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Synthesis and Structural Characterization of Manganese(II) Complexes with *N,N'*-Bis(2-pyridylmethylene)-1,3-diaminopropan-2-ol or *N,N'*-Bis(2-pyridylmethylene)-1,3-propanediamine

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Manganese(II) complexes with *N,N'*-bis(2-pyridylmethylene)-1,3-diaminopropan-2-ol (HL^1) or *N,N'*-bis(2-pyridylmethylene)-1,3-propanediamine (L^2), $[Mn(HL^1)(NO_3)_2]$ (**1**) and $[Mn(HL^1)(NCS)_2]$ (**2**), $[Mn(HL^1)(phen)](ClO_4)_2$ (**3**), $[Mn_2(L^1)(CH_3COO)(phen)_2](ClO_4)_2$ (**4**), $[Mn(L^2)(NO_3)_2]$ (**5**), $[Mn(L^2)(bpy)(CH_3OH)](ClO_4)_2$ (**6**), $[Mn(L^2)(NCS)_2]$ (**7**), $[Mn(L^2)(phen)](ClO_4)_2$ (**8**), have been synthesized and characterized by measurements of the infrared, electronic, and ESR spectra, and magnetic susceptibilities. The molecular structures of these complexes were determined by the single-crystal X-ray structure analysis. The complexes $\mathbf{1}\cdot C_2H_5OH$ and **5** have an eight-coordinated manganese atom with a square antiprism geometry. The complex **6** is seven-coordinated in a monocapped trigonal prism. The manganese atoms of **2**, **7**, and **8** are six-coordinated in a trigonal prism environment. The coordination environment of **3** is disordered between the seven- and six-coordinate geometries. The complex $\mathbf{4}\cdot H_2O$ is a dinuclear molecule comprising two octahedral Mn(II) atoms.

There has been considerable interest in the coordination chemistry of manganese compounds because of their potential utilities as model compounds of manganese containing proteins which would show significant involvement of manganese in various biological systems.1) This results in a number of reports on manganese(II) complexes. Manganese(II) ion takes usually a high-spin d^5 electronic configuration, which gives no crystal field stabilization energies for any coordination geometries. This configuration may enable us various coordination geometries for manganese(II) complexes. However, surprisingly, most manganese(II) complexes take an octahedral geometry and only few examples are known to take the other coordination geometries.2) Especially coordination numbers exceeding six are uncommon for manganese(II). These facts show that manganese(II) ion prefers a limited number of coordination geometries which minimize ligand–ligand repulsions. As part of a continuing project on manganese complexes,3—11) we reported on the synthesis and characterization of several manganese complexes with organic ligands. From these studies, we felt that pyridyl group seems to favor the manganese(II) state.11) In fact, we obtained some manganese(II) complexes with pyridyl-containing ligands, which have an octahedral geometry around the manganese(II) atom.3,4) During this activity, we have found novel eight-, seven-, and six-coordinate manganese(II) geometries are formed in the cases for the two pyridyl-containing Schiff-base ligands: *N,N'*-bis(2-pyridylmethylene)-1,3-diaminopropan-2-ol (HL^1) and *N,N'*-bis(2-pyridylmethylene)-1,3-propanediamine (L^2) (Chart 1). As for the latter ligand, Chiswell and Taylor reported a series of manganese(II) complexes involving $[Mn(L^2)X_2]$ ($X = ClO_4$, Cl, Br, I, NCS).12) However, their structural characterization is limited to the solid state IR or ESR spectral features and they did not elucidate any crystal structures by the X-ray crystallography. Herein we report our findings on X-ray crystal structures of manganese(II) complexes with these ligands. A preliminary account of this study has been previously reported.13)

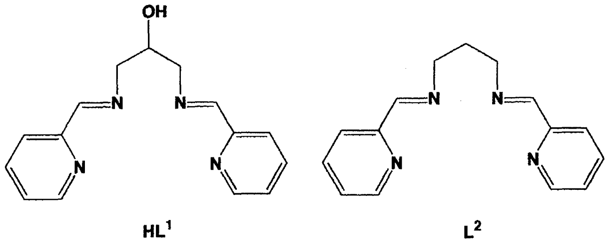

Chart 1.

