Synthesis and Characterization of Mononuclear (Mn(II) and Mn(III)) and Dinuclear (Mn(II)Mn(II) and Mn(II)Mn(III)) Complexes with 2,6-Bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol

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Mononuclear and dinuclear manganese complexes with2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol (HL), $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**), $[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (**2**), $[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**), $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(CH_3OH)_2](ClO_4)_2$ (**4**), $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(NCS)_2]$ (**5**), $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**), and $[Mn^{III}(HL)(N_3)_3]$ (**7**), have been prepared and characterized by infrared, electronic, and ESR spectra, as well as the temperature dependence of the magnetic susceptibilities (80—300 K). The molecular structures of **1**, **2**, **3**, **6**, and **7** were determined by single-crystal X-ray structure analyses. Complexes **1** and **2** have a μ-phenoxo-di-μ-acetato-bridged dinuclear structure, in which one manganese atom is five-coordinated and the other six-coordinated. Complex **6** is a μ-phenoxo-di-μ-acetato-bridged dinuclear molecule comprising an octahedral Mn(II) atom and an elongated-octahedral Mn(III) atom. The manganese atoms of **3** and **7** are six-coordinated in a distorted octahedral environment. The spectral and magnetic properties are discussed in relation to the crystal structures.

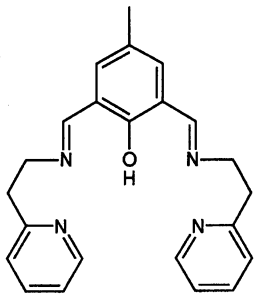
The coordination chemistry of manganese has achieved remarkable progress during the last decade due to an increased recognition of this metal's role in biological systems. Dinuclear manganese complexes are of current interest, since such systems are known to exist at the active site of some manganese-containing enzymes, such as manganese catalase, ribonucleotide reductase of certain bacteria, and the photosystem II of green plants.[1—9] As part of continuing projects concerning dinuclear manganese complexes, we recently reported on the synthesis and characterization of several manganese complexes with pentadentate ligands: 1,5-bis(salicylideneamino)-3-pentanol,[10—13] 1,3-bis(salicylideneamino)-2-propanol,[14] and 1-salicylideneamino-3-salicylamino-2-propanol.[15] These dinucleating ligands afford interesting μ-alkoxo-bridged dinuclear manganese(III) complexes which contain a variety of anions or solvent molecules. Concerning these complexes, we have also tried to isolate μ-phenoxo-bridged manganese complexes with a related pentadentate Schiff-base ligand, 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol (HL), which was expected to hold two manganese atoms in close proximity (Chart 1). This dinucleating ligand has two pyridyl side-arms in addition to a phenoxo-oxygen as a bridging group, and has been used to obtain phenoxo-bridged dinuclear copper complexes,[16,17] where the two copper atoms are bridged by the phenoxo-oxygen atom and by another bridging ligand X^-, such as the pyrazolate anion. By using this ligand, we have isolated various manganese complexes containing mononuclear Mn(II), mononuclear Mn(III), dinuclear Mn(II)Mn(II), and dinuclear Mn(II)Mn(III). Here, we present complete details concerning the synthesis and characterization of these complexes.[18,19]

Experimental

Synthesis of the Complexes. 2,6-Diformyl-4-methylphenol was synthesized according to a method reported by Okawa and Kida.[20]

$[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (1).

2,6-Diformyl-4-mehtylphenol (41 mg, 0.25 mmol) and 2-(2-aminoethyl)pyridine (61 mg, 0.50 mmol) were dissolved in 10 ml of methanol. The solution was stirred and heated at ca 70 °C for 1 h. To the resulting yellow solution were successively added manganese(II) acetate tetrahydrate (120 mg, 0.50 mmol) and sodium perchlorate (180 mg, 0.50 mmol). After the reaction mixture had been stirred and filtered while hot, diethyl ether (ca. 10 ml) was layered onto the filtrate and the mixture placed in a refrigerator for several days. Yellow prisms were deposited and collected by filtration and dried in vacuo over P_2O_5 (yield 100 mg, 55%). Anal. Calcd for $C_{28}H_{33}ClMn_2N_4O_{10}$: C, 46.01; H, 4.55; N, 7.66%. Found: C, 45.86; H, 4.62; N, 7.58%. IR



HL

Chart 1.

(KBr) ν/cm^{-1} ν (C=N) 1643, 1625; ν_{as} (COO) 1584; ν_s (COO) 1409; ν (ClO_4) 1105. Λ_M (DMF)/S mol^{-1} cm^2 98 (lit, range for 1:1 electrolytes,[21] 65—90 S mol^{-1} cm^2). Electronic spectrum in DMF: λ_{max}/nm (ε per Mn/dm^3 mol^{-1} cm^{-1}) 381 (3910). Diffuse reflectance spectrum: λ_{max}/nm 247, 367, 648 (very weak), 1137 (very weak), 1185 (very weak), 1380 (very weak). μ_{eff} per Mn (288 K)/B.M. 5.56.

$[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (2). This complex was prepared in the same way as that for **1**, except for using an equimolecuar amount of ammonium thiocyanate instead of sodium perchlorate (orange prisms, yield 67%). Anal. Calcd for $C_{28}H_{29}Mn_2N_5O_5S$: C, 51.15; H, 4.45; N, 10.65%. Found: C, 51.35; H, 4.62; N, 10.82%. IR (KBr) ν/cm^{-1} ν (NCS) 2080, 2060; ν (C=N) 1640, 1626; ν_{as} (COO) 1588; ν_s (COO) 1421. Λ_M (DMF)/S mol^{-1} cm^2 93 (lit, range for 1:1 electrolytes,[21] 65—90 S mol^{-1} cm^2). Electronic spectrum in DMF: λ_{max}/nm (ε per Mn/dm^3 mol^{-1} cm^{-1}) 381 (4520). Diffuse reflectance spectrum: λ_{max}/nm 248, 381, 447 sh, 1135 (very weak), 1186 (very weak), 1380 (very weak). μ_{eff} per Mn(297 K)/B.M. 5.60.

$[Mn^{II}(HL)(NCS)_2(H_2O)]$ (3). After 2,6-diformyl-4-methylphenol (33 mg, 0.20 mmol) and 2-(2-aminoethyl)pyridine (49 mg, 0.40 mmol) had been dissolved in 5.0 ml of methanol and the solution was heated for 1 h, manganese(II) acetate tetrahydrate (99 mg, 0.40 mmol) and ammonium thiocyanate (150 mg, 2.0 mmol) were added. The solution was filtered. Diethyl ether (1 ml) was layered onto the filtrate and the solution placed in a refrigerator. Vermillion prisms were deposited, collected by filtration and dried in vacuo over P_2O_5 (yield 85 mg, 76%). Anal. Calcd for $C_{25}H_{26}MnN_6O_2S_2$: C, 53.46; H, 4.66; N, 14.96%. Found: C, 53.27; H, 4.74; N, 14.84%. IR (KBr) ν/cm^{-1} ν (NCS) 2060; ν (C=N) 1646, 1630. Λ_M (DMF)/S mol^{-1} cm^2 132 (lit, range for 2:1 electrolytes,[21] 130—170 S mol^{-1} cm^2). Electronic spectrum in DMF: λ_{max}/nm (ε per Mn/dm^3 mol^{-1} cm^{-1}) 355 (3770), 417 (4830). Diffuse reflectance spectrum: λ_{max}/nm 243, 411, 538, 1137 (very weak), 1189 (very weak), 1375 (very weak). μ_{eff} per Mn (287 K)/B.M. 5.92.

$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(CH_3OH)_2](ClO_4)_2$ (4). To a hot solution of 2,6-diformyl-4-methylphenol (33 mg, 0.20 mmol) and 2-(2-aminoethyl)pyridine (49 mg, 0.40 mmol) in 4 ml of methanol were successively added manganese(III) acetate dihydrate (110 mg, 0.40 mmol) and sodium perchlorate (49 mg, 0.40 mmol). The reaction mixture was stirred and filtered while hot. The mixture was allowed to stand at room temperature for several days. Dark-brown needles were collected by filtration and dried in vacuo over P_2O_5 (yield 58 mg, 34%). Since these crystals were prone to lose solvent molecules and slowly decompose, no characterization was performed. Anal. Calcd for $C_{29}H_{37}Cl_2Mn_2N_4O_{15}$: C, 40.39; H, 4.32; N, 6.50%. Found: C, 40.72; H, 4.38; N, 6.50%. IR (KBr) ν/cm^{-1} ν (C=N) 1656, ν_{as} (COO) 1554; ν_s (COO) 1394; ν (ClO_4) 1144, 1114, 1084.

$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(NCS)_2]$ (5). This complex was prepared in the same way as that for **4**, except for using ammonium thiocyanate instead of sodium perchlorate (brown needles, yield 57%). Anal. Calcd for $C_{29}H_{29}Mn_2N_6O_5S_2$: C, 48.67; H, 4.08; N, 11.74%. Found: C, 48.71; H, 4.18; N, 11.64%. IR (KBr) ν/cm^{-1} ν (NCS) 2056; ν (C=N) 1631; ν_{as} (COO) 1553; ν_s (COO) 1398. Diffuse reflectance spectrum: λ_{max}/nm 242, 353, 420sh, 502sh, 1051. μ_{eff} per Mn (291 K)/B.M. 5.21.

