Synthesis and Characterization of Tetranuclear Manganese(III) Complexes with 2,6-Bis(salicylideneaminomethyl)-4-methylphenol

Masahiro Mikuriya,* Keiichi Nakadera, Takanori Kotera, Tadashi Tokii,† and Wasuke Mori††

Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662

†Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840

††Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Tetranuclear manganese(III) complexes with 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (**1**) and $[Mn_4(L)_2(O)_2(C_6H_5COO)_2]\cdot 2CH_3OH$ (**2**), have been synthesized and characterized by infrared and electronic spectra, cyclic voltammetry, and temperature dependence of magnetic susceptibilities (4—300 K). The molecular structure of **1** was determined by single-crystal X-ray structure analysis. Complex **1** has a tetranuclear structure, in which two incomplete cubanes are sharing faces by the oxo-bridges. The magnetic susceptibility data show an overall antiferromagnetic interaction.

There is considerable current interest in the synthesis of mononuclear, dinuclear, trinuclear, and tetranuclear manganese complexes, since such manganese systems are believed to occur at the active sites of manganese-binding enzymes such as manganese catalase, ribonucleotide reductase of certain bacteria, and the photosystem II of green plants.[1—9] Many manganese complexes have been reported as the model compounds.[1—9] However, the examples of tetranuclear manganese complexes are still limited.[10—37] As part of a continuing project on manganese complexes, we recently reported on the synthesis and characterization of several manganese complexes with pentadentate Schiff-base ligands: 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol,[38] 1,3-bis(salicylideneamino)-2-propanol,[39] 1-salicylideneamino-3-salicylamino-2-propanol,[40] bis(benzoylacetone)-1,3-diiminopropan-2-ol,[41] and 1,5-bis(salicylideneamino)-3-pentanol.[37,42] These dinucleating ligands afford interesting mononuclear ($[Mn^{II}]$[38] and $[Mn^{III}]$[38]), dinuclear ($[Mn^{II}_2]$,[38] $[Mn^{II}Mn^{III}]$,[38] and $[Mn^{III}_2]$[37,39,40,42]), trinuclear ($[Mn^{III}_3]$[41]), and tetranuclear ($[Mn^{III}_4]$[37]) complexes. Concerning these complexes, we have also tried to isolate μ-phenoxo-bridged manganese complexes with a related pentadentate Schiff-base ligand, 2,6-bis(salicylideneaminomethyl)-4-methylphenol (H_3L), which was expected to hold two manganese atoms in close proximity. This dinucleating ligand has two terminal phenoxo-oxygen atoms in addition to a phenoxo-oxygen atom as a bridging group. These phenoxo-oxygen atoms are potential donor groups which may stabilize higher oxidation states.[43] In fact we obtained a series of manganese(IV) complexes by using similar tridentate Schiff-base ligands, *o*-(salicylideneaminomethyl)phenol and its substituted derivatives.[44] Interestingly we have found that the pentadentate Schiff-base ligand (H_3L) forms a novel tetranuclear nickel(II) complex with a mixed-spin state generated by association of the two dinuclear molecules by virtue of the phenoxo-bridges.[45] We therefore expected that interesting tetranuclear manganese complexes with high oxidation state would be formed by the donor and bridging properties of H_3L. In this study we have successfully isolated tetranuclear manganese complexes by using this pentadentate ligand; however, they are not high-oxidation manganese complexes but manganese(III) complexes similar to the Mn^{III}_4 complex with 1,5-bis(salicylideneamino)-3-pentanol.[37] Here, we present complete details concerning the synthesis and characterization of these complexes.

Experimental

Synthesis of the Complexes. 2,6-Bis(salicylideneaminomethyl)-4-methylphenol was synthesized according to a method reported by Mazurek et al.[46] Manganese(II) benzoate dihydrate was prepared by a literature method.[19a]

$[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (1). To an acetonitrile solution (4 ml) of 2,6-bis(salicylideneaminomethyl)-4-methylphenol (36 mg, 0.10 mmol), manganese(II) acetate tetrahydrate (48 mg, 0.20 mmol), triethylamine (30 mg, 0.30 mmol) and 1 ml of dimethylformamide were successively added with stirring. The resulting black solution was filtered. Diethyl ether was layered onto the filtrate and the solution was left to stand for several days. Black prisms

were deposited; they were collected by filtration, washed with acetonitrile, and dried in vacuo over P_2O_5 (yield 31 mg, 25%). Anal. Calcd for $C_{54}H_{50}Mn_4N_6O_{12}$: C, 54.28; H, 4.22; N, 7.03%. Found: C, 54.08; H, 4.40; N, 7.28%. IR (KBr) ν/cm^{-1} ν(C=N) 1627; ν_{as}(COO) 1565; ν_s(COO) 1400.