Experimental

Synthesis of the Complexes. *N,N'*-Bis(2-pyridylmethylene)-1,3-diaminopropan-2-ol (HL^1) and *N,N'*-bis(2-pyridylmethylene)-1,3-propanediamine (L^2) were synthesized according to a method reported by Campbell and Urbach.14)

$[Mn(HL^1)(NO_3)_2]$ (1). Ligand HL^1 (53 mg, 0.20 mmol) was dissolved in ethanol (11 cm^3), then manganese(II) nitrate hexahydrate (43 mg, 0.15 mmol) was added with stirring. After the solution had been filtered, the filtrate was kept at room temperature for several days. Pale yellow plates were deposited and collected by filtration and dried in vacuo over P_2O_5 to remove the solvent: Yield, 53 mg (80% on the basis of manganese(II) nitrate hexahydrate used).

Found: C, 40.25; H, 3.56; N, 18.78%. Calcd for $C_{15}H_{16}MnN_6O_7$: C, 40.28; H, 3.61; N, 18.79%. IR (Nujol mull) ν(OH) 3374(br); ν(C=N) 1649(m), 1592(s), $\nu(NO_3)$ 1459(s), 1326(s), 1301(s) cm^{-1}. μ_{eff} (295 K, B.M.) 5.73. λ_M (CH_3OH)/S mol^{-1} cm^2 140 (lit, range for 2 : 1 electrolytes,[15] 160—220 S mol^{-1} cm^2). λ_M (DMF (*N*,*N*-dimethylformamide))/S mol^{-1} cm^2 134 (lit, range for 2 : 1 electrolytes,[15] 130—170 S mol^{-1} cm^2). Diffuse reflectance spectrum: λ_{max}/nm 269, 310sh, 375sh, 405sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 281 (12400).

[Mn(HL^1)(NCS)$_2$] (2). Ligand HL^1 (27 mg, 0.10 mmol) was dissolved in a mixed solvent of ethanol (3 cm^3) and methanol (7 cm^3); then manganese(II) bromide tetrahydrate (29 mg, 0.10 mmol) and sodium thiocyanate (16 mg, 0.20 mmol) were added. After the solution was allowed to stand for several days at room temperature, yellow needles resulted, which were filtered and dried in vacuo over P_2O_5: Yield, 25 mg (57% on the basis of manganese(II) bromide tetrahydrate used). Found: C, 46.19; H, 3.52; N, 18.75%. Calcd for $C_{17}H_{16}MnN_6OS_2$: C, 46.47; H, 3.67; N, 19.13%. IR (Nujol mull) ν(OH) 3366(br); ν(NCS) 2069(s), 2052(s); ν(C=N) 1644(m), 1591(s) cm^{-1}. μ_{eff} (285 K, B.M.) 5.98. λ_M(CH_3OH)/S mol^{-1} cm^2 100 (lit, range for 1 : 1 electrolytes,[15] 80—115 S mol^{-1} cm^2). λ_M(DMF)/S mol^{-1} cm^2 88 (lit, range for 1 : 1 electrolytes,[15] 65—90 S mol^{-1} cm^2). Diffuse reflectance spectrum: λ_{max}/nm 268, 330, 400, 570sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 267 (14900).

[Mn(HL^1)(phen)](ClO$_4$)$_2$ (3). Ligand HL^1 (27 mg, 0.10 mmol) was dissolved in a mixture of 1-propanol (10 cm^3) and water (0.5 ml). While the solution was stirred, manganese(II) perchlorate hexahydrate (35 mg, 0.097 mmol) and 1,10-phenanthroline monohydrate (20 mg, 0.10 mmol) were added, and the resulting solution was filtered. The filtrate was allowed to stand for several days at room temperature to give yellow needles. These were collected by filtration and dried in vacuo over P_2O_5: Yield, 33 mg (48% on the basis of manganese(II) perchlorate hexahydrate used). Found: C, 45.98; H, 3.46; N, 11.90%. Calcd for $C_{27}H_{24}Cl_2MnN_6O_9$: C, 46.17; H, 3.44; N, 11.97%. IR (Nujol mull) ν(OH) 3380(br); ν(C=N) 1659(m), 1596(s), $\nu(ClO_4)$ 1080; δ(CH(phen)) 846(s), 730(s) cm^{-1}. μ_{eff} (286 K, B.M.) 5.92. λ_M (CH_3OH)/S mol^{-1} cm^2 210. λ_M (DMF)/S mol^{-1} cm^2 170. Diffuse reflectance spectrum: λ_{max}/nm 261, 329, 400sh, 580sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 265 (36200).

