4)	O2–Mn2–O4	80.1(4)	O2–Mn2–N2	94.8(5)
O6–Mn2–O2	91.9(4)	O6–Mn2–O3	95.3(4)	O6–Mn2–O2	85.1(4)	O6–Mn2–O3	89.6(4)
O6–Mn2–O4	93.5(4)	O6–Mn2–N2	95.9(5)	O6–Mn2–O4	88.1(4)	O6–Mn2–N2	89.6(4)
O7–Mn2–O2	85.4(4)	O7–Mn2–O3	87.4(4)	N4–Mn2–O2	89.5(4)	N4–Mn2–O3	95.9(5)
O7–Mn2–O4	86.0(4)	O7–Mn2–N2	84.3(4)	N4–Mn2–O4	92.2(4)	N4–Mn2–N2	89.6(5)

Table 3. (Continued)

$[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (8)							
Mn1–Mn2	2.933(1)	Mn1–Mn2′	3.122(1)	O2–Mn1–N1	94.8(3)	O4–Mn1–O1	91.2(2)
Mn2–Mn2′	2.875(1)	Mn1–N1	2.021(5)	O4–Mn1–O2	89.4(2)	O4–Mn1–Ox	89.4(2)
Mn1–Ox	1.941(4)	Mn1–O1	1.889(5)	O4–Mn1–N1	97.9(3)	O3′–Mn1–O1	93.3(2)
Mn1–O2	1.888(5)	Mn1–O4	2.201(5)	O3′–Mn1–O2	85.0(2)	O3′–Mn1–Ox	79.5(2)
Mn1–O3′	2.359(5)	Mn2–N2	2.067(6)	O3′–Mn1–N1	93.1(2)	O3–Mn2–Ox	104.3(2)
Mn2–Ox	1.892(4)	Mn2–Ox′	1.934(4)	O3–Mn2–N2	86.8(2)	O2–Mn2–Ox	78.6(2)
Mn2–O2	2.168(4)	Mn2–O3	2.142(4)	O2–Mn2–N2	90.0(2)	O5–Mn2–O2	91.3(2)
Mn2–O5	2.002(5)			O5–Mn2–O3	91.3(2)	O5–Mn2–Ox	93.3(2)
Mn1–O2–Mn2	92.4(2)	Mn1–Ox–Mn2	99.9(2)	O5–Mn2–N2	89.6(2)	Ox′–Mn2–O2	92.3(2)
Mn1–Ox–Mn2′	107.4(2)	Mn1–O3′–Mn2′	87.7(2)	Ox′–Mn2–O3	85.4(2)	Ox′–Mn2–Ox	82.6(2)
Mn2–Ox–Mn2′	97.4(2)	O1–Mn1–Ox	89.0(2)	Ox′–Mn2–N2	95.3(2)		
O1–Mn1–N1	91.3(2)	O2–Mn1–Ox	84.8(2)				

(Mn–O 1.844(5)—1.944(5) Å, Mn–N 2.001(6), 2.004(6) Å) are comparable to those reported for other alkoxo-bridged[22–27] and phenoxo-bridged[28,29] dinuclear manganese(III) complexes. We can find the Mn–O (phenoxo) distances (1.855(5), 1.844(5) Å) are significantly shorter than those of the Mn–O (alkoxo) bonds (1.937(5)—1.944(5) Å). At present, it is hard to say which the difference comes from the distinction between the bridging and terminal Mn–O bonds or the alkoxo oxygen and phenoxo oxygen atoms. The elongated octahedral coordination is achieved by the weak coordination of chloride ion and methanol molecule at the apical positions. This elongation results from expected Jahn–Teller distortions for a high-spin d^4 ion.[22,30] It is to be noted that there are hydrogen bonds between the chloride ions and the methanol molecules (Cl1···O6 3.023(6) Å, Cl2···O5 3.055(7) Å). A similar hydrogen bonding between chloride ion and coordinated water molecule is found in an alkoxo-bridged dinuclear copper(II) complex with *N*-(2-ethylthioethyl)-3-aminopropanol.[31]