$[Mn_4(L)_2(O)_2(C_6H_5COO)_2]\cdot 2CH_3OH$ (2). After 2,6-bis(salicylideneaminomethyl)-4-methylphenol (36 mg, 0.10 mmol) had been dissolved in 4.0 ml of methanol, manganese(II) benzoate dihydrate (66 mg, 0.20 mmol) and triethylamine (50 mg, 0.50 mmol) were added. The solution was filtered and the filtrate was placed in a refrigerator. Black prisms were deposited; they were collected by filtration, washed with methanol, and dried in vacuo over P_2O_5 (yield 27 mg, 20%). Anal. Calcd for $C_{62}H_{56}Mn_4N_4O_{14}$: C, 57.24; H, 4.33; N, 4.30%. Found: C, 57.72; H, 4.04; N, 4.48%. IR (KBr) ν/cm^{-1} ν(C=N) 1630; ν_{as}(COO) 1553; ν_s(COO) 1391.

Measurements. Carbon, Hydrogen, and nitrogen analyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the 4000—400 cm^{-1} region on a KBr disk. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. Electric conductivities were measured on a Horiba conductivity meter DS-14. Cyclic voltammetric measurements were carried out on a BAS 100B Electrochemical Analyzer. A three-electrode cell comprising a glassy carbon electrode, a platinum-wire counter electrode, and a nonaqueous Ag/Ag^+ electrode was used. The magnetic susceptibilities were measured by the Faraday method over the 4—300 K temperature range. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[47] The effective magnetic moments were calculated from the equation $\mu_{eff}=2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analysis of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (1). Single crystals of **1** grew from methanol. A black crystal with dimensions of $0.21\times0.30\times0.11$ mm^3 was used for the X-ray structure analysis. The unit-cell parameters and intensities were measured on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20\leq 2\theta\leq 30°$. The intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: $C_{54}H_{50}Mn_4N_6O_{12}$, F.W.=1194.80, triclinic, $P\bar{1}$, $a=11.821(2)$, $b=12.635(5)$, $c=10.515(3)$ Å, $\alpha=112.53(3)$, $\beta=116.16(2)$, $\gamma=71.80(2)°$, $V=1282.4(7)$ Å^3, $D_m=1.53$, $D_c=1.55$ g cm^{-3}, $Z=1$, μ(Mo $K\alpha$)=9.94 cm^{-1}.

Of the 4499 reflections ($2\leq 2\theta\leq 50°$) measured, the unique 3306 reflections with $I>3\sigma(I)$ were considered as observed. The structures were solved by the direct methods. Refinements were carried out by the full-matrix least-squares methods. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from difference Fourier maps and fixed at their positions. The weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. The final discrepancy factors are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.045$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.050$.

All of the calculations were carried out on a Micro-VAXII computer using an Enraf–Nonius SDP program package.[48] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the F_o-F_c tables were deposited as Document No. 68058 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

In an earlier report, we describe the use of 1,5-bis(salicylideneamino)-3-pentanol (H_3L') to prepare