[Mn$_2$(L^1)(CH$_3$COO)(phen)$_2$](ClO$_4$)$_2$ (4). Ligand HL^1 (27 mg, 0.10 mmol) was dissolved in a mixture of ethanol (8 cm^3) and methanol (2 cm^3); then triethylamine (21 mg, 0.21 mmol), manganese(II) acetate tetrahydrate (51 mg, 0.21 mmol), 1,10-phenanthroline monohydrate (41 mg, 0.21 mmol), and sodium perchrolate (24 mg, 0.20 mmol) were successively added with stirring. After the solution had been filtered, the filtrate was placed at room temperature for several days. Dark reddish-orange columns were deposited. They were collected by filtration and dried in vacuo over P_2O_5: Yield, 46 mg (46% on the basis of HL^1 used). Found: C, 49.32; H, 3.76; N, 10.81%. Calcd for $C_{41}H_{34}Cl_2Mn_2N_8O_{11}$: C, 49.47; H, 3.44; N, 11.26%. IR (Nujol mull) ν(C=N) 1661(sh), 1589(m); ν_{as}(COO) 1559(s), ν_s(COO) 1422(m), $\nu(ClO_4)$ 1089(s, br); δ(CH(phen)) 844(s), 729(s) cm^{-1}. μ_{eff} (289 K, B.M.)/Mn 5.20. λ_M (CH_3OH)/S mol^{-1} cm^2 235. λ_M (DMF)/S mol^{-1} cm^2 158. Diffuse reflectance spectrum: λ_{max}/nm 259, 325sh, 425sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 264 (75500).

[Mn(L^2)(NO$_3$)$_2$] (5). A solution of L^2 (31 mg, 0.12 mmol) in ethanol (5 cm^3) was slowly added to an ethanol solution (5 cm^3) of manganese(II) nitrate hexahydrate (37 mg, 0.13 mmol). The mixture was allowed to stand for several days at room temperature to give pale yellow plates. They were collected by filtration and dried in vacuo over P_2O_5: Yield, 41 mg (79% on the basis of L^2 used). Found: C, 41.76; H, 3.68; N. 19.50%. Calcd for $C_{15}H_{16}MnN_6O_6$: C, 41.78; H, 3.74; N, 19.49%. IR (Nujol mull) ν(C=N) 1648(m), 1592(s); $\nu(NO_3)$ 1427(sh), 1313(sh), 1304(s) cm^{-1}. μ_{eff} (289 K, B.M.) 5.98. λ_M (CH_3OH)/S mol^{-1} cm^2 147. λ_M (DMF)/S mol^{-1} cm^2 135. Diffuse reflectance spectrum: λ_{max}/nm 270, 300sh, 350sh, 410sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 281 (15100).

[Mn(L^2)(bpy)(CH$_3$OH)](ClO$_4$)$_2$ (6). To a solution of L^2 (29 mg, 0.11 mmol) in ethanol (7 ml)–methanol (3 ml), manganese(II) perchlorate hexahydrate (36 mg, 0.099 mmol) and 2,2′-bipyridyl (17 mg, 0.10 mmol) were added with stirring. Then the solution was filtered and the filtrate was kept at room temperature for several days to give pale yellow plates. They were collected by filtration and dried in vacuo over P_2O_5: Yield, 36 mg (53% on the basis of manganese(II) perchlorate hexahydrate used). Found: C, 44.77; H, 3.65; N, 12.38%. Calcd for $C_{26}H_{28}Cl_2MnN_6O_9$: C, 44.97; H, 4.06; N, 12.10%. IR (Nujol mull) ν(OH) 3364(br); ν(C=N) 1654(m), 1593(s); $\nu(ClO_4)$ 1089(s, br); δ(CH(bipy)) 762(s) cm^{-1}. μ_{eff} (295 K, B.M.) 5.89. λ_M (CH_3OH)/S mol^{-1} cm^2 202. λ_M (DMF)/S mol^{-1} cm^2 160. Diffuse reflectance spectrum: λ_{max}/nm 273, 325, 370. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 281 (27700).