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)$_2$]Br (2). The crystal structure consists of dinuclear complex cations and bromide ions. A perspective view of the cation and bromide ion is shown in Fig. 2. The two manganese ions are bridged by an alkoxo oxygen atom of L, the methoxo oxygen atom, and the oxygen atoms of the acetate ion. The acetate ion bridges the manganese ions in a syn–syn configuration[32] with Mn–O distances of 2.140(10) and 2.173(10) Å. In addition, a methanol molecule is weakly bonded to each manganese ion with distance of 2.306(10) or 2.339(10) Å. Each manganese ion possesses an elongated-octahedral MnO_5N geometry. The in-plane-bond distances (Mn–O 1.841(9)—1.958(7) Å, Mn–N 2.002(11), 2.012(10) Å) are comparable to those reported for other dinuclear manganese(III) complexes.[22–29] The Mn···Mn separation is 2.943(3) Å and the Mn–O–Mn angles are 97.8(4) and 98.0(4)°. Bromide ion does not participate in any coordination but forms hydrogen bonds with the coordinating methanols (Br···O7 3.212(10), Br···O8 3.267(9) Å). These hydrogen bonds may contribute to the stabilization of the crystal structure.

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)$_2$]I (3). The crystal and molecular structure of **3** is similar to that of **2**; they are isomorphous. The Mn···Mn separation is 2.933(2) Å and the Mn–O–Mn angles are 97.8(3) and 99.4(4)°. The iodide ion is hydrogen-bonded to the coordinated methanol molecules (I···O7 3.482(9), I···O8 3.444(8) Å).

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)NCS] (4). The molecular structure of the complex is illustrated in Fig. 3. The two manganese ions are bridged by the alkoxo oxygen atom of L, the methoxo oxygen atom, and the acetate ion (syn–syn configuration). In addition, the methanol is weakly bonded to the Mn1 atom with the Mn1–O7 distance of 2.411(7) Å and the thiocyanate ion is bound to the Mn2 atom with the Mn2–N3 distance of 2.329(8) Å. There is no hydrogen bond between the thiocyanate ion and the methanol molecule, the Mn2–N3–C24 angle being 157.5(8)° (cf. the Mn1–N3–N4 angle of **5** (122.0(10)°). Both Mn1 and Mn2 atoms possess elongated-octahedral geometries. The Mn1···Mn2 separation is 2.940(2) Å and the Mn–O–Mn angles are 97.7(2) and 99.0(3)°.

[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)N_3] (5). The

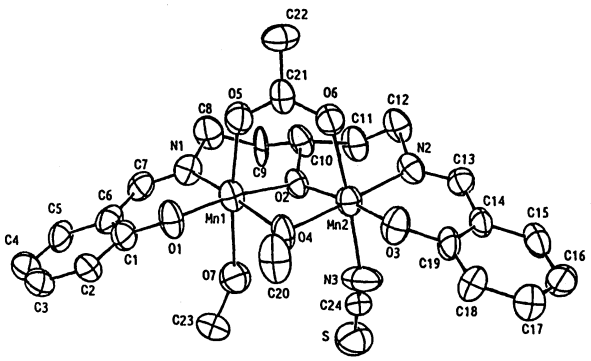

Fig. 3. A perspective view of [Mn_2(L)(CH_3O)-(CH_3COO)(CH_3OH)(NCS)] (**4**). Hydrogen atoms are not shown for clarity.

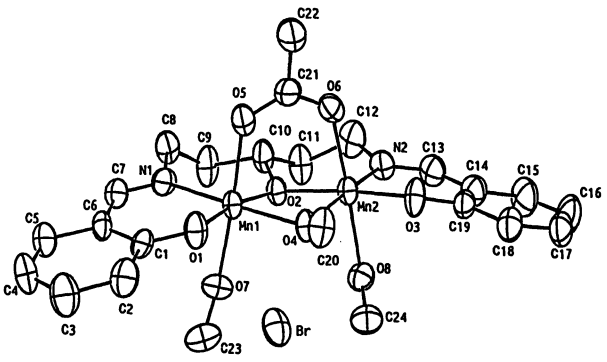

Fig. 2. A perspective view of [Mn_2(L)(CH_3O)-(CH_3COO)(CH_3OH)$_2$]Br (**2**). Hydrogen atoms are not shown for clarity.