$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (6). To a hot solution of 2,6-diformyl-4-methylphenol (33 mg, 0.20 mmol) and 2-(2-aminoethyl)pyridine (49 mg, 0.40 mmol) in 4 ml of methanol were successively added manganese(II) acetate tetrahydrate (99 mg, 0.40 mmol), manganese(III) acetate dihydrate (110 mg, 0.40 mmol), and sodium azide (26 mg, 0.40 mmol). The reaction mixture was stirred and filtered while hot. Dark-brown prisms were deposited and collected by filtration, and then dried in vacuo over P_2O_5 (yield 58 mg, 41%). Anal. Calcd for $C_{29}H_{37}Mn_2N_{10}O_7$: C, 46.59; H, 4.99; N, 18.74%. Found: C, 46.14; H, 4.65; N, 19.03%. IR (KBr) ν/cm^{-1} ν (N_3) 2038; ν (C=N) 1631; ν_{as} (COO) 1545; ν_s (COO) 1401. Diffuse reflectance spectrum: λ_{max}/nm 238, 357, 445sh, 1011. μ_{eff} per Mn (290 K)/B.M. 5.22.

$[Mn^{III}(HL)(N_3)_3]$ (7). To a hot solution of 2,6-diformyl-4-methylphenol (33 mg, 0.20 mmol) and 2-(2-aminoethyl)pyridine (49 mg, 0.40 mmol) in 5 ml of methanol were successively added manganese(III) acetate dihydrate (110 mg, 0.40 mmol) and sodium azide (26 mg, 0.40 mmol). The reaction mixture was stirred and filtered while hot. Dark-brown prisms were deposited and collected by filtration, and then dried in vacuo over P_2O_5 (yield 74 mg, 76%). Anal. Calcd for $C_{23}H_{24}MnN_{13}O$: C, 49.91; H, 4.37; N, 32.90%. Found: C, 49.95; H, 4.40; N, 32.05%. IR (KBr) ν/cm^{-1} ν (N_3) 2060, 2034; ν (C=N) 1653, 1624. Diffuse reflectance spectrum: λ_{max}/nm: 250, 346, 399, 461sh, 570sh, 1021. μ_{eff} per Mn (300 K)/B.M. 4.90.

Caution: Perchlorate or azide salts are explosive, and care should be exercised in handling these complexes, even though we experienced no problems.

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 4000—400 cm^{-1} region on a KBr disk. Electric conductivities were measured on a Horiba conductivity meter (DS-14). Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). The magnetic susceptibilities were measured by the Faraday method over the 80—300 K temperature range. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[22] The effective

Table 1. Crystal Data and Data Collection Details

Complexes	$[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**)	$[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (**2**)	$[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**)	$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**)	$[Mn^{III}(HL)(N_3)_3]$ (**7**)
Formula	$Mn_2ClO_{10}N_4C_{28}H_{33}$	$Mn_2SO_5N_5C_{28}H_{29}$	$MnS_2O_2N_6C_{25}H_{26}$	$Mn_2O_7N_{10}C_{29}H_{37}$	$MnON_{13}C_{23}H_{24}$
F.W.	730.9	657.5	561.6	747.6	553.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P1$	$P2_1/n$
a/Å	17.706(4)	21.220(1)	9.289(3)	13.421(2)	14.241(8)
b/Å	15.174(2)	15.947(2)	19.685(5)	16.220(3)	13.347(2)
c/Å	11.777(3)	17.912(1)	14.670(5)	9.060(4)	14.164(8)
α/°				90.69(3)	
β/°	91.91(1)	101.38(3)	94.86(2)	99.62(2)	99.83(3)
γ/°				66.97(1)	
V/Å^3	3162.3	5942.1	2672.9	1786.4(9)	2652.6
Z	4	8	4	2	4
D_c/g cm^{-3}	1.54	1.47	1.40	1.39	1.39
D_m/g m^{-3}	1.55	1.45	1.38	1.44	1.39
$F(000)$	1504	2704	1164	774	1144
μ(Mo $K\alpha$)/cm^{-1}	9.10	9.27	6.49	7.32	5.18
Crystal dimensions (mm)	0.30×0.32×0.46	0.29×0.32×0.35	0.37×0.39×0.45	0.07×0.29×0.68	0.18×0.36×0.55
2θ range/°	2.0—48.0	2.0—48.0	2.0—48.0	2.0—48.0	2.0—48.0
Total no. of observed reflections	5173	9693	4331	5599	4354
No. of unique reflections with $I>3\sigma(I)$	2957	5948	2461	2576	2142
Final no. of variables	406	739	325	433	343
Final rediduals					
R	0.060	0.057	0.054	0.049	0.064
R_w	0.066	0.064	0.059	0.054	0.067

magnetic moments were calculated from the equation $\mu_{eff}=2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility. The ESR spectra were recorded at liquid-nitrogen or liquid-helium temperature on a Varian E109 ESR spectrometer.

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 concerning data collection are given in Table 1. The lattice constants were determined by a 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 direct methods. Refinements were carried out by the full-matrix least-squares methods. Hydrogen atoms were not included in the calculation for **1**, **2**, and **7**. For **3**, hydrogen atoms of the protonated imine nitrogen (N3) and water molecule were located from difference Fourier maps; the Schiff-base's hydrogens were included at the calculated positions. The hydrogen atoms of **6** were inserted into their calculated positions. All of the hydrogen atoms were 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, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are listed in Table 1. All of the calculations were carried out on a Micro-VAXII computer using an Enraf-Nonius SDP program package.[23] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 2. 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. 66015 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Dinuclear Mn(II)Mn(II) Complexes. Under the reaction of 2,6-diformyl-4-methylphenol, 2-(2-aminoethyl)pyridine, manganese(II) acetate, and sodium perchlorate or ammonium thiocyanate with the 1 : 2 : 2 : 2 molar ratio, dinuclear manganese(II) complex, $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**) or $[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (**2**) was formed. At an early stage[18] we assumed a μ-phenoxo-μ-methoxo-μ-acetato-bridged dinuclear structure of $[Mn_2^{II}(L)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)]$ for the former complex based on an elemental analysis and IR spectral data, with reference to the X-ray structure of the μ-alkoxo-μ-methoxo-μ-acetato-bridged dinuclear manganese(III) complex with 1,5-bis(salicylideneamino)-3-pentanol.[10]

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)
$[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**)				
Mn1	0.77013(7)	0.02582(8)	0.6655(1)	3.49(3)
Mn2	0.60038(7)	−0.03718(8)	0.7614(1)	3.35(2)
Cl	0.7914(2)	0.2512(2)	0.2906(2)	5.18(6)
O1	0.6520(3)	0.0699(3)	0.6743(5)	3.8(1)
O2	0.7879(3)	0.0232(4)	0.8464(5)	4.6(1)
O3	0.6748(3)	−0.0207(5)	0.8983(5)	5.3(2)
O4	0.7473(3)	−0.1094(4)	0.6460(6)	5.0(1)
O5	0.6263(3)	−0.1439(4)	0.6568(5)	4.8(1)
O6	0.7577(4)	0.0340(4)	0.4700(5)	5.4(2)
O7	0.8522(6)	0.2637(9)	0.2219(8)	14.2(4)
O8	0.7277(5)	0.2891(7)	0.250(1)	13.5(3)
O9	0.8090(7)	0.282(1)	0.3932(9)	20.7(6)
O10	0.7759(8)	0.1646(8)	0.313(1)	18.2(5)
N1	0.7955(4)	0.1662(4)	0.6507(6)	3.8(2)
N2	0.8965(4)	−0.0053(5)	0.6583(6)	4.3(2)
N3	0.4956(4)	0.0069(5)	0.6757(5)	3.7(1)
N4	0.5240(4)	−0.1059(4)	0.8877(6)	3.6(1)
C1	0.6222(5)	0.1414(5)	0.6279(6)	3.5(2)
C2	0.6664(5)	0.2165(5)	0.6030(7)	3.7(2)
C3	0.6331(6)	0.2932(6)	0.5539(8)	5.1(2)
C4	0.5554(6)	0.2956(6)	0.5236(8)	5.4(2)
C5	0.5117(6)	0.2227(6)	0.5471(7)	4.8(2)
C6	0.5428(5)	0.1473(6)	0.5996(7)	3.9(2)
C7	0.5206(8)	0.3789(8)	0.468(1)	8.9(4)
C8	0.7477(5)	0.2264(5)	0.6231(7)	4.0(2)
C9	0.8748(5)	0.1942(6)	0.6648(9)	5.2(2)
C10	0.9246(6)	0.1432(6)	0.5842(9)	5.6(2)
C11	0.9504(5)	0.0542(6)	0.6338(8)	4.9(2)
C12	1.0266(5)	0.0345(7)	0.6514(9)	6.2(3)
C13	1.0495(6)	−0.0481(8)	0.694(1)	6.5(3)
C14	0.9940(6)	−0.1085(8)	0.7144(9)	6.1(3)
C15	0.9175(6)	−0.0851(7)	0.6957(9)	5.5(2)
C16	0.4868(5)	0.0778(6)	0.6176(7)	4.1(2)
C17	0.4244(5)	−0.0468(7)	0.6812(8)	5.0(2)
C18	0.4402(5)	−0.1404(6)	0.7235(8)	4.6(2)
C19	0.4580(5)	−0.1432(6)	0.8506(8)	4.0(2)
C20	0.4080(5)	−0.1806(7)	0.9255(8)	5.2(2)
C21	0.4281(6)	−0.1840(7)	1.0412(9)	5.8(3)
C22	0.4968(6)	−0.1486(7)	1.0789(8)	5.3(2)
C23	0.5440(5)	−0.1095(6)	0.9985(7)	4.4(2)
C24	0.7410(5)	0.0065(5)	0.9203(7)	3.8(2)
C25	0.7655(6)	0.0173(7)	1.0452(7)	5.3(2)
C26	0.6932(5)	−0.1599(5)	0.6273(7)	3.8(2)
C27	0.7071(5)	−0.2468(6)	0.5662(8)	4.8(2)
C28	0.7625(6)	−0.0382(7)	0.3926(8)	5.4(2)