[Mn(L^2)(NCS)$_2$] (7). Ligand L^2 (25 mg, 0.099 mmol) was dissolved in methanol (4 cm^3), then manganese(II) bromide tetrahydrate (30 mg, 0.10 mmol) and sodium thiocyanate (17 mg, 0.21 mmol) were added. After the mixture was allowed to stand for several days at room temperature, yellow needles resulted; these were filtered and dried in vacuo over P_2O_5: Yield, 23 mg (55% on the basis of L^2 used). Found: C, 48.18; H, 3.75; N, 20.00%. Calcd for $C_{17}H_{16}MnN_6S_2$: C, 48.22; H, 3.81; N, 19.85%. IR (Nujol mull) ν(NCS) 2066(s), 2052(s); ν(C=N) 1652(m), 1591(s) cm^{-1}. μ_{eff} (289 K, B.M.) 5.85. λ_M (CH_3OH)/S mol^{-1} cm^2 100. λ_M (DMF)/S mol^{-1} cm^2 90. Diffuse reflectance spectrum: λ_{max}/nm 270, 320, 390sh, 600sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 280 (14000).

[Mn(L^2)(phen)](ClO$_4$)$_2$ (8). Ligand L^2 (28 mg, 0.11 mmol) was dissolved in methanol (10 cm^3). While the mixture was stirred, manganese(II) perchlorate hexahydrate (35 mg, 0.097 mmol) and 1, 10-phenanthroline monohydrate (19 mg, 0.096 mmol) were added. The solution was allowed to stand for several days at room temperature to give yellow needles. These were collected by filtration and dried in vacuo over P_2O_5: Yield, 47 mg (71% on the basis of 1,10-phenanthroline monohydrate used). Found: C, 47.13; H, 3.53; N, 11.96%. Calcd for $C_{27}H_{24}Cl_2MnN_6O_8$: C, 47.25; H, 3.52; N, 12.24%. IR (Nujol mull) ν(C=N) 1653(m), 1595(s); $\nu(ClO_4)$ 1083(s, br); δ(CH(phen)) 849(s), 730(s) cm^{-1}. μ_{eff} (285 K, B.M.) 5.88. λ_M (CH_3OH)/S mol^{-1} cm^2 222. λ_M (DMF)/S mol^{-1} cm^2 171. Diffuse reflectance spectrum: λ_{max}/nm 262, 322, 400sh, 600sh. Electronic spectrum in CH_3OH: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 264 (45600).

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 Spectrophotometer model IR700 in the 4000—400 cm^{-1} region. Electronic 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. Magnetic moments at room temperature were measured by a magnetic susceptibility balance MSB-AUTO. Temperature dependence of magnetic susceptibilities was measured over the 80—300 K temperature range by the Faraday method. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[16] The effective magnetic moments were calculated from the equation $\mu_{\mathrm{eff}} = 2.828\sqrt{\chi_{\mathrm{A}}T}$, where χ_{A} is the atomic magnetic susceptibility. ESR spectra were recorded at liquid-nitrogen temperature on a ESR spectrometer JES-TE 300.

X-Ray Crystal Structure Analysis. X-Ray quality crystals were collected from each solution and were not dried. The crystals were sealed in a glass capillary together with the mother liquor and mounted on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. Unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \leq 2\theta \leq 30°$. Crystal data and details of the date collection are given in Table 1. Intensity data were corrected for Lorentz-polarization effects and absorption. The structures were solved by the direct methods and refined by the full-matrix least-squares methods. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were inserted at their calculated positions and fixed at their positions. The final discrepancy factors, $R = \Sigma||F_{\mathrm{o}}| - |F_{\mathrm{c}}||/\Sigma|F_{\mathrm{o}}|$,