Table 1. 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)
Mn1	0.60551(5)	0.02813(5)	0.99642(6)	2.03(1)
Mn2	0.40744(6)	0.22616(5)	1.06632(7)	2.37(1)
Ox	0.5048(2)	0.0842(2)	1.1150(3)	2.07(6)
O1	0.7462(2)	−0.1103(2)	1.0650(3)	2.45(7)
O2	0.4489(3)	0.1603(2)	0.8910(3)	2.69(7)
O3	0.3609(3)	0.2764(3)	1.2324(3)	3.25(8)
O4	0.5820(3)	0.3020(3)	1.1843(4)	3.66(9)
O5	0.7201(3)	0.1422(3)	1.1242(3)	2.94(7)
N1	0.6753(3)	−0.0109(3)	0.8347(4)	2.47(8)
N2	0.3087(3)	0.3717(3)	1.0108(4)	2.99(9)
N3	1.1464(9)	0.159(1)	1.5142(9)	16.1(3)
C1	0.4718(4)	0.2195(4)	0.8222(4)	2.6(1)
C2	0.5438(4)	0.1551(4)	0.7318(4)	2.5(1)
C3	0.5697(4)	0.2135(4)	0.6599(4)	3.0(1)
C4	0.5274(4)	0.3301(4)	0.6759(5)	3.3(1)
C5	0.4551(5)	0.3911(4)	0.7629(5)	3.8(1)
C6	0.4238(4)	0.3363(4)	0.8357(5)	3.3(1)
C7	0.5561(5)	0.3920(4)	0.5975(5)	4.6(1)
C8	0.5851(4)	0.0263(4)	0.7022(4)	2.8(1)
C9	0.7876(4)	−0.0638(4)	0.8388(4)	2.7(1)
C10	0.8862(4)	−0.1138(4)	0.9521(4)	2.5(1)
C11	1.0111(4)	−0.1479(4)	0.9507(5)	3.5(1)
C12	1.1091(4)	−0.1980(5)	1.0511(6)	3.9(1)
C13	1.0865(5)	−0.2186(5)	1.1580(6)	3.8(1)
C14	0.9644(4)	−0.1891(4)	1.1611(5)	3.2(1)
C15	0.8621(4)	−0.1362(4)	1.0608(4)	2.3(1)
C16	0.3310(6)	0.4114(5)	0.9096(6)	8.3(2)
C17	0.2237(4)	0.4420(4)	1.0634(5)	3.1(1)
C18	0.1892(4)	0.4308(4)	1.1737(5)	3.0(1)
C19	0.0846(5)	0.5107(5)	1.2054(6)	4.2(1)
C20	0.0493(5)	0.5062(6)	1.3123(6)	4.9(2)
C21	0.1195(5)	0.4249(5)	1.3890(6)	4.5(2)
C22	0.2224(5)	0.3483(5)	1.3629(5)	3.7(1)
C23	0.2598(4)	0.3504(4)	1.2522(5)	2.8(1)
C24	0.6914(4)	0.2467(4)	1.1958(5)	3.1(1)
C25	0.8018(6)	0.3088(6)	1.3037(8)	5.8(2)
C26	1.1718(7)	0.0725(9)	1.5445(7)	9.9(3)
C27	1.2034(8)	−0.0290(9)	1.5893(8)	8.4(3)

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

the tetranuclear complex $[Mn_4(L')_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$.[37] This compound was obtained as a byproduct for the dinuclear manganese complex containing cyanate ion or by treating the dinuclear manganese species with an aqueous solution of triethylamine. In both cases, an alkaline aqueous condition is required for the tetranuclear formation. Interestingly, such a tetranuclear complex, $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (**1**), is readily formed in an acetonitrile solution containing manganese(II) acetate and 2,6-bis(salicylideneaminomethyl)-4-methylphenol in the presence of triethylamine. Thus in the absence of any further addition of aqueous solution, which can be a source of oxo ions, the two dinuclear units associate to the tetranuclear complex by virtue of the phenoxo-oxygens of the Schiff-base ligands and oxo-ions which might be generated from traces of water in the solvent. The corresponding benzoate complex, $[Mn_4(L)_2(O)_2(C_6H_5COO)_2]\cdot 2CH_3OH$ (**2**), was obtained in an analogous manner. The IR spectra of **1** and **2** show an absorption which confirmed the presence of a coordinated C=N group of L and two stretching bands, the difference in energy of which is characteristic of a bridging carboxylate group.[49]