However, the present X-ray crystal structure analysis revealed that the proposed structure is incorrect; complex **1** has a μ-phenoxo-di-μ-acetato-bridged dinuclear core. A perspective drawing of the molecular structure of **1** is given in Fig. 1. Selected bond distances and angles are listed in Table 3. The two manganese atoms (Mn1 and Mn2) are bridged by the central phenoxo-oxygen atom (O1) of the pentadentate Schiff-base ligand (L) and the two didentate acetate ions. The Mn1···Mn2 separation

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} a)
$[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (**2**)				
Mn1a	0.57095(5)	0.58568(7)	0.18649(6)	3.58(2)
Mn1b	0.92680(5)	0.43496(8)	0.29383(6)	3.60(2)
Mn2a	0.42915(5)	0.53832(7)	0.22944(6)	3.40(2)
Mn2b	1.07174(5)	0.45912(7)	0.25010(6)	3.50(2)
S1a	0.2699(2)	0.6636(2)	0.0209(2)	9.16(9)
S1b	1.2190(1)	0.3642(2)	0.4866(1)	5.84(6)
O1a	0.4952(2)	0.4919(3)	0.1598(3)	3.6(1)
O1b	1.0082(2)	0.5177(3)	0.3181(3)	3.7(1)
O2a	0.5304(3)	0.7066(4)	0.1506(4)	5.9(2)
O2b	0.9628(3)	0.3152(4)	0.3301(4)	5.5(1)
O3a	0.4729(3)	0.6595(4)	0.2282(3)	5.9(2)
O3b	1.0304(3)	0.3380(4)	0.2555(3)	7.1(2)
O4a	0.5922(3)	0.5443(4)	0.2982(3)	5.9(2)
O4b	0.9105(3)	0.4731(5)	0.1813(3)	6.0(2)
O5a	0.5010(2)	0.5138(4)	0.3334(3)	4.4(1)
O5b	1.0034(3)	0.4863(4)	0.1448(3)	4.8(1)
N1a	0.5941(3)	0.5424(4)	0.0785(3)	3.8(1)
N1b	0.9080(3)	0.4810(4)	0.4036(3)	3.8(1)
N2a	0.6753(3)	0.6320(4)	0.2110(4)	4.3(2)
N2b	0.8199(3)	0.4014(5)	0.2680(4)	4.5(2)
N3a	0.3970(3)	0.4069(4)	0.2316(3)	3.7(1)
N3b	1.1098(3)	0.5871(4)	0.2455(3)	3.7(1)
N4a	0.3619(3)	0.5725(4)	0.3093(3)	3.9(1)
N4b	1.1348(3)	0.4150(4)	0.1683(3)	3.9(1)
N5a	0.3580(3)	0.5799(5)	0.1302(4)	5.0(2)
N5b	1.1422(4)	0.4260(5)	0.3537(4)	5.8(2)
C1a	0.4987(3)	0.4183(5)	0.1285(4)	3.3(2)
C1b	1.0181(3)	0.5853(5)	0.3600(4)	3.3(2)
C2a	0.5397(4)	0.4063(5)	0.0739(4)	3.6(2)
C2b	0.9841(4)	0.6004(5)	0.4202(4)	3.6(2)
C3a	0.5444(4)	0.3274(5)	0.0409(4)	4.4(2)
C3b	0.9967(4)	0.6721(5)	0.4665(4)	4.3(2)
C4a	0.5117(4)	0.2575(5)	0.0600(4)	4.8(2)
C4b	1.0402(4)	0.7338(5)	0.4537(5)	4.6(2)
C5a	0.4708(4)	0.2684(5)	0.1126(4)	4.7(2)
C5b	1.0726(4)	0.7211(5)	0.3940(5)	4.4(2)
C6a	0.4628(4)	0.3472(5)	0.1454(4)	3.7(2)
C6b	1.0640(4)	0.6485(5)	0.3491(4)	3.8(2)
C7a	0.5194(6)	0.1710(5)	0.0262(5)	6.7(3)
C7b	1.0516(5)	0.8136(6)	0.5020(5)	6.1(3)
C8a	0.5778(4)	0.4715(5)	0.0473(4)	3.8(2)
C8b	0.9358(4)	0.5444(5)	0.4410(4)	3.8(2)
C9a	0.6370(4)	0.5935(6)	0.0384(4)	4.7(2)
C9b	0.8604(4)	0.4389(6)	0.4428(4)	4.6(2)
C10a	0.6552(4)	0.6779(5)	0.0775(5)	4.7(2)
C10b	0.8345(4)	0.3580(5)	0.4012(5)	4.7(2)
C11a	0.6991(4)	0.6677(5)	0.1538(4)	4.5(2)
C11b	0.7917(4)	0.3751(5)	0.3249(5)	4.2(2)
C12a	0.7617(5)	0.6965(8)	0.1652(6)	8.2(3)
C12b	0.7248(4)	0.3670(6)	0.3141(5)	5.5(2)
C13a	0.8009(5)	0.686(1)	0.2380(7)	11.6(4)
C13b	0.6877(4)	0.3842(7)	0.2421(6)	6.2(3)
C14a	0.7773(5)	0.6448(9)	0.2958(6)	8.3(3)
C14b	0.7173(4)	0.4087(6)	0.1828(6)	5.5(2)
C15a	0.7130(4)	0.6216(6)	0.2798(5)	5.1(2)
C15b	0.7836(4)	0.4165(6)	0.1986(5)	5.0(2)
C16a	0.4174(4)	0.3449(5)	0.1964(4)	3.8(2)
C16b	1.1028(4)	0.6481(5)	0.2890(4)	4.0(2)
C17a	0.3492(4)	0.3839(5)	0.2791(5)	4.6(2)
C17b	1.1506(4)	0.6026(5)	0.1885(5)	4.9(2)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} a)
C18a	0.3659(4)	0.4270(5)	0.3580(4)	4.6(2)
C18b	1.2055(4)	0.5376(5)	0.1982(4)	4.5(2)
C19a	0.3419(3)	0.5165(5)	0.3570(4)	3.9(2)
C19b	1.1869(4)	0.4569(5)	0.1557(4)	4.0(2)
C20a	0.3008(4)	0.5418(6)	0.4053(4)	4.7(2)
C20b	1.2238(4)	0.4255(6)	0.1051(5)	5.0(2)
C21a	0.2805(4)	0.6248(6)	0.4044(5)	5.7(2)
C21b	1.2061(4)	0.3493(6)	0.0682(5)	5.3(2)
C22a	0.3011(5)	0.6818(6)	0.3550(6)	6.4(2)
C22b	1.1516(4)	0.3076(6)	0.0803(5)	5.2(2)
C23a	0.3413(4)	0.6527(6)	0.3078(5)	5.2(2)
C23b	1.1167(4)	0.3431(5)	0.1303(5)	4.6(2)
C24a	0.4840(4)	0.7145(5)	0.1833(4)	4.0(2)
C24b	1.0102(4)	0.2936(5)	0.3030(5)	4.3(2)
C25a	0.4428(4)	0.7919(6)	0.1688(5)	5.5(2)
C25b	1.0436(4)	0.2119(6)	0.3283(6)	6.1(2)
C26a	0.5599(4)	0.5213(5)	0.3470(4)	4.1(2)
C26b	0.9440(4)	0.4912(5)	0.1322(5)	4.5(2)
C27a	0.5984(5)	0.5032(7)	0.4266(5)	5.7(2)
C27b	0.9073(5)	0.5217(6)	0.0557(5)	5.8(2)
C28a	0.3218(4)	0.6156(6)	0.0853(4)	4.5(2)
C28b	1.1741(4)	0.3995(5)	0.4088(4)	4.2(2)
$[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**)				
Mn	0.3210(1)	0.03813(5)	0.71170(7)	4.08(2)
S1	0.8239(2)	0.1173(1)	0.7742(2)	6.29(5)
S2	0.1477(3)	0.2095(1)	0.9053(2)	8.31(6)
O1	0.3290(5)	−0.0170(2)	0.8379(3)	4.6(1)
O2	0.0797(5)	0.0180(2)	0.6997(3)	5.1(1)
N1	0.3509(5)	−0.0640(3)	0.6502(3)	3.7(1)
N2	0.2945(5)	0.0812(3)	0.5678(3)	4.7(1)
N3	0.2945(6)	0.0073(3)	1.0087(3)	4.6(1)
N4	−0.0031(6)	0.1050(3)	1.2213(4)	4.7(1)
N5	0.5556(6)	0.0604(3)	0.7200(4)	5.8(1)
N6	0.2714(8)	0.1307(3)	0.7797(5)	7.4(2)
C1	0.3681(6)	−0.0782(3)	0.8586(4)	3.8(1)
C2	0.4038(6)	−0.1278(3)	0.7937(4)	3.8(1)
C3	0.4495(7)	−0.1922(3)	0.8234(4)	4.2(1)
C4	0.4657(7)	−0.2110(3)	0.9156(4)	4.3(1)
C5	0.4287(7)	−0.1646(4)	0.9780(4)	4.8(2)
C6	0.3792(7)	−0.0984(4)	0.9533(4)	4.2(1)
C7	0.5225(8)	−0.2812(4)	0.9423(5)	5.9(2)
C8	0.3867(7)	−0.1178(3)	0.6948(4)	4.0(1)
C9	0.3407(7)	−0.0703(4)	0.5497(4)	4.6(2)
C10	0.2179(7)	−0.0282(4)	0.5032(4)	5.1(2)
C11	0.2565(6)	0.0465(4)	0.4925(4)	4.6(1)
C12	0.2551(8)	0.0746(4)	0.4056(4)	5.9(2)
C13	0.2934(8)	0.1421(5)	0.3974(5)	6.9(2)
C14	0.3320(8)	0.1789(4)	0.4743(6)	6.6(2)
C15	0.3312(8)	0.1478(4)	0.5591(5)	5.8(2)
C16	0.3438(7)	−0.0531(4)	1.0231(4)	4.6(2)
C17	0.2606(7)	0.0545(4)	1.0827(4)	5.0(2)
C18	0.1001(8)	0.0667(4)	1.0844(5)	5.1(2)
C19	0.0690(7)	0.1217(3)	1.1504(4)	4.3(1)
C20	0.1155(9)	0.1873(4)	1.1387(5)	6.2(2)
C21	0.079(1)	0.2374(4)	1.1984(6)	7.0(2)
C22	−0.0007(8)	0.2201(4)	1.2697(5)	6.2(2)
C23	−0.0362(7)	0.1540(4)	1.2790(5)	5.8(2)
C24	0.6675(7)	0.0839(3)	0.7400(5)	4.7(1)
C25	0.2207(7)	0.1629(3)	0.8317(5)	4.7(2)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} a)
$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**)				
Mn1	0.32398(9)	0.29993(8)	0.3209(2)	3.78(3)
Mn2	0.10741(9)	0.22447(7)	0.2344(1)	3.11(2)
Om1	0.6064(7)	0.1312(6)	−0.062(1)	10.7(3)
Om2	0.4897(7)	0.3098(6)	−0.0190(9)	10.4(3)
O1	0.1509(3)	0.3349(3)	0.2724(5)	3.3(1)
O2	0.3467(4)	0.1857(3)	0.4738(7)	5.2(2)
O3	0.2091(4)	0.1442(3)	0.3965(6)	4.4(1)
O4	0.3503(4)	0.2023(4)	0.1546(7)	5.7(2)
O5	0.2059(4)	0.1663(3)	0.0956(6)	4.5(1)
N1	0.2789(5)	0.3985(4)	0.4914(7)	4.0(2)
N2	0.5025(5)	0.2725(4)	0.4125(8)	4.7(2)
N3	−0.0038(4)	0.3010(4)	0.0599(6)	3.1(1)
N4	0.0279(5)	0.1176(4)	0.1784(7)	3.8(2)
N5	0.3228(5)	0.4011(4)	0.1598(8)	4.9(2)
N6	0.3123(5)	0.4758(4)	0.1813(8)	5.2(2)
N7	0.3010(7)	0.5487(5)	0.200(1)	8.0(3)
N8	−0.0060(5)	0.2737(4)	0.3641(7)	4.0(2)
N9	0.0017(5)	0.2293(4)	0.4749(8)	4.5(2)
N10	0.0046(6)	0.1908(5)	0.5823(9)	7.2(2)
Cm1	0.608(1)	0.124(1)	−0.214(2)	11.4(5)
Cm2	0.556(1)	0.362(1)	0.021(2)	13.5(6)
C1	0.0778(5)	0.4175(4)	0.2657(8)	2.9(2)
C2	0.0930(5)	0.4833(4)	0.3606(8)	3.1(2)
C3	0.0113(6)	0.5697(5)	0.3515(9)	3.9(2)
C4	−0.0857(6)	0.5971(5)	0.2448(8)	3.8(2)
C5	−0.0998(6)	0.5343(5)	0.1493(9)	3.5(2)
C6	−0.0218(5)	0.4462(5)	0.1596(8)	3.2(2)
C7	−0.1722(7)	0.6912(5)	0.239(1)	5.2(2)
C8	0.1895(6)	0.4657(5)	0.4776(9)	3.7(2)
C9	0.3669(7)	0.3938(6)	0.617(1)	5.4(2)
C10	0.4611(7)	0.4065(6)	0.561(1)	5.7(2)
C11	0.5408(6)	0.3251(6)	0.498(1)	5.3(2)
C12	0.6526(8)	0.3066(7)	0.531(1)	7.7(3)
C13	0.7259(8)	0.2331(8)	0.471(2)	9.1(4)
C14	0.6869(8)	0.1795(8)	0.384(1)	8.5(4)
C15	0.5751(7)	0.2017(6)	0.357(1)	6.0(3)
C16	−0.0466(5)	0.3861(5)	0.0543(8)	3.4(2)
C17	−0.0431(7)	0.2536(5)	−0.0601(9)	4.5(2)
C18	−0.1210(6)	0.2164(5)	−0.013(1)	5.1(2)
C19	−0.0686(6)	0.1335(5)	0.0905(9)	4.2(2)
C20	−0.1233(6)	0.0765(6)	0.094(1)	5.7(2)
C21	−0.0752(7)	−0.0001(6)	0.189(1)	6.0(2)
C22	0.0249(7)	−0.0163(6)	0.277(1)	5.8(2)
C23	0.0726(7)	0.0430(5)	0.270(1)	5.1(2)
C24	0.3008(6)	0.1348(5)	0.4741(8)	3.5(2)
C25	0.3537(7)	0.0489(6)	0.573(1)	6.1(3)
C26	0.2996(6)	0.1602(5)	0.0850(9)	4.0(2)
C27	0.3566(7)	0.0950(6)	−0.023(1)	6.8(3)