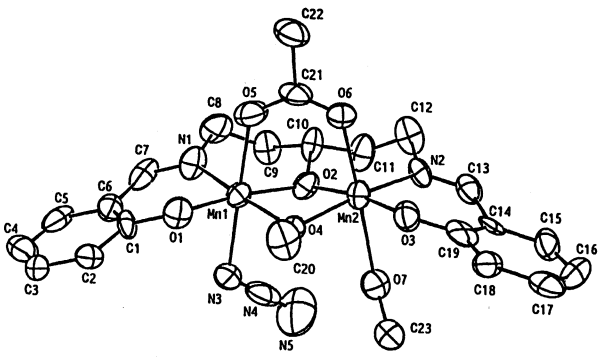

Fig. 4. A perspective view of [Mn_2(L)(CH_3O)-(CH_3COO)(CH_3OH)(N_3)] (**5**). Hydrogen atoms are not shown for clarity.

molecular structure of the complex is illustrated in Fig. 4. The structure is similar to that of **4**. The Mn···Mn separation is 2.955(3) Å and the Mn–O–Mn angles are 97.9(3) and 99.0(4)°. The azide ion is weakly coordinated to the Mn1 atom with the Mn1–N3 distance of 2.358(12) Å and the methanol molecule is bound to the Mn2 atom with the Mn2–O7 distance of 2.446(11) Å. There is a hydrogen bond between the N5 atom of the azide ion and the coordinated methanol (N5···O7 2.841(21) Å) probably causing the tilting of the azide ion (Mn1–N3–N4 122.0(10)°) toward the methanol oxygen.

$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (7). The molecular structure of the complex is illustrated in Fig. 5. The structure is similar to that of **1**, the apical positions of the elongated octahedron being occupied by cyanate ion and water molecule. There is a hydrogen bond between the cyanate ion and the water molecule (N3···O6 2.803(14) Å, N4···O7 2.810(14) Å). The Mn···Mn separation is 2.980(3) Å and the Mn–O–Mn angles are 99.5(5) and 101.0(5)°.

$[Mn_4(L)_2(O)_2(CH_3COO)_2]$ (8). A perspective view of the molecule is shown in Fig. 6. The molecule has a layered tetranuclear structure consisting of four pseudooctahedra MnO_5N sharing the five edges, Ox–O2, Ox′–O2′, Ox–O3′, Ox′–O3, and Ox–Ox′. The tetranuclear molecule is located at the crystallographic inversion center. In the dinuclear 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 dinuclear 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 O_2N 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 other dinuclear manganese(III) complexes.[22–29] Short Mn···Mn separations are 2.875(1) Å for Mn2···Mn2′, 2.933(1) Å for Mn1···Mn2, and 3.122(1) Å for Mn1···Mn2′. Several tetranuclear manganese complexes with adamantane,[33–35] cubane,[36–41] butterfly,[42–48] linear,[49–52] and trapezoid[53–57] structures have been reported as model componds of the OEC recently, however, this type of tetranuclear structure has not been observed for any manganese complexes yet.

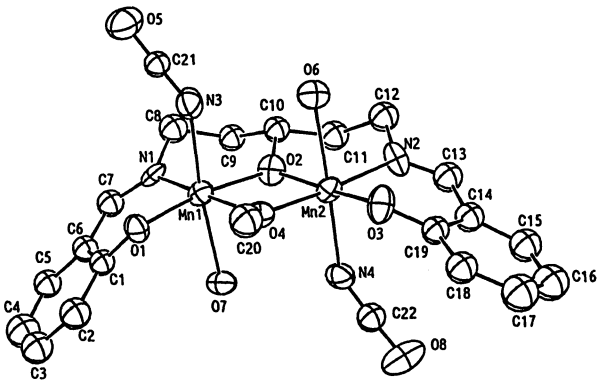

Fig. 5. A perspective view of $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (7). Hydrogen atoms are not shown for clarity.