The X-ray crystal structure of **1** has been determined. A perspective drawing of the molecular structure of **1** is given in Fig. 1. Bond distances and angles are listed in Table 2. The molecule has a tetranuclear structure similar to that of $[Mn_4(L')_2(O)_2(CH_3COO)_2]\cdot 4H_2O\cdot 2CH_3OH$ (**3**).[37] The tetranuclear molecule has a crystallographic inversion center at the midpoint between the Mn1 and Mn1′ atoms or the Ox and Ox′ atoms. In the dinuclear half, the two manganese atoms (Mn1 and Mn2) are bridged by the central phenoxo-oxygen atom (O2) of L, the oxo ion (Ox), and the acetate ion. These two dinuclear halves are associated to form the tetranuclear molecule by the oxo ions (Ox and Ox′) and the terminal phenoxo-oxygen atoms (O1 and O1′) of L. Both the Mn1 and Mn2 atoms take elongated-octahedral geometries. The square plane around the Mn1 atom is formed by the N1 atom of L, the two oxo ions Ox and Ox′, and the O5 atom of the acetate ion, whereas the plane for the Mn2 atom consists of the O2, O3, and N2 atoms of L and the oxo ion Ox. These in-plane-bond distances (Mn–O 1.880(4)—1.957(3) Å, Mn–N 1.989(4), 2.039(4) Å) are slightly shorter than those of **3** (Mn–O 1.888(5)—2.002(5) Å, Mn–N 2.021(5), 2.067(6) Å),[38] although comparable to those found in dinuclear manganese(III) complexes with pentadentate Schiff-base ligands.[37—42] The elongated axes are O1–Mn1–O2 and O4–Mn2–O1′, the Mn–O distances ranging from 2.105(3) to 2.286(3) Å. These distances are also slightly shorter than the corresponding Mn–O distances (2.142(4)—2.359(5) Å) of **3**.[37] These facts mean that substitution of the phenoxo-oxygen for the alkoxo-oxygen in the Schiff-base ligand results in slight shortenings of the Mn–O and Mn–N bonds. The Mn···Mn separations are 2.831(1) Å for Mn1···Mn1′, 2.954(1) Å for Mn1···Mn2, and 3.051(1) Å for Mn1···Mn2′; these are slightly different from the corresponding Mn···Mn separations (2.875(1), 2.933(1), 3.122(1) Å) of **3**[37] and the Mn–O–Mn angles are 88.0(1)—106.1(1)°. This type of tetranuclear structure is very rare for manganese system.[35—37] So far, several tetranuclear structures including adamantane,[10,11] cubane,[12—17] butterfly,[18—21] linear,[22—27] trapezoid,[28—32] tetrahedral,[33] and cyclic[34] arrangements have been found and reported as model compounds of the oxygen evolution center (OEC) of the photosystem II. Our tetranuclear structure is interesting, because it, also, can explain the two types of Mn–Mn separations which are found in the EXAFS data for the OEC.[4—9]

Diffuse reflectance spectra of the tetranuclear Mn(III)

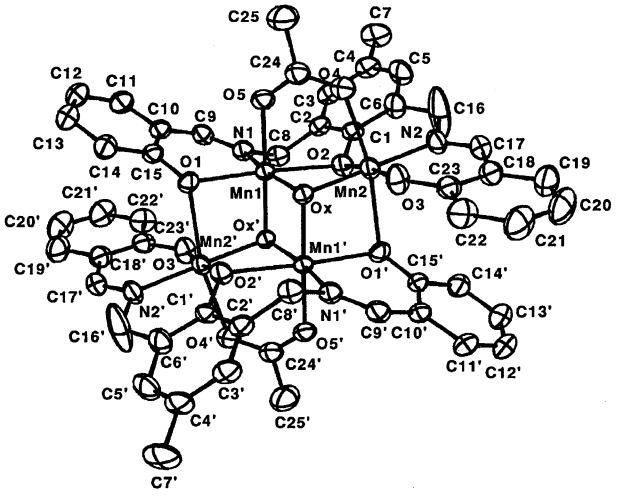

Fig. 1. A perspective view of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (**1**). Solvent molecules are not shown.