is 3.366(2) Å, and the Mn1–O1–Mn2 angle is 101.9(2)°. It is noteworthy that the two manganese environments are different. The coordination geometry of the Mn1 atom is a distorted octahedron formed by the N1, N2, and O1 atoms of ligand L, the O2 and O4 atoms of the two acetate ions, and the O6 atoms of the methanol molecule. On the other hand, the Mn2 atom is in a distorted square pyramid. The basal plane is formed by the N3, N4, and O1 atoms from ligand L and the O3 atom of the acetate ion, and the fifth coordination site is

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^{2} a)
$[Mn^{III}(HL)(N_3)_3]$ (**7**)				
Mn	0.26739(9)	0.4121(1)	0.1364(1)	4.36(2)
O	0.4031(3)	0.4804(4)	0.1362(4)	4.5(1)
N1	0.2236(5)	0.5501(5)	0.1746(5)	5.7(2)
N2	0.1147(4)	0.3472(5)	0.1357(5)	4.7(2)
N3	0.5804(4)	0.4381(5)	0.1209(4)	4.2(2)
N4	0.7838(5)	0.4860(6)	0.2679(6)	5.8(2)
N5	0.3135(5)	0.2810(6)	0.0940(7)	6.7(2)
N6	0.3929(5)	0.2546(6)	0.1183(5)	5.4(2)
N7	0.4700(6)	0.2269(7)	0.1384(7)	7.5(2)
N8	0.2206(5)	0.4518(5)	0.0009(5)	5.3(2)
N9	0.1826(5)	0.3889(6)	−0.0546(5)	6.0(2)
N10	0.1473(8)	0.3330(8)	−0.1099(7)	10.5(3)
N11	0.3041(5)	0.3732(7)	0.2734(6)	7.3(2)
N12	0.3677(6)	0.4070(8)	0.3232(6)	8.3(2)
N13	0.432(1)	0.433(1)	0.3730(9)	18.9(5)
C1	0.4227(5)	0.5751(6)	0.1298(5)	3.6(2)
C2	0.3566(5)	0.6530(6)	0.1398(5)	3.9(2)
C3	0.3812(5)	0.7543(6)	0.1294(5)	4.1(2)
C4	0.4696(6)	0.7819(6)	0.1081(6)	4.5(2)
C5	0.5366(6)	0.7069(6)	0.1009(6)	4.4(2)
C6	0.5149(5)	0.6049(6)	0.1122(5)	3.7(2)
C7	0.4945(7)	0.8917(6)	0.0945(8)	6.3(3)
C8	0.2645(6)	0.6361(7)	0.1667(6)	5.1(2)
C9	0.1336(7)	0.5496(8)	0.2176(8)	8.9(3)
C10	0.0518(7)	0.5169(8)	0.1508(9)	8.5(3)
C11	0.0397(5)	0.4042(8)	0.1400(7)	5.9(2)
C12	−0.0525(7)	0.3637(9)	0.1315(9)	8.1(3)
C13	−0.0641(7)	0.2633(9)	0.1130(9)	8.2(3)
C14	0.0142(7)	0.2013(8)	0.1066(8)	7.3(3)
C15	0.1031(6)	0.2477(7)	0.1187(6)	5.5(2)
C16	0.5892(5)	0.5341(6)	0.1087(5)	4.0(2)
C17	0.6608(5)	0.3672(6)	0.1233(6)	4.8(2)
C18	0.6929(6)	0.3308(7)	0.2277(6)	5.4(2)
C19	0.7237(6)	0.4191(7)	0.2950(6)	5.0(2)
C20	0.6881(9)	0.4281(9)	0.3799(8)	8.8(3)
C21	0.721(1)	0.511(1)	0.4420(9)	10.3(4)
C22	0.7841(8)	0.5787(8)	0.4102(8)	8.4(3)
C23	0.8136(7)	0.5652(7)	0.3236(7)	6.9(3)

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

occupied by the O5 atom of the other acetate ion. The two square planes around Mn1 and Mn2 (O1–N1–N2–O4 and O1–N3–N4–O3) are twisted by 60.4° each other. The Mn–O (phenoxo) (2.200(5), 2.135(5) Å), Mn–O (acetato) (2.081(6)—2.149(6) Å), Mn–O (methanol) (2.313(6) Å), Mn–N (imine) (2.184(7), 2.202(7) Å), and Mn–N (pyridyl) (2.289(7), 2.278(7) Å) distances fall within the ranges of the corresponding bonds found for other dinuclear or polynuclear manganese(II) complexes (Mn–O (phenoxo) 2.041(3)—2.218(3) Å,[24—29] Mn–O (carboxylato) 2.099(8)—2.246(3) Å,[29—34] Mn–O (alcohol) 2.213(12)—2.318(2) Å,[35,36] Mn–N (imine) 2.150(5)—2.308(2) Å,[27,28,36,37] Mn–N (pyridyl) 2.203(14)—2.411(3) Å.[24,29,31,35,36,38] There have been very few structural reports concerning five-coordinate manganese complexes.[39] Considering the general trend of the manganese(II) ion toward six-coordination, this is a novel example of dinuclear complexes having different coordination environments with a symmetric dinucleating ligand. The analytical data (C, 46.14; H, 4.73; N, 7.97; Mn, 15.63%) of the formula $[Mn_2^{II}(L)(CH_3O)(CH_3COO)(ClO_4)(CH_3OH)]$ are similar to those for the correct formula $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (C, 46.01; H, 4.55; N, 7.66; Mn, 15.03%). Thus, we could not distinguish between them based on the analytical data before undertaking an X-ray crystal structure analysis of **1**.