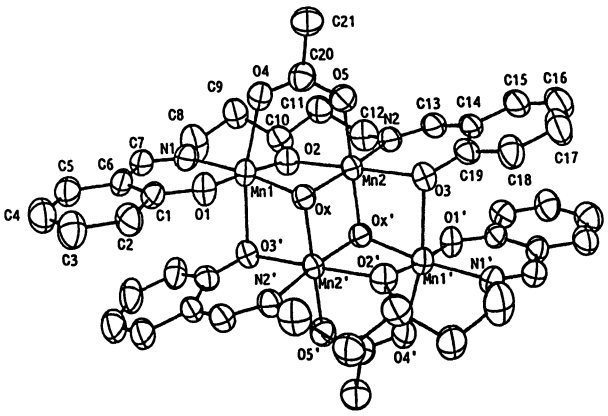

Fig. 6. A perspective view of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**). Hydrogen atoms are not shown for clarity.

Electronic Spectra. Diffuse reflectance spectrum of the dinuclear manganese complex, **1**, is shown in Fig. 7 together with that of the tetranuclear manganese complex, **8**. The complex, **1**, shows three bands in the visible region (381, 470sh, and 635 nm). In methanol solution, the complex displays three absorptions at 374, 430sh, and 627 nm with molar extinction coefficients of 2860, 775, and 145 $dm^3\,mol^{-1}\,cm^{-1}/Mn$, respectively.

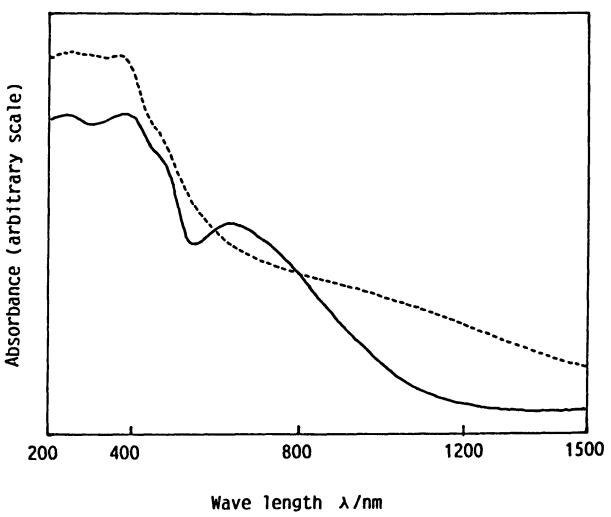

Fig. 7. Diffused reflectance spectra of $[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**) (——) and $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**) (------).

Table 4. Electronic Spectral Data

Complex	Reflectance λ_{max}/nm			Methanol solution λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})		
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (**6**)	606	460sh[a]	379	611(141)	433sh(600)	373(3070)
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]I$ (**3**)	612	450sh	385	610(135)	420sh(650)	373(2880)
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (**2**)	615	450sh	383	610(137)	427sh(651)	373(2910)
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (**5**)	615	460sh	362	612(136)	430sh(624)	370(2870)
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(NCS)]$ (**4**)	629	450sh	383	611(143)	430sh(616)	373(2950)
$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**)	630	435sh	371	610(160)	433sh(765)	377(2910)
$[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**)	635	470sh	381	627(145)	430sh(775)	374(2860)
$[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**)	800	460sh	372	570(170)	436sh(610)	374(3060)

a) sh=shoulder.

It is reasonable to assign the lower-energy two bands to d–d transitions for Mn(III) ion in an elongated octahedral environment.[58,59] The diffuse reflectance spectra of the other dinuclear manganese complexes, **2**—**7**, are essentially similar to that of **1** (Table 4). The absorption maxima of the lowest-energy d–d band in the solid state shifts to longer wave length with the change of X in the order ClO_4(**6**)>I(**3**)≈Br(**2**)≈N_3(**5**)>NCS(**4**)≈NCO(**7**)>Cl(**1**). Since the equatorial coordination spheres are virtually invariant MnO_3N, the shifting of the absorption maxima should reflects the change of the apical coordination environments. Noting the coordinated atoms of the apical ligands, we find a shifting of the d–d bands to longer wavelengths in the order O>N>Cl. It is not clear why the order does not agree with that of the spectrochemical series.[60] In solution, solvent exchange at the axial sites in the dinuclear manganese complexes may be quite facile, and its effects can be seen in the solution spectra. The absorption spectra in methanol are very similar to one another (Table 4). This fact is consistent with the electronic conductivities data (The Λ_M values are 79—132 S mol^{-1} cm^2 corresponding to 1 : 1 electrolyte.[61])