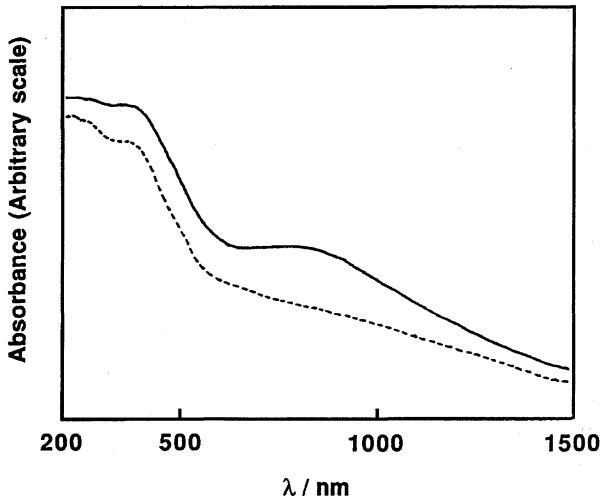

Fig. 2. Diffuse reflectance spectra of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (**1**) (—) and $[Mn_4(L)_2(O)_2(C_6H_5COO)_2]\cdot 2CH_3OH$ (**2**) (---).

Table 2. Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

(a) Manganese coordination spheres			
Mn1–Mn1′	2.831(1)	Mn1–Mn2	2.954(1)
Mn1–Mn2′	3.051(1)	Mn1–Ox	1.891(3)
Mn1–Ox′	1.899(3)	Mn1–O1	2.105(3)
Mn1–O2	2.262(3)	Mn1–O5	1.957(3)
Mn1–N1	2.039(4)	Mn2–Ox	1.920(3)
Mn2–O1′	2.286(3)	Mn2–O2	1.923(3)
Mn2–O3	1.880(4)	Mn2–O4	2.182(3)
Mn2–N2	1.989(4)		
Mn1–Ox–Mn1′	96.7(1)	Mn1–Ox–Mn2	101.7(2)
Mn1′–Ox–Mn2	106.1(1)	Mn1–O1–Mn2′	88.0(1)
Mn1–O2–Mn2	89.4(1)	Ox–Mn1–Ox′	83.3(1)
Ox–Mn1–O1	107.6(1)	Ox–Mn1–O2	77.6(1)
Ox–Mn1–O5	93.7(1)	Ox–Mn1–N1	165.5(1)
Ox′–Mn1–O1	85.5(1)	Ox′–Mn1–O2	89.3(1)
Ox′–Mn1–O5	175.8(2)	Ox′–Mn1–N1	93.5(1)
O1–Mn1–O2	172.2(1)	O1–Mn1–O5	92.6(1)
O1–Mn1–N1	86.2(1)	O2–Mn1–O5	92.8(1)
O2–Mn1–N1	88.2(1)	O5–Mn1–N1	90.1(2)
Ox–Mn2–O1′	80.2(1)	Ox–Mn2–O2	85.9(1)
Ox–Mn2–O3	90.5(1)	Ox–Mn2–O4	89.1(1)
Ox–Mn2–N2	178.2(2)	O1′–Mn2–O2	83.8(1)
O1′–Mn2–O3	91.0(1)	O1′–Mn2–O4	167.8(1)
O1′–Mn2–N2	100.0(1)	O2–Mn2–O3	174.2(2)
O2–Mn2–O4	89.8(1)	O2–Mn2–N2	92.3(2)
O3–Mn2–O4	94.7(1)	O3–Mn2–N2	91.3(2)
O4–Mn2–N2	90.6(1)		
(b) Ligand L moiety			
O1–C15	1.321(6)	O2–C1	1.365(7)
O3–C23	1.311(5)	C1–C2	1.407(7)
C1–C6	1.378(6)	C2–C3	1.405(9)
C2–C8	1.491(6)	C3–C4	1.365(6)
C4–C5	1.379(8)	C4–C7	1.52(1)
C5–C6	1.42(1)	C6–C16	1.498(9)
C9–C10	1.439(6)	C10–C11	1.408(7)
C10–C15	1.431(8)	C11–C12	1.354(7)
C12–C13	1.39(1)	C13–C14	1.384(8)
C14–C15	1.390(6)	C17–C18	1.453(9)
C18–C19	1.409(7)	C18–C23	1.382(7)
C19–C20	1.38(1)	C20–C21	1.379(9)
C21–C22	1.359(7)	C22–C23	1.426(9)
Mn–O1–C15	124.2(3)	Mn2′–O1–C15	126.1(2)
Mn1–O2–C1	120.7(2)	Mn2–O2–C1	126.5(2)
Mn2–O3–C23	127.8(3)	Mn2–O4–C24	125.1(3)
Mn1–O5–C24	127.5(3)	Mn1–N1–C8	115.5(3)
Mn1–N1–C9	125.9(3)	C8–N1–C9	118.7(4)
Mn2–N2–C16	122.4(3)	Mn2–N2–C17	123.6(4)
C16–N2–C17	113.9(4)	O2–C1–C2	117.0(4)
O2–C1–C6	122.2(5)	C2–C1–C6	120.8(5)
C1–C2–C3	118.4(4)	C1–C2–C8	122.0(5)
C3–C2–C8	119.4(4)	C2–C3–C4	121.9(5)
C3–C4–C5	118.6(6)	C3–C4–C7	121.3(5)
C5–C4–C7	120.1(4)	C4–C5–C6	122.0(4)
C1–C6–C5	118.2(5)	C1–C6–C16	126.6(6)
C5–C6–C16	115.0(5)	N1–C8–C2	114.0(3)
N1–C9–C10	127.3(5)	C9–C10–C11	118.1(5)
C9–C10–C15	123.3(4)	C11–C10–C15	118.6(4)
C10–C11–C12	122.1(6)	C11–C12–C13	119.5(5)
C12–C13–C14	120.3(5)	C13–C14–C15	121.6(6)
O1–C15–C10	121.7(3)	O1–C15–C14	120.4(5)
C10–C15–C14	117.9(4)	N2–C16–C6	119.8(5)
N2–C17–C18	126.2(5)	C17–C18–C19	117.2(5)
C17–C18–C23	122.1(4)	C19–C18–C23	120.5(6)
C18–C19–C20	119.8(6)	C19–C20–C21	119.2(5)
C20–C21–C22	122.2(7)	C21–C22–C23	119.7(5)
O3–C23–C18	123.8(6)	O3–C23–C22	117.7(4)
C18–C23–C22	118.5(4)		
(c) Acetate group			
O4–C24	1.240(5)	O5–C24	1.267(5)
C24–C25	1.500(7)		
O4–C24–O5	126.5(4)	O4–C24–C25	117.6(4)
O5–C24–C25	116.0(4)		
(d) Solvent molecule			
N3–C26	1.16(2)	C26–C27	1.42(2)
N3–C26–C27	176.9(8)		