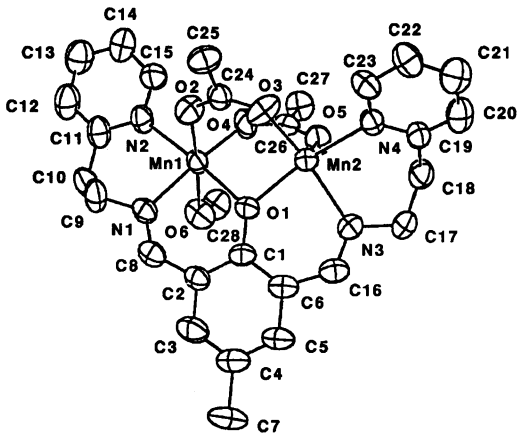


Fig. 1. ORTEP view of the structure of $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**).

The molecular structure of **2** was also determined by X-ray crystallography. The crystal contains two crystallographically independent dinuclear molecules; they are represented by a and b. Their structures are essentially the same. A perspective view of molecule a is given in Fig. 2. This structure is similar to that of **1**. The two manganese atoms are bridged by a phenoxo-oxygen of the Schiff-base ligand L and two acetate ions (Mn1a–Mn2a 3.337(2) Å, Mn1b–Mn2b 3.343(2) Å, Mn1a–O1a–Mn2a 99.9(2)°, Mn1b–O1b–Mn2b 100.6(2)°). Two N-donor atoms from either side-arm of the pentadentate ligand coordinate and complete N_2O_3 coordination about each manganese atom. The sixth coordination site of Mn2 is occupied by the nitrogen atom of the thiocyanate ion. The Mn2–N5 (thiocyanate) bond lengths are 2.195(6) and 2.205(7) Å for molecules a and b, respectively. These are slightly longer than the values typically found for Mn(II)–N (thiocyanate) (2.100(4)—2.174(4) Å).[24,35,36,40] The infrared spectrum of **2** shows a splitting of the ν_{CN} (NCS) stretching band. This fact is in harmony with the crystal structure of **2**, which contains two crystallographically independent molecules (a and b). The other Mn–N (2.202(6)—2.294(6) Å) and the Mn–O (2.069(6)—2.197(5) Å) lengths are comparable to those of **1**.

The electronic spectra of the dinuclear Mn(II)Mn(II) complexes, **1** and **2**, in DMF show no detectable d–d transitions in the visible region, being consistent

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

$[Mn^{II}_2(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**)			
Mn1–Mn2	3.366(2)	Mn1–O1	2.200(5)
Mn1–O2	2.149(6)	Mn1–O4	2.103(6)
Mn1–O6	2.313(6)	Mn1–N1	2.184(7)
Mn1–N2	2.289(7)	Mn2–O1	2.135(5)
Mn2–O3	2.081(6)	Mn2–O5	2.091(6)
Mn2–N3	2.202(7)	Mn2–N4	2.278(7)
Mn1–O1–Mn2	101.9(2)	O1–Mn1–O2	94.8(2)
O1–Mn1–O4	96.9(2)	O1–Mn1–O6	87.4(2)
O1–Mn1–N1	84.5(2)	O1–Mn1–N2	174.1(2)
O2–Mn1–O4	96.6(3)	O2–Mn1–O6	176.4(2)
O2–Mn1–N1	94.0(2)	O2–Mn1–N2	84.6(2)
O4–Mn1–O6	85.9(2)	O4–Mn1–N1	169.1(3)
O4–Mn1–N2	88.9(2)	O6–Mn1–N1	83.4(2)
O6–Mn1–N2	92.9(2)	N1–Mn1–N2	89.8(3)
O1–Mn2–O3	90.6(2)	O1–Mn2–O5	101.9(2)
O1–Mn2–N3	85.0(2)	O1–Mn2–N4	157.7(2)
O3–Mn2–O5	114.0(2)	O3–Mn2–N3	146.9(3)
O3–Mn2–N4	85.7(2)	O5–Mn2–N3	99.0(2)
O5–Mn2–N4	99.7(2)	N3–Mn2–N4	86.2(3)
$[Mn^{II}_2(L)(CH_3COO)_2(NCS)]$ (**2**)			
Mn1a–Mn2a	3.337(2)	Mn1b–Mn2b	3.343(2)
Mn1a–O1a	2.178(5)	Mn1b–O1b	2.149(5)
Mn1a–O2a	2.158(6)	Mn1b–O2b	2.112(6)
Mn1a–O4a	2.069(6)	Mn1b–O4b	2.069(6)
Mn1a–N1a	2.198(6)	Mn1b–N1b	2.207(6)
Mn1a–N2a	2.294(6)	Mn1b–N2b	2.289(6)
Mn2a–O1a	2.181(5)	Mn2b–O1b	2.197(5)
Mn2a–O3a	2.145(6)	Mn2b–O3b	2.132(7)
Mn2a–O5a	2.196(5)	Mn2b–O5b	2.183(5)
Mn2a–N3a	2.207(6)	Mn2b–N3b	2.202(6)
Mn2a–N4a	2.278(7)	Mn2b–N4b	2.282(7)
Mn2a–N5a	2.195(6)	Mn2b–N5b	2.205(7)
Mn1a–O1a–Mn2a	99.9(2)	Mn1b–O1b–Mn2b	100.6(2)
O1a–Mn1a–O2a	108.4(2)	O1b–Mn1b–O2b	105.4(2)
O1a–Mn1a–O4a	90.2(2)	O1b–Mn1b–O4b	89.4(2)
O1a–Mn1a–N1a	82.8(2)	O1b–Mn1b–N1b	84.0(2)
O1a–Mn1a–N2a	155.0(2)	O1b–Mn1b–N2b	155.5(2)
O2a–Mn1a–O4a	124.8(3)	O2b–Mn1b–O4b	123.2(3)
O2a–Mn1a–N1a	99.4(2)	O2b–Mn1b–N1b	98.3(2)
O2a–Mn1a–N2a	94.7(2)	O2b–Mn1b–N2b	97.7(2)
O4a–Mn1a–N1a	134.9(2)	O4b–Mn1b–N1b	138.2(3)
O4a–Mn1a–N2a	84.3(2)	O4b–Mn1b–N2b	84.5(2)
N1a–Mn1a–N2a	83.9(2)	N1b–Mn1b–N2b	84.9(2)
O1a–Mn2a–O3a	88.3(2)	O1b–Mn2b–O3b	93.3(2)
O1a–Mn2a–O5a	90.4(2)	O1b–Mn2b–O5b	91.1(2)
O1a–Mn2a–N3a	85.6(2)	O1b–Mn2b–N3b	84.0(2)
O1a–Mn2a–N4a	173.5(2)	O1b–Mn2b–N4b	171.7(2)
O1a–Mn2a–N5a	93.2(2)	O1b–Mn2b–N5b	91.3(2)
O3a–Mn2a–O5a	86.6(2)	O3b–Mn2b–O5b	90.6(2)
O3a–Mn2a–N3a	172.4(2)	O3b–Mn2b–N3b	177.0(3)
O3a–Mn2a–N4a	96.7(2)	O3b–Mn2b–N4b	92.8(3)
O3a–Mn2a–N5a	87.1(3)	O3b–Mn2b–N5b	87.8(3)
O5a–Mn2a–N3a	88.9(2)	O5b–Mn2b–N3b	88.2(2)
O5a–Mn2a–N4a	85.8(2)	O5b–Mn2b–N4b	83.1(2)
O5a–Mn2a–N5a	172.6(3)	O5b–Mn2b–N5b	177.1(3)
N3a–Mn2a–N4a	89.0(2)	N3b–Mn2b–N4b	89.8(2)
N3a–Mn2a–N5a	97.8(2)	N3b–Mn2b–N5b	93.5(3)
N4a–Mn2a–N5a	91.2(2)	N4b–Mn2b–N5b	94.6(3)

Table 3. (Continued)