The reflectance spectrum of the tetranuclear manganese complex **8** is different from those of the dinuclear manganese complexes (Fig. 7). While the spectrum contains bands at 372 and 460 (shoulder) nm corresponding to the high energy bands in the spectra of the dinuclear manganese complexes **1**—**7**, a very broad feature appears at ca. 800 nm. The difference may be attributed to the presence of the oxo-bridges in **8**. This spectrum is comparable to those of the di-oxo-bridged dinuclear manganese(III) complexes which have appeared recently.[62,63]

Magnetic Susceptibilities. Temperature dependence of magnetic susceptibilities of the dinuclear manganese(III) complexes **1**—**7** were measured on powdered samples in the temperature range 80—300 K, and one of the results is shown in Fig. 8. The effective magnetic moments at room temperature fall in the range 4.08—4.29 BM/Mn, decreasing monotonically to the values 2.47—3.08 BM/Mn at liquid nitrogen temperature. The susceptibility data were analyzed with the van Vleck equation based on the Heisenberg model $\mathcal{H}=-2JS_{Mn1}\cdot S_{Mn2}$ ($S_{Mn1}=S_{Mn2}=2$) and the best fitting parameters are listed in Table 5. The values of the magnetic exchange coupling constants J for **1**—**7** are in the range −10.6 to −16.5 cm^{-1}. The observation of an antiferromagnetic interaction in the present complexes is consistent with the reported interactions in analogous dinuclear manganese(III) complexes. In the di-μ-alkoxo-bridged dinuclear systems, J is in the range −13.5 to −20.4 cm^{-1}.[30] Structural and magnetic data for these complexes are listed in Table 5. Although no clear relationship is found for the J value against the Mn···Mn separation and the Mn–O–Mn angle, the variation in the dihedral angle between the two coordination planes, τ, follows the trend in J values, with good coplanarity correlating to stronger antiferromagnetic interaction. The J values for the chloro and cyanate complexes, **1**

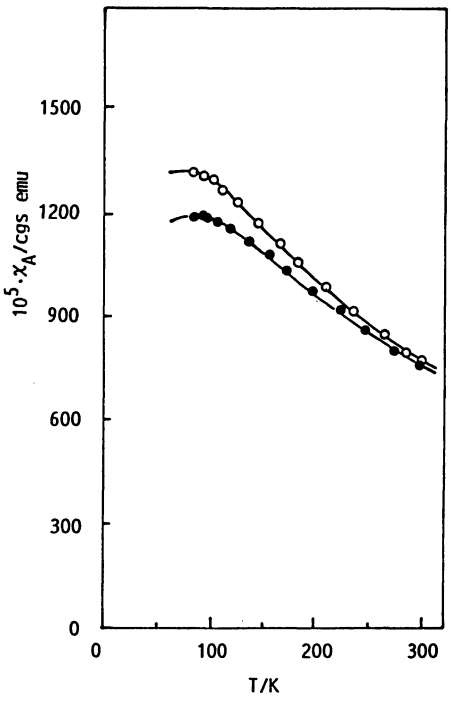

Fig. 8. Plots of magnetic susceptibilities of $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (**2**) (●) and $[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (**5**) (○). The solid lines represent the calculated fits with van Vleck equation for the S=2—S=2 system.

Table 5. Magnetic and Structural Data

Complex	μ_{eff}/BM(T/K)	J/cm^{-1} g	Mn1–Mn2/Å	Mn1–O2–Mn2/°	Mn1–O4–Mn2/°	τ[a]/°
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (**6**)	4.28(298)[b]	−10.6[b] 1.99[b]	2.931(2)[b]	97.2(2)[b]	99.0(2)[b]	
$[Mn_2(L')(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$[c]	4.26(292)	−11.8 2.00	2.921(2)[d]	98.0(2)[d]	99.4(2)[d]	167.4[d]
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (**5**)	4.29(298)	−11.8 2.00	2.955(3)	97.9(3)	99.0(4)	163.4
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]I$ (**3**)	4.29(297)	−12.9 2.01	2.933(2)	97.8(3)	99.4(3)	164.8
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(NCS)]$ (**4**)	4.23(297)	−13.0 2.01	2.940(2)	97.7(2)	99.0(3)	166.6
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (**2**)	4.21(295)	−13.2 2.00	2.943(3)	97.8(4)	98.0(4)	163.8
$[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**)	4.16(292)	−15.6 2.01	3.006(2)	101.6(2)	101.6(2)	178.0
$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**)	4.08(202)	−16.5 2.00	2.980(3)	99.5(5)	101.0(5)	177.3