complexes, **1** and **2**, are shown in Fig. 2. In both complexes, an intense charge-transfer transition is observed around 380 nm; it tails into the visible region. In the visible region, a very broad feature appears at ca. 800 nm. Although this may be due to d–d transitions for Mn(III) ion in an elongated octahedral environment, the broad feature seems to be characteristic of oxo-bridged Mn(III) species. Similar spectra are found in the related tetranuclear complex **3**[37] which has oxo-bridged structure.

The complex **1** is soluble in DMF; unfortunately, the complex **2** is only sparingly soluble. Thus, conductivity measurements were performed for complex **1**. The conductivity data show that complex **1** is nonelectrolyte, in agreement with the formulation as neutral tetranuclear molecule. Cyclic voltammetric measurements were also carried out for **1** in DMF solution. The cyclic voltammogram was featureless in the range 1.0——2.0 V vs. Ag/Ag^+ in both anodic and cathodic scans, suggesting that the complex is stable at the Mn(III) oxidation level. This is in contrast to the quasi-reversible electrochemical behavior found in the tetranuclear complex **3**, which shows the $[Mn^{III}Mn^{III}Mn^{III}Mn^{IV}]/[Mn^{III}Mn^{III}]_2$, $[Mn^{III}Mn^{III}]_2/[Mn^{II}Mn^{III}]_2$, and $[Mn^{II}Mn^{III}]_2/[Mn^{II}Mn^{II}]_2$ couples.[37] Judging from the structural similarity between the present complex and complex **3**, we conclude that substitution of the phenoxo-oxygen for the alkoxo-oxygen can greatly influence the electrochemical behavior in this type of tetranuclear Mn complexes.