$[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**)			
Mn–O1	2.142(4)	Mn–O2	2.269(4)
Mn–N1	2.229(5)	Mn–N2	2.270(5)
Mn–N5	2.216(6)	Mn–N6	2.146(7)
O1–Mn–O2	86.5(2)	O1–Mn–N1	84.1(2)
O1–Mn–N2	170.6(2)	O1–Mn–N5	95.3(2)
O1–Mn–N6	91.2(2)	O2–Mn–N1	88.1(2)
O2–Mn–N2	88.0(2)	O2–Mn–N5	178.1(2)
O2–Mn–N6	86.2(2)	N1–Mn–N2	88.1(2)
N1–Mn–N5	92.5(2)	N1–Mn–N6	172.8(2)
N2–Mn–N5	90.3(2)	N2–Mn–N6	96.1(2)
N5–Mn–N6	93.2(3)		
$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**)			
Mn1–Mn2	3.544(2)	Mn1–O1	2.132(5)
Mn1–O2	2.220(6)	Mn1–O4	2.141(6)
Mn1–N1	2.191(6)	Mn1–N2	2.266(6)
Mn1–N5	2.203(8)	Mn2–O1	2.098(5)
Mn2–O3	1.924(5)	Mn2–O5	1.941(5)
Mn2–N3	2.019(5)	Mn2–N4	2.376(7)
Mn2–N8	1.989(6)		
Mn1–O1–Mn2	113.8(2)	O1–Mn1–O2	90.9(2)
O1–Mn1–O4	91.2(2)	O1–Mn1–N1	82.6(2)
O1–Mn1–N2	169.9(2)	O1–Mn1–N5	95.3(2)
O2–Mn1–O4	84.0(2)	O2–Mn1–N1	93.6(2)
O2–Mn1–N2	86.1(2)	O2–Mn1–N5	172.1(2)
O4–Mn1–N1	173.4(3)	O4–Mn1–N2	98.1(3)
O4–Mn1–N5	91.0(3)	N1–Mn1–N2	87.9(2)
N1–Mn1–N5	92.0(2)	N2–Mn1–N5	88.6(3)
O1–Mn2–O3	98.8(2)	O1–Mn2–O5	97.9(2)
O1–Mn2–N3	85.7(2)	O1–Mn2–N4	170.4(2)
O1–Mn2–N8	89.9(2)	O3–Mn2–O5	90.5(2)
O3–Mn2–N3	175.5(3)	O3–Mn2–N4	89.1(2)
O3–Mn2–N8	91.2(2)	O5–Mn2–N3	88.9(2)
O5–Mn2–N4	87.3(2)	O5–Mn2–N8	171.7(3)
N3–Mn2–N4	86.4(2)	N3–Mn2–N8	88.7(2)
N4–Mn2–N8	84.5(2)		
$[Mn^{III}(HL)(N_3)_3]$ (**7**)			
Mn–O	2.138(5)	Mn–N1	2.047(7)
Mn–N2	2.339(6)	Mn–N5	1.998(8)
Mn–N8	1.993(7)	Mn–N11	1.990(8)
O–Mn–N1	86.2(2)	O–Mn–N2	176.5(2)
O–Mn–N5	91.7(3)	O–Mn–N8	92.2(3)
O–Mn–N11	91.4(3)	N1–Mn–N2	90.5(3)
N1–Mn–N5	177.0(3)	N1–Mn–N8	87.0(3)
N1–Mn–N11	91.0(3)	N2–Mn–N5	91.6(2)
N2–Mn–N8	86.4(3)	N2–Mn–N11	89.8(3)
N5–Mn–N8	90.9(3)	N5–Mn–N11	91.1(4)
N8–Mn–N11	175.7(3)		

with the high-spin d^5 electronic configuration of the manganese(II) ion. Intense absorption is observed at ca. 380 nm (ε ca. 4000 $dm^3\ mol^{-1}\ cm^{-1}$/Mn). This may be assigned to a CT transition band. Diffuse reflectance spectra were also measured. The electronic spectra in the solid state are similar to those in DMF. However, in the solid state, very weak absorptions which can be ascribed to spin-forbidden d–d transitions[41] are observed in the visible region (Fig. 3).

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

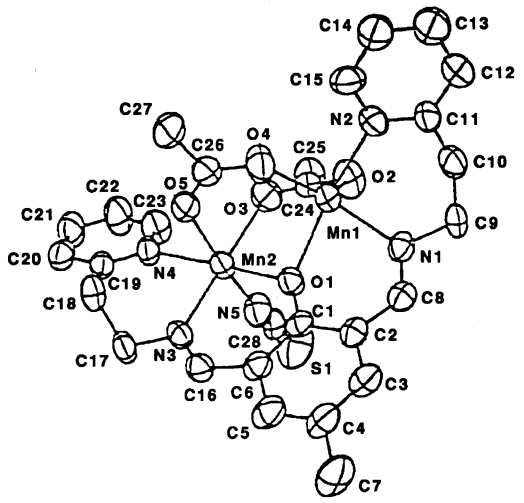


Fig. 2. ORTEP view of the structure of $[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (**2**).

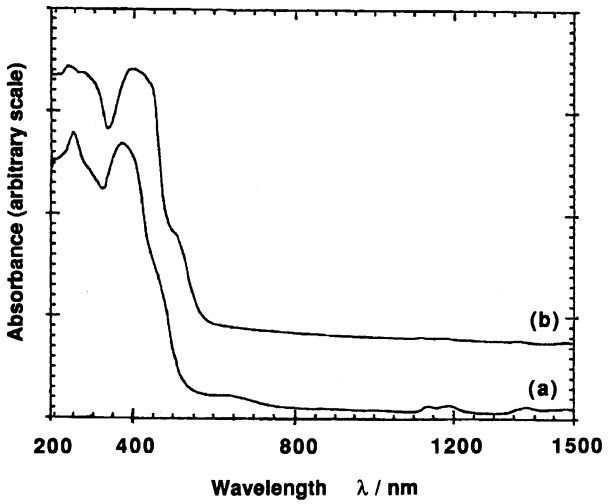


Fig. 3. Diffuse reflectance spectra of $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**) (a) and $[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**) (b).

5.56 and 5.60 B.M./Mn at room temperature, respectively, which are lower than those of normal high-spin manganese(II) complexes. The temperature dependence of the magnetic susceptibilities of **1** and **2** were measured on powdered samples over the temperature range 80—300 K; the results are shown in Fig. 4. The susceptibility data were analyzed using the van Vleck equation for the ($S_{Mn1}=5/2$)-($S_{Mn2}=5/2$) system based on the Heisenberg model

$$\mathcal{H} = -2J\boldsymbol{S}_{Mn1}\cdot\boldsymbol{S}_{Mn2}:$$

$$\chi_A = (Ng^2\beta^2/kT)\{(55+30X^{10}+14X^{18}+5X^{24}+X^{28})/(11+9X^{10}+7X^{18}+5X^{24}+3X^{28}+X^{30})\},$$

where $X=\exp(-J/kT)$ and the other symbols have their usual meanings. The best fitting parameters are $J=-3.4$ cm^{-1}, $g=1.99$ for **1**; $J=-2.5$ cm^{-1}, $g=2.00$ for **2**. The solid curves in Fig. 4 are those calculated using these parameters. This indicates that the two high-spin manganese ions are antiferromagnetically coupled. The antiferromagnetic interactions in these complexes are comparable to those of similar dinuclear manganese(II) complexes with 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol ($J=-4.9$ and -5.5 cm^{-1}).[42]

The X-Band ESR spectrum was measured for a frozen-solution sample of **1** in DMF–toluene at 4.2 K (Fig. 5). Two peaks with an eleven-line hyperfine-type structure were observed at near $g=2.0$ and $g=2.4$. The hyperfine coupling constants are both about 48 G, which is close to half that found in the mononuclear Mn(II) complex **3** (vide infra). This means that the two Mn(II) ions are coupled with each other by an electron spin-exchange interaction.[43] This is a rare example of dinuclear manganese(II) complexes showing a multiline ESR signal. The ESR spectrum of a frozen DMF/toluene solution glass of **2** is similar to that of **1**.[19] Molar conductance data indicate that complex **2** is a 1 : 1 electrolyte in DMF, like **1**. Therefore, the thiocyanate ion may be dissociated and replaced by the solvent molecule in the frozen solution. The similarity between the ESR spectra of **1** and **2** can be understandable, assuming that the coordinated methanol molecule is replaced by DMF in a frozen solution of **1**.

Mononuclear Mn(II) Complex. It is interesting that only one thiocyanate ion is trapped in a dinuclear unit of **2** under the reaction of 2,6-diformyl-4-methylphenol, 2-(2-aminoethyl)pyridine, manganese(II) ace-

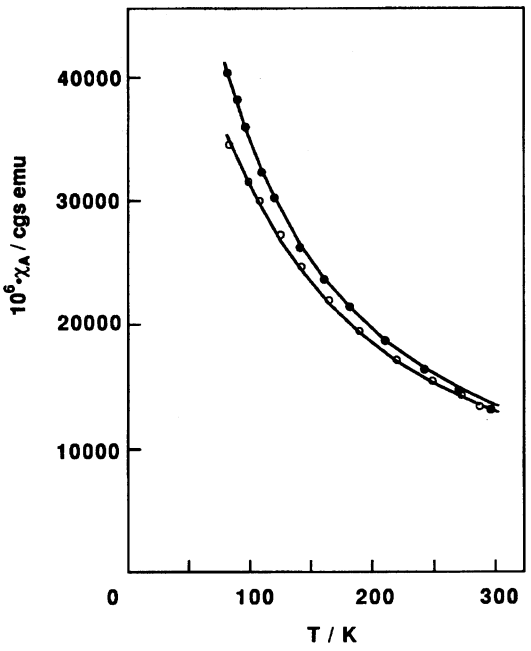


Fig. 4. Magnetic susceptibility data of $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**) (○) and $[Mn_2^{II}(L)(CH_3COO)_2(NCS)]$ (**2**) (●).