a) Dihedral angle between the two coordination planes. b) Ref. 15. c) H_3L'=1,5-bis(5-chlorosalicylideneamino)-3-pentanol. d) Ref. 14.

and **7**, which have τ values of 178.0 and 177.3°, respectively, are lower than those for the other complexes, **2**—**5** which have smaller τ values. As pointed out by Nishida et al.,[15] a direct interaction between the two d_{xy} orbitals might be a main contribution for the antiferromagnetism of this type of dinuclear manganese(III) complexes, since the $d_{x^2-y^2}$ orbitals along the in-plane Mn–O and Mn–N bonds are unoccupied. The stronger antiferromagnetic interaction in **1** and **7** may be a consequence of a good overlapping of the two d_{xy} orbitals on the almost same plane.

The magnetic moment of the tetranuclear manganese(III) complex **8** decreases from 4.32 BM/Mn at 291 K to 3.56 BM/Mn at 81 K (Fig. 9). To simplify the analysis, the coupling between manganese(III) ions is assumed to be equivalent (J') for all four pairs (Mn1–Mn2, Mn1–Mn2′, Mn2–Mn1′, Mn1′–Mn2′), regardless of the difference between the alkoxo-bridge and the phenoxo-bridge. The resulting spin Hamiltonian is thus

$$\mathcal{H} = -2JS_{Mn2} \cdot S_{Mn2'} - 2J'(S_{Mn1} \cdot S_{Mn2} + S_{Mn1} \cdot S_{Mn2'} + S_{Mn2} \cdot S_{Mn1'} + S_{Mn1'} \cdot S_{Mn2'})$$
$$(S_{Mn1} = S_{Mn2} = S_{Mn1'} = S_{Mn2'} = 2)$$

An expression for χ_A was derived from the van Vleck equation.[44,45] For fitting the data, g was fixed at 2.0 and the parameters J and J' were varied. A good fit was obtained for J=−10.0 cm^{-1} and J'=−3.7 cm^{-1}.

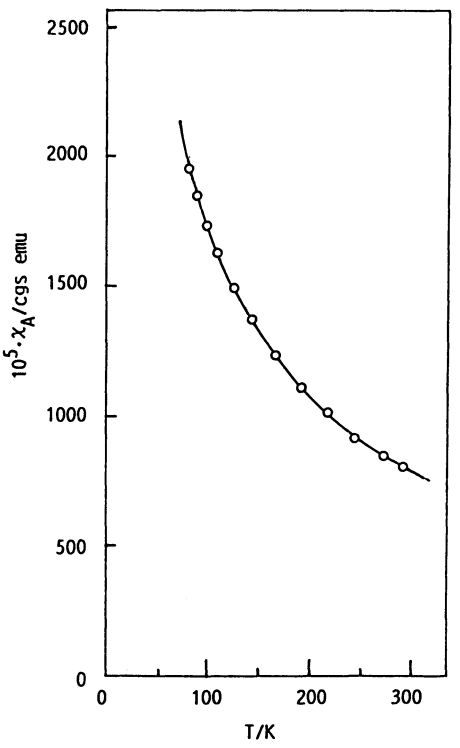

Fig. 9. Plots of magnetic susceptibilities of $[Mn_4(L)_2(O)_2(CH_3COO)_2] \cdot 4H_2O \cdot 2CH_3OH$ (**8**) (○). The solid line represents the calculated fit with van Vleck equation for the tetranuclear system.