The effective magnetic moments of **1** and **2** are

Table 3. Comparison of Structural Parameters and Exchange Coupling Constants for $[Mn_4(\mu_3\text{-}O)_2]$ Cores

Complex	Bridging mode	J or J'/cm^{-1}	Mn–Mn/Å	Mn–O–Mn/°	Mn–O/Å	Reference
1	Di-μ-oxo $Mn^{III}Mn^{III}$	−2.51	2.831	96.7	1.891, 1.899	This work
	Mono-μ-oxo $Mn^{III}Mn^{III}$	−2.13	2.954, 3.051	101.7, 106.1	1.891—1.920	
3	Di-μ-oxo $Mn^{III}Mn^{III}$	−10.0	2.875	97.4	1.892, 1.934	37
	Mono-μ-oxo $Mn^{III}Mn^{III}$	−3.7	2.933, 3.122	99.9, 107.4	1.892—1.941	
$[Mn_4O_2(O_2CMe)_7(bipy)_2](ClO_4)$	Di-μ-oxo $Mn^{III}Mn^{III}$	−23.5	2.848	95.7, 96.8	1.89—1.93	18d
	Mono-μ-oxo $Mn^{III}Mn^{III}$	−7.8	3.299—3.385	123.3—131.3	1.80—1.93	
$(n\text{-}Bu_4N)[Mn_4O_2(O_2CMe)_7(pic)_2]$	Di-μ-oxo $Mn^{III}Mn^{III}$	−24.6	2.842	96.9	1.888—1.910	19a
	Mono-μ-oxo $Mn^{III}Mn^{III}$	−5.3	3.308, 3.406	124.6—130.2	1.840—1.910	
$[Mn_4O_2(O_2CMe)_6(bipy)_2]$	Di-μ-oxo $Mn^{III}Mn^{III}$	−3.12	2.779	97.1	1.851, 1.856	18d
	Mono-μ-oxo $Mn^{II}Mn^{III}$	−1.97	3.288, 3.481	112.4, 123.0	1.851—2.103	
$[Mn_4O_2(O_2CCPh_3)_6(OEt_2)_2]$	Di-μ-oxo $Mn^{III}Mn^{III}$	−2.8	2.770	97.6	1.828, 1.852	20
	Mono-μ-oxo $Mn^{II}Mn^{III}$	−1.5	3.265	113.3, 119.7	1.828—2.077	

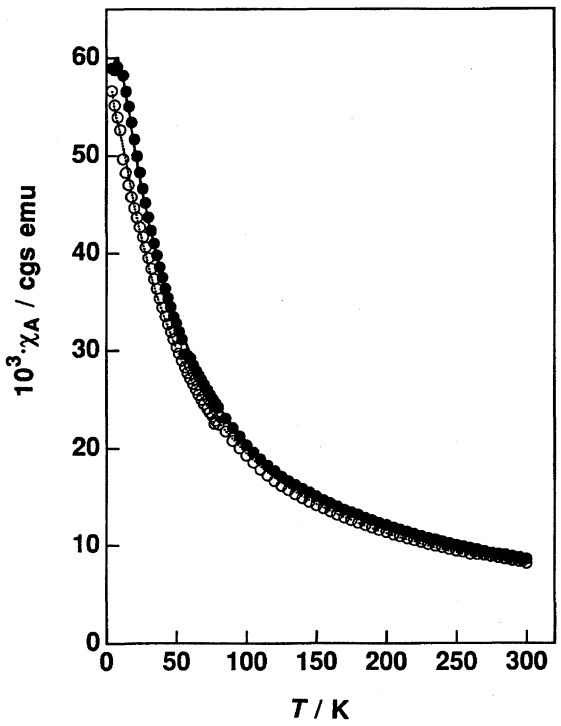

Fig. 3. Plots of magnetic susceptibilities of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (**1**) (○) and $[Mn_4(L)_2(O)_2(C_6H_5COO)_2]\cdot 2CH_3OH$ (**2**) (●). The dotted and solid lines represent the calculated fits with van Vleck equation for the tetranuclear Mn(III) system.