Table 1. Crystal Data and Data Collection Details

Complex	$[\mathrm{Mn(HL^1)(NO_3)_2}]\cdot\mathrm{C_2H_5OH}$ (**1**·$\mathrm{C_2H_5OH}$)	$[\mathrm{Mn(HL^1)(NCS)_2}]$ (**2**)	$[\mathrm{Mn(HL^1)(phen)}]\mathrm{(ClO_4)_2}$ (**3**)	$[\mathrm{Mn_2(L^1)(CH_3COO)(phen)_2}]\mathrm{(ClO_4)_2}\cdot\mathrm{H_2O}$ (**4**·$\mathrm{H_2O}$)
Formula	$C_{17}H_{22}MnN_6O_8$	$C_{17}H_{16}MnN_6OS_2$	$C_{27}H_{24}Cl_2MnN_6O_9$	$C_{41}H_{36}Cl_2Mn_2N_8O_{12}$
F.W.	493.3	439.4	702.4	1013.6
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/a$	$P2_1/a$	$Pnma$	$P\bar{1}$
a/Å	9.618(2)	18.276(4)	19.660(4)	11.843(8)
b/Å	27.984(3)	8.673(1)	11.805(3)	12.067(12)
c/Å	8.255(2)	13.511(3)	12.941(4)	16.835(17)
α/°				84.51(6)
β/°	99.85(1)	110.14(1)		76.01(7)
γ/°				82.58(6)
V/Å^3	2189.8(8)	2010.5(7)	3003.4(12)	2310(4)
Z	4	4	4	2
D_c/g cm^{-3}	1.50	1.45	1.55	1.46
D_m/g cm^{-3}	1.49	1.46	1.55	1.50
μ(Mo $K\alpha$)/cm^{-1}	6.31	8.48	6.61	7.06
Crystal size /mm	0.50 × 0.48 × 0.20	0.41 × 0.40 × 0.25	0.50 × 0.31 × 0.16	0.55 × 0.46 × 0.40
2θ range/°	2.0—52.0	2.0—48.0	2.0—49.0	2.0—44.0
Total no. of reflections measured	4397	3388	2849	5654
No. of unique reflections with $I \geq 3\sigma(I)$	2847	2239	1148	2608
R	0.057	0.036	0.080	0.069
R_{w}	0.069	0.041	0.087	0.085
Complex	$[\mathrm{Mn(L^2)(NO_3)_2}]$ (**5**)	$[\mathrm{Mn(L^2)(bipy)(CH_3OH)}]\mathrm{(ClO_4)_2}$ (**6**)	$[\mathrm{Mn(L^2)(NCS)_2}]$ (**7**)	$[\mathrm{Mn(L^2)(phen)}]\mathrm{(ClO_4)_2}$ (**8**)
Formula	$C_{15}H_{16}MnN_6O_6$	$C_{26}H_{28}Cl_2MnN_6O_9$	$C_{17}H_{16}MnN_6S_2$	$C_{27}H_{24}Cl_2MnN_6O_8$
F.W.	431.3	694.4	423.4	686.4
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$P2_1/a$	$P2_1/n$	$Pnma$
a/Å	19.098(4)	18.173(2)	24.294(4)	18.846(4)
b/Å	7.277(1)	10.416(1)	8.644(1)	11.628(1)
c/Å	13.585(3)	17.688(2)	9.482(1)	13.483(2)
α/°				
β/°	106.06(1)	113.68(1)	97.295(5)	
γ/°				
V/Å^3	1814.3(6)	3066.1(6)	1975.2(5)	2944.8(8)
Z	4	4	4	4
D_c/g cm^{-3}	1.58	1.50	1.42	1.55
D_m/g cm^{-3}	1.60	1.51	1.43	1.53
μ(Mo $K\alpha$)/cm^{-1}	7.43	6.47	8.57	6.70
Crystal size /mm	0.40 × 0.25 × 0.11	0.68 × 0.60 × 0.52	0.60 × 0.43 × 0.40	0.52 × 0.29 × 0.20
2θ range/°	2.0—49.0	2.0—48.0	2.0—47.0	2.0—49.0
Total no. of reflections measured	3277	5112	3145	2790
No. of unique reflections with $I \geq 3\sigma(I)$	1503	3553	2039	1276
R	0.044	0.052	0.039	0.046
R_{w}	0.052	0.060	0.045	0.052