Table 6. Cyclic Voltammetric Data[a)]

Complex	E_{pc}[b)]	E_{pa}[c)]	ΔE_p[d)]/mV	$E_{1/2}$[e)]
$[Mn_2(L)(CH_3O)Cl_2(CH_3OH)_2]$ (**1**)	0.01	0.18	170	0.09
	−0.42	−0.24	180	−0.33
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]Br$ (**2**)	−0.02	0.14	160	0.06
	−0.46	−0.23	230	−0.34
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)_2]I$ (**3**)	−0.02	0.14	160	0.06
	−0.48	−0.22	260	−0.35
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(NCS)]$ (**4**)	0.01	0.14	130	0.08
	−0.42	−0.25	170	−0.33
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(N_3)]$ (**5**)	0.01	0.14	130	0.07
	−0.45	−0.24	210	−0.34
$[Mn_2(L)(CH_3O)(CH_3COO)(CH_3OH)(ClO_4)]$ (**6**)	0.02	0.14	120	0.08
	−0.43	−0.24	190	−0.33
$[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**)	0.02	0.18	160	0.10
	−0.44	−0.26	180	−0.35
$[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**)	0.31	0.42	110	0.36
	−0.01	0.12	130	0.05
	−0.45	−0.23	220	−0.34

a) In methanol. Scan rate=100 mV s^{-1}, V vs. Ag/AgCl. b) E_{pc}=cathodic peak potential. c) E_{pa}=anodic peak potential. d) $\Delta E_p = |E_{pc} - E_{pa}|$. e) $E_{1/2} = (E_{pa} + E_{pc})/2$.

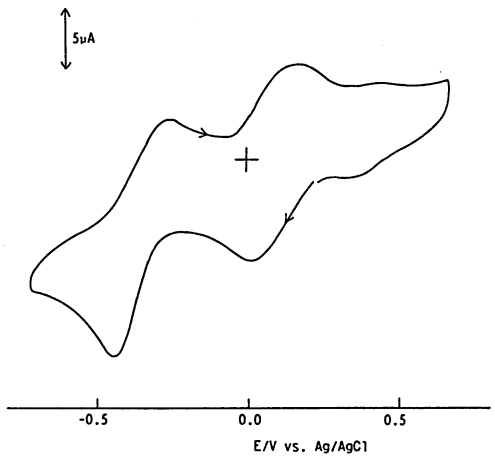

Fig. 10. Cyclic voltammogram of $[Mn_2(L)(CH_3O)(NCO)_2(H_2O)_2]$ (**7**).

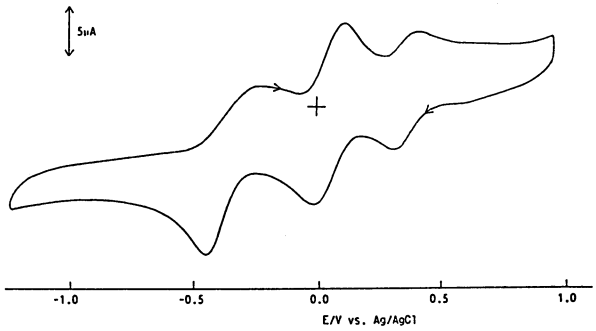

Fig. 11. Cyclic voltammogram of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**8**).

The fit confirms the observation of net antiferromagnetic coupling.

Electrochemistry. The cyclic voltammograms of the dinuclear complexes **1**—**7** have been measured in methanol solution. All the dinuclear complexes give similar results like the solution spectra (Table 6); the cyclic voltammogram of **7** is shown in Fig. 10. The first of these reduction processes ($E_{1/2}$=0.06—0.10 V vs. Ag/AgCl) has the characteristic of an electrochemically quasi-reversible couple, the peak separation being 120—170 mV. The second reduction process at −0.33—−0.35 V appears partially irreversible. The former may be assigned to the Mn(III)Mn(III)/Mn(II)Mn(III) couple, and the latter may be due to the Mn(II)Mn(III)/Mn(II)Mn(II) couple. Although there are no other dialkoxo-bridged manganese(III) complexes whose redox behavior can be compared to those of the present complexes, these cyclic voltammograms are comparable to that of a diphenoxo-bridged dinuclear manganese(II) complex of 2-(bis(salicylideneamino)methyl)phenolate; their oxidations to the Mn(II)Mn(III) and Mn(III)Mn(III) states occur at ca. −0.4 and −0.04 V vs. SCE, respectively.[29)]