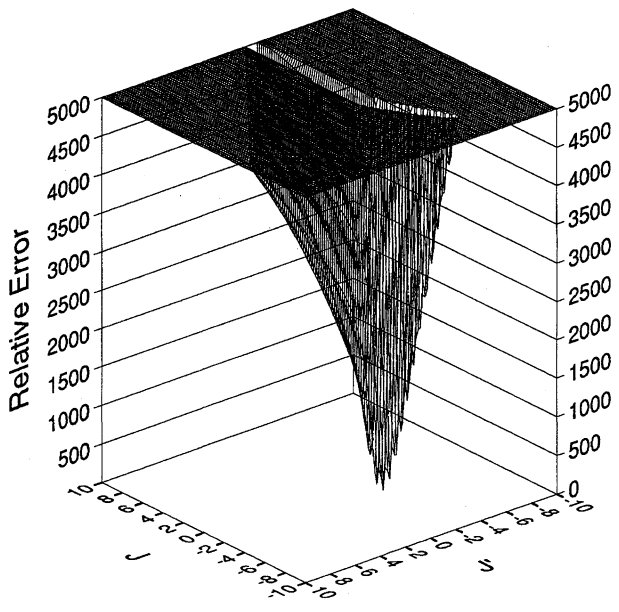

Fig. 4. A plot of the relative error surface for fitting the susceptibility data of $[Mn_4(L)_2(O)_2(CH_3COO)_2]\cdot 2CH_3CN$ (**1**) as a function of the coupling parameters J and J'.

4.42 and 4.58 B.M./Mn at room temperature, respectively; these values are lower than those of normal high-spin manganese(III) complexes. The tem-

perature dependence of the magnetic susceptibilities of **1** and **2** were measured in the temperature range 4—300 K (Fig. 3). The magnetic data were analyzed using the van Vleck equation for the ($S_{Mn1}=2$)–($S_{Mn2}=2$)–($S_{Mn1'}=2$)–($S_{Mn2'}=2$) system based on the Heisenberg model

$$\mathscr{H}=-2JS_{Mn1}\cdot S_{Mn1'}-2J'(S_{Mn1}\cdot S_{Mn2}+S_{Mn1}\cdot S_{Mn2'}+S_{Mn1'}\cdot S_{Mn2}+S_{Mn1'}\cdot S_{Mn2'}). \quad (1)$$

The Kambe vector-coupling method[50] allows for determination of the eigenvalues using the following scheme:

$$S_A=S_{Mn1}+S_{Mn1'},\ S_B=S_{Mn2}+S_{Mn2'},\ S_T=S_A+S_B. \quad (2)$$

The energies of the spin states are given in Eq. 3.

$$E=-J[S_A(S_A+1)]-J'[S_T(S_T+1)-(S_A(S_A+1)-S_B(S_B+1))]. \quad (3)$$

Since $S_T=0,1,2,\cdots,8$, there are 85 individual spin states. The best fitting parameters are $g=1.872(5)$, $J=-2.51(3)$ cm^{-1}, $J'=-2.13(2)$ cm^{-1} for **1**; $g=1.874(5)$, $J=-1.90(3)$ cm^{-1}, $J'=-1.75(2)$ cm^{-1} for **2**. The dotted and solid lines in Fig. 3 are those calculated using these parameters. A plot of the relative error for fitting the data is shown in Fig. 4 as one of the examples. It can be confirmed that the fitting parameters show a well-defined minimum for this system. These results suggest that the ground state for these exchange parameters in a singlet ($S_T=0$) state. In Table 3, exchange parameters for Mn–Mn interactions in analogous tetranuclear complexes with the $Mn_4(\mu_3\text{-}O)_2$ cores are listed together with their structural parameters. The di-μ-oxo Mn^{III}–Mn^{III} interactions are antiferromagnetic with J in the -2.51 to -24.6 cm^{-1} range. The Mn^{III}–O–Mn^{III} angles are in the range of 95.7 to 97.6°. The mono-μ-oxo Mn^{III}–Mn^{III} interactions are also antiferromagnetic, but slightly weak with $J'=-1.5$ to -7.8 cm^{-1}. The Mn^{III}–O–Mn^{III} angles are 99.9—131.3°. The net antiferromagnetic interactions in the present complexes are comparable to those of the similar tetranuclear complex **3**.[37]

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