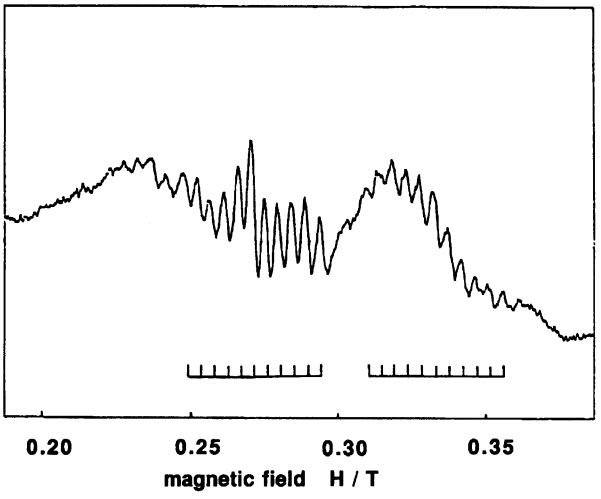


Fig. 5. X-Band ESR spectrum of $[Mn_2^{II}(L)(CH_3COO)_2(CH_3OH)](ClO_4)$ (**1**), DMF/toluene glass at 4.2 K.

tate, and ammonium thiocyanate with a 1 : 2 : 2 : 2 molar ratio. In order to attain the formation of a six-coordinate dinuclear complex in which both manganese(II) ions are coordinated by thiocyanate ions, we used an excess of thiocyanate ions. However, a mononuclear manganese(II) complex $[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**) was obtained as vermillion crystals from the 1 : 2 : 2 : 10 reaction mixture of 2,6-diformyl-4-methylphenol, 2-(2-aminoethyl)pyridine, manganese(II) acetate tetrahydrate, and ammonium thiocyanate in methanol. The X-ray structure determination of **3** revealed a unique mononuclear structure in which the octahedral coordination around the manganese ion is formed by a phenolate oxygen, an imino nitrogen, and a pyridyl nitrogen atoms of the Schiff base ligand (HL) two nitrogen atoms of the thiocyanate ions, and an oxygen atom of the water molecule (Fig. 6). One of the side-arm pyridyl nitrogens of the dinucleating ligand is not coordinated. The Mn–O (phenolate) (2.142(4) Å), Mn–O (water) (2.269(4) Å), Mn–N (imine) (2.229(5) Å), Mn–N (pyridyl) (2.270(5) Å), and Mn–N (thiocyanate) (2.216 (6), 2.146(7) Å) lengths are comparable to the corresponding values reported for dinuclear and polynuclear Mn(II) complexes.[24—38] The difference Fourier map of **3** shows that the phenol proton of Schiff base ligand HL is close to the imino nitrogen atom (N3) rather than the pyridyl nitrogen atom. A similar mononuclear structure is found in an iron(III) complex of the dinucleating ligand HL, $[Fe(HL)Cl_3]$.[44]

As shown in Fig. 3, the diffuse reflectance spectra of **3** are characterized by very weak absorptions in the visible region, which can be associated with spin-forbidden d–d transitions, and intense absorptions at 411 nm with a shoulder at 538 nm, which may represent charge-transfer transitions in origin. The shoulder at 538 nm disappears in the electronic spectra in DMF. Since the thiocyanate ions can be considered to dissociate in DMF, based on conductivity data (2 : 1 electrolyte), the shoulder may be assigned to an N (NCS)→Mn(II) CT transition.

The magnetic moment of **3** is 5.92 B.M./Mn at room temperature, and is in excellent agreement with the spin-only value of 5.92 B.M. for a high-spin d^5 system. The magnetic susceptibility was measured over the 80—300 K temperature range. The susceptibility data obey the Curie law. The frozen solution ESR spectrum of **3** (Fig. 7) shows a six-line hyperfine structure at $g=2.0$. The hyperfine constant is about 97 G, which is common for mononuclear Mn(II) complexes.[45]

Dinuclear Mn(II)Mn(III) Complexes. When manganese(III) acetate dihydrate dissolved in methanol, with the Schiff base ligand being used as starting materials, mixed-valence Mn(II)Mn(III) dinuclear complexes were isolated as brown ClO_4, NCS or N_3 salts, $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(CH_3OH)_2](ClO_4)_2$ (**4**), $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(NCS)_2]$ (**5**), or

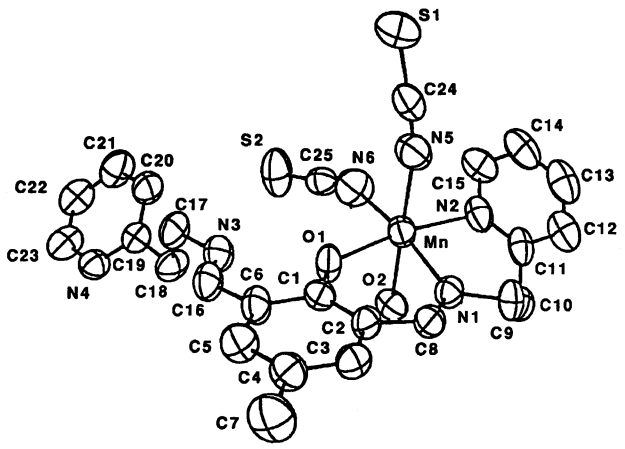


Fig. 6. ORTEP view of the structure of $[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**).

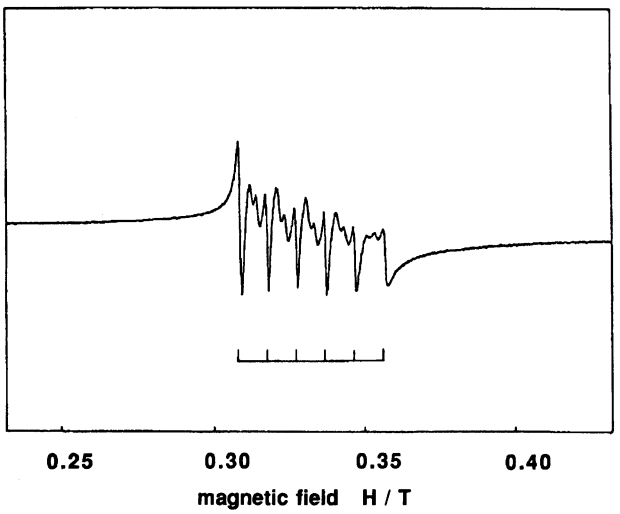


Fig. 7. X-Band ESR spectrum of $[Mn^{II}(HL)(NCS)_2(H_2O)]$ (**3**), DMF/toluene glass at 78 K.

$[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**). In the case of the N_3 salt, a reaction mixture of manganese(II) acetate tetrahydrate, manganese(III) acetate dihydrate, and sodium azide containing the Schiff base ligand gave a dark-red solution, from which pure, highly crystalline $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]H_2O$ (**6**) was obtained in good yield (41%). The X-ray crystal structure of **6** shows a novel dinuclear Mn(II)Mn(III) core (Fig. 8). The two manganese ions are bridged by the central phenoxo-oxygen atom of the Schiff base ligand L and by two didentate acetate ions. Both manganese atoms are in a distorted octahedral coordination with a phenoxo-oxygen, an imino nitrogen, and a pyridyl nitrogen atom of the dinucleating ligand L, two oxygen atoms of the acetate ions, and a nitrogen atom of the azide ion. However, the structural parameters of Mn1 and Mn2 are significantly different. This difference permits differentiation between the two oxidation states, since the ionic radii of the Mn(II) and Mn(III) ions differ significantly; it has been established that the equatorial Mn–O and Mn–N lengths for Mn(III) are generally shorter than those for Mn(II).[42,46,47] The Mn1 atom shows structural parameters that are consistent with its assignment as Mn(II) with a distorted octahedral coordination geometry. The Mn1–O distances range from 2.132(5) to 2.220(6) Å. They fall within the range previously reported for other dinuclear and polynuclear manganese(II) complexes.[24—34] The Mn1–N distances (2.191(6)—2.266(6) Å) lie within the range reported for the Mn(II)–N lengths.[24,27—29,31,35—38] On the other hand, the Mn2 atom has an elongated octahedral coordination geometry with structural parameters typical of Mn(III). The Mn2–O1 (phenoxo) distance (2.098(5) Å) is longer than either the Mn2–O (carboxylate) distance (1.924(5), 1.941(5) Å), while the Mn2–N4 (pyridyl) distance (2.376(7) Å) trans to Mn2–O1 is longer than the other two Mn–N distances (2.019 (5), 1.989(6) Å). This feature is consistent with the Jahn–Teller distortion expected for high-spin d^4 Mn(III) complexes.[10—15,48] The shorter in-plane Mn1–O and Mn1–N distances are comparable to those reported for manganese(III) complexes.[10—15,42,46—48] The present structural data clearly show that **6** is a valence-trapped Mn(II)Mn(III) species. This core is further characterized by an Mn···Mn distance of 3.544(2) Å and an Mn(II)–O (phenoxo)–Mn(III) angle of 113.8 (2)°, which are similar to analogous μ-phenoxo-di-μ-acetato-Mn(II)Mn(III) complexes.[42,49,50] In the crystal, there are hydrogen bonds among the azide ions and the methanol molecules (N5···Om2 2.898(11) Å, Oml···Om2 2.761(12) Å).

The present Mn(II)Mn(III)complexes could not be dissolved in organic solvents without significant decomposition. Diffused reflectance spectra were measured; and the result for **6** is shown in Fig. 9. The absorptions at around 360 nm may be assigned to O (phenoxo)→Mn(II) or Mn(III) LMCT transitions. Since the Mn(II)Mn(II) complexes are spectrally transparent at wavelengths longer than 500 nm, the electronic absorptions in the visible region must originate from the Mn(III) subunit. The shoulder at around 445 nm and the absorption at around 1011 nm can be assigned to be d–d transitions. This spectral feature is similar to that of the mononuclear Mn(III) complex **7** (Fig. 9, vide infra). Therefore, it is not reasonable to regard the broad band around 1011 nm as being an intervalence charge-transfer transition. The interpretation that complex **6** does not show an IT band in the near-infrared region is consistent with the valence-trapped Mn(II)Mn(III) structure. A similar spectrum was obtained for **5**.