A cyclic voltammogram of the tetranuclear complex **8** in CH_3OH is similar to those of the dinuclear complexes except for the region 0.25 to 0.60 V (Fig. 11). The waves at 0.05 and −0.34 V can be assigned to the $(Mn(III)Mn(III))_2/(Mn(II)Mn(III))_2$ and $(Mn(II)Mn(III))_2/(Mn(II)Mn(II))_2$ couples, respectively. Besides, there is a quasi-reversible oxidation at 0.36 V which may be assigned to oxidation to the (Mn(III)Mn(III))-(Mn(III)Mn(IV))/((Mn(III)Mn(III))$_2$ couple as judged by the peak heights. The Mn(III)Mn(III) to Mn(III)-Mn(IV) oxidation potential is comparable to those for the couple in the dinuclear dioxo-bridged manganese(III) complexes (0.568, 0.678 V vs. Ag/AgCl).[62,63)] The observation that **8** can be electrochemically oxidized to the (Mn(III)Mn(III))(Mn(III)Mn(IV)) form may be understood in terms of the coordination environment for the oxo-bridged manganese ion. It is well known

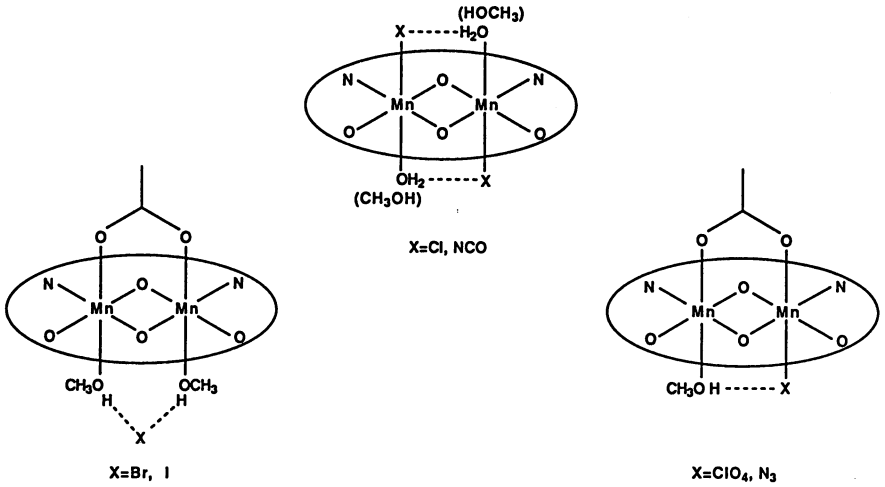

Fig. 12. Structures of the present dinuclear manganese complexes.

that the bridging oxo-group stabilize the higher oxidation state to a remarkable extent and a number of di-μ-oxo-Mn(III)Mn(IV) dinuclear complexes have been reported.[5-8]

Concluding Comments

A series of dinuclear manganese complexes containing various anions have been synthesized. Their electronic, magnetic, and electrochemical properties have been studied. X-Ray structure analyses of the present complexes show that there are three ways of anion binding mode as shown in Fig. 12. All the binding modes except for **4** are made up by hydrogen bonds between the anions and solvent molecules which may stabilize the anion binding to the dinuclear unit. Complex **1** is a rare example of dinuclear manganese cluster with a Mn–Cl bonding. If a methanol molecule is replaced by a water molecule, the chloride ion will occupy an adjacent position to the water molecule forming a hydrogen bond between them. It is recognized that chloride ion is an important cofactor at the OEC and has been proposed to bind to the manganese atoms.

Addition of strong base, such as Et_3N, to a solution of the dinuclear unit results in further dimerization to a tetranuclear species **8**. The X-ray structure of **8** is the first example of manganese complex which has a layered structure consisting of edge-sharing pseudooctahedra,[17] although a similar tetranuclear structure has appeared very recently.[64] The intriguing aspects of this structure are (i) the Mn···Mn separarions 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 donor mainly. These features are in harmony with those observed for the natural system.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 03640532 from the Ministry of Education, Science and Culture.

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