The effective magnetic moments of **5** and **6** at room temperature are 5.21 and 5.22 B.M., respectively, which are somewhat less than those of the dinuclear Mn(II)-Mn(II) complexes. These values decrease to 4.54 and

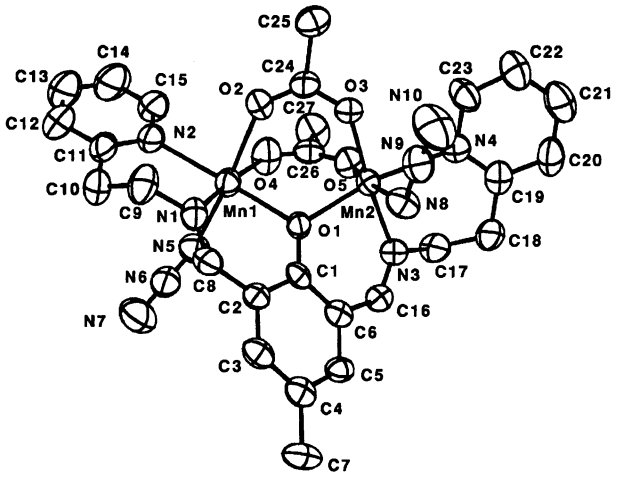


Fig. 8. ORTEP view of the structure of $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**).

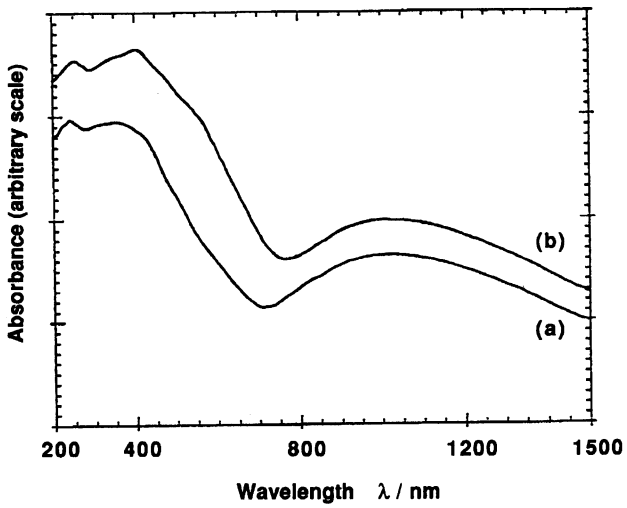


Fig. 9. Diffuse reflectance spectra of $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**) (a) and $[Mn^{III}(HL)(N_3)_3]$ (**7**) (b).

4.44 B.M. at liquid-nitrogen temperature for **5** and **6**, respectively. The susceptibility data were analyzed using the van Vleck equation based on the Heisenberg model

$$\mathscr{H} = -2J\boldsymbol{S}_{Mn1}\cdot\boldsymbol{S}_{Mn2}(S_{Mn1} = 5/2, S_{Mn2} = 2):$$

$$\chi_A = (Ng^2\beta^2/8kT)\{(165 + 84X^9 + 35X^{16} + 10X^{21} + X^{24})/(5 + 4X^9 + 3X^{16} + 2X^{21} + X^{24})\},$$

where $X = \exp(-J/kT)$; the other symbols have their usual meanings. The parameters obtained from the best fitting are: $J = -3.6$ cm^{-1}, $g = 2.00$ for **5**; $J = -4.0$ cm^{-1}, $g = 2.00$ for **6** (Fig. 10). To our knowledge, there are six other known structurally characterized Mn(II)-Mn(III) complexes.[42,49—52] Magnetic exchange parameters (J) in the range from 0.89 to -7.7 cm^{-1} have been found for these complexes. In the case of Mn(II)Mn(III) complexes having μ-phenoxo-di-μ-acetato-bridged cores,[42,49,50] the J values range from -4.5 to -7.7 cm^{-1}. The present J values for **5** and **6** are comparable to those for the latter case.

Mononuclear Mn(III) Complex. While the Mn(II)Mn(III) dinuclear complex **6** forms from a treatment of the Schiff base ligand with a mixture of Mn(II) acetate and Mn(III) acetate, the dinucleating ligand (HL) reacts with manganese(III) acetate in the presence of sodium azide to yield a mononuclear Mn(III) species, $[Mn^{III}(HL)(N_3)_3]$ (**7**). The X-ray structure determination confirms the monomeric nature of **7** (Fig. 11). The manganese atom is coordinated by a phenolate oxygen, an imino nitrogen, and a pyridyl nitrogen atoms of the dinucleating ligand (L), and three nitrogen atoms of the azide ions. The general coordination geometry around Mn is similar to that observed in **3**, but with a Jahn–Teller elongation along the N2–Mn–O axis (Mn–N2 2.339(6) Å, Mn–O 2.138(5) Å). The in-plane-bond distances (Mn–N 1.990(8)—2.047(7) Å) are comparable to those found for other Mn(III) Schiff base complexes.[10—15,46—48]

The diffuse reflectance spectrum of **7** shows absorptions at 346, 399, 461 (shoulder), 570 (shoulder), and 1021 nm (Fig. 9). The lower-energy three bands may be assigned to d–d transitions for the Mn(III) ion in an elongated octahedral environment.[41]

The magnetic moment of **7** (4.90 B.M. at 300 K) is very close to the spin-only value of 4.90 B.M. for a high-spin d^4 ion. This complex followed the Curie law at 80—300 K, in agreement with the results concerning the X-ray crystal structure.

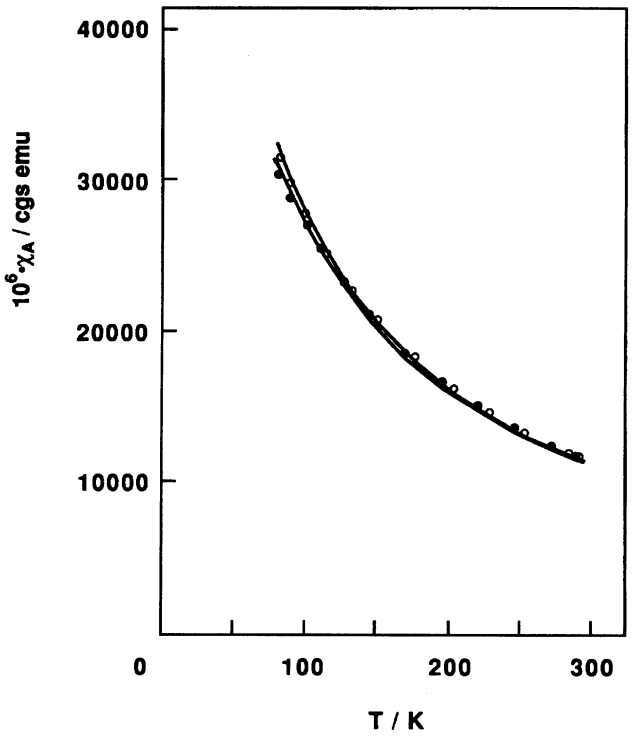


Fig. 10. Magnetic susceptibility data of $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(NCS)_2]$ (**5**) (○) and $[Mn^{II}Mn^{III}(L)(CH_3COO)_2(N_3)_2]\cdot 2CH_3OH$ (**6**) (●).

Concluding Remarks

Use of the dinucleating ligand, 2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-4-methylphenol HL, in conjunction with carboxylate or other anionic ligands leads to the formation of a variety of manganese complexes, dinuclear Mn(II)Mn(II), mononuclear Mn(II), dinuclear Mn(II)Mn(III), and mononuclear Mn(III) complexes. This is in striking contrast to the dinucleating ligands having an alkoxo-oxygen atom, such as 1,5-bis(salicylideneamino)-3-pentanol, which give μ-alkoxo-bridged dinuclear manganese(III) complexes exclusively.[10—15] X-Ray structure analyses of the present complexes show that there are two binding-mode forms of the dinucleating ligand: an anionic form (L) and neutral type (HL) which differ in the orientations of the flexible side arms.

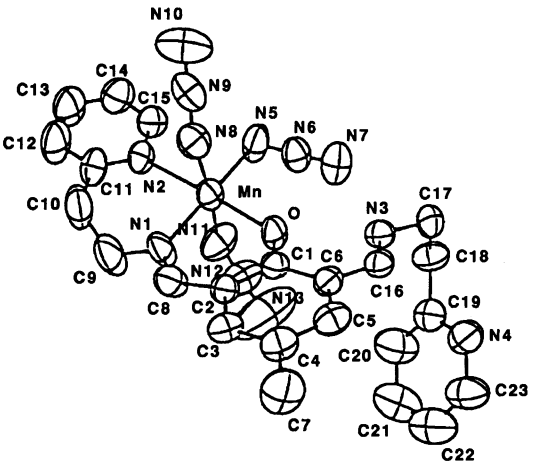


Fig. 11. ORTEP view of the structure of $[Mn^{III}(HL)(N_3)_3]$ (**7**).

The subtle role of the mononegative anionic ligand, such as N_3^- or NCS^-, can be emphasized based on the following facts: (1) the addition of excess thiocyanate ion to the reaction solution of the dinuclear species gave the corresponding mononuclear complex, and (2) the azide ion seems to stabilize the higher oxidation state Mn(III), resulting in the formation of mononuclear Mn(III) or dinuclear Mn(III)Mn(II) species.

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