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	*B*/Å^2
$[Mn(HL^1)(NO_3)_2]\cdot C_2H_5OH$ (**1**$\cdot C_2H_5OH$)				
Mn	0.76882(7)	0.12265(3)	0.07354(9)	3.31(1)
O1	0.8437(4)	0.0442(2)	0.5274(5)	5.7(1)
O2	0.5855(5)	0.0712(2)	−0.0438(5)	7.2(1)
O3	0.7522(5)	0.0693(2)	−0.1790(5)	7.4(1)
O4	0.5750(5)	0.0239(2)	−0.2537(6)	7.2(1)
O5	0.7368(4)	0.1785(2)	−0.1326(5)	5.5(1)
O6	0.5630(4)	0.1775(2)	−0.0047(5)	7.0(1)
O7	0.5797(7)	0.2338(2)	−0.1769(7)	9.6(2)
O8	0.128(2)	0.1291(5)	−0.477(2)	23.4(5)$^{a)}$
N1	0.9987(4)	0.1201(2)	0.0367(5)	3.96(9)
N2	0.8665(4)	0.0510(2)	0.1820(5)	4.09(9)
N3	0.6893(4)	0.1143(2)	0.3159(5)	3.75(9)
N4	0.8325(4)	0.1911(2)	0.2352(5)	3.73(9)
N5	0.6344(5)	0.0539(2)	−0.1603(5)	4.5(1)
N6	0.6243(5)	0.1979(2)	−0.1078(5)	4.7(1)
C1	1.0670(6)	0.1546(2)	−0.0316(7)	4.9(1)
C2	1.2125(6)	0.1532(3)	−0.0308(8)	5.9(2)
C3	1.2857(6)	0.1141(3)	0.0353(9)	6.9(2)
C4	1.2177(6)	0.0779(3)	0.1007(8)	5.8(2)
C5	1.0733(5)	0.0821(2)	0.1021(7)	4.2(1)
C6	0.9962(6)	0.0456(2)	0.1753(7)	4.8(1)
C7	0.7939(6)	0.0132(2)	0.2565(7)	5.0(1)
C8	0.7325(6)	0.0306(2)	0.4035(7)	4.5(1)
C9	0.6242(5)	0.0705(2)	0.3644(7)	4.4(1)
C10	0.7271(6)	0.1456(2)	0.4254(6)	4.0(1)
C11	0.8025(5)	0.1886(2)	0.3887(6)	3.9(1)
C12	0.8386(7)	0.2239(2)	0.5029(7)	5.5(2)
C13	0.9049(8)	0.2641(3)	0.4601(8)	6.6(2)
C14	0.9334(7)	0.2679(2)	0.3035(8)	5.7(2)
C15	0.8964(6)	0.2310(2)	0.1962(7)	4.7(1)
C16	0.271(2)	0.1104(6)	−0.449(2)	16.6(5)$^{a)}$
C17	0.391(2)	0.1278(5)	−0.372(2)	14.7(4)$^{a)}$
$[Mn(HL^1)(NCS)_2]$ (**2**)				
Mn	0.97747(3)	0.03890(6)	0.76418(4)	3.49(1)
N1	1.0952(2)	0.0936(4)	0.8991(2)	3.79(7)
N2	0.9523(2)	0.1737(4)	0.8933(2)	4.15(7)
N3	0.9032(2)	0.2427(4)	0.6710(2)	3.82(7)
N4	1.0276(2)	0.1167(3)	0.6380(2)	3.37(6)
N5	0.8662(2)	−0.0770(4)	0.7153(3)	5.38(9)
N6	1.0319(2)	−0.1878(4)	0.7754(3)	5.01(9)
S1	0.73415(8)	−0.2566(2)	0.6317(1)	7.96(4)
S2	1.07124(7)	−0.4965(1)	0.8001(1)	6.33(3)
O	0.8997(2)	0.4823(4)	0.8296(3)	7.13(9)
C1	1.1662(2)	0.0416(5)	0.9078(3)	4.59(9)
C2	1.2325(2)	0.0725(5)	0.9940(3)	4.7(1)
C3	1.2254(2)	0.1628(5)	1.0736(3)	5.1(1)
C4	1.1533(2)	0.2194(5)	1.0666(3)	4.5(1)
C5	1.0893(2)	0.1802(4)	0.9781(3)	3.71(8)
C6	1.0099(2)	0.2261(5)	0.9683(3)	4.27(9)
C7	0.8739(2)	0.2302(6)	0.8823(3)	5.5(1)
C8	0.8482(2)	0.3572(5)	0.7989(3)	5.3(1)
C9	0.8332(2)	0.3036(6)	0.6865(4)	5.2(1)
C10	0.9234(2)	0.2988(4)	0.5985(3)	3.83(9)
C11	0.9913(2)	0.2365(4)	0.5772(3)	3.42(8)
C12	1.0139(2)	0.2945(4)	0.4975(3)	4.20(9)
C13	1.0790(2)	0.2327(5)	0.4814(3)	4.8(1)
C14	1.1170(2)	0.1116(5)	0.5438(3)	4.48(9)
C15	1.0889(2)	0.0557(5)	0.6202(3)	3.99(8)
C16	0.8109(2)	−0.1502(5)	0.6802(3)	4.48(9)
C17	1.0479(2)	−0.3144(5)	0.7855(3)	3.88(9)
$[Mn(HL^1)(phen)](ClO_4)_2$ (**3**)				
Mn	0.7538(1)	0.25	0.0762(2)	4.85(5)$^{b)}$
Cl1	1.0192(2)	0.25	0.2730(5)	8.3(1)$^{b)}$
Cl2	0.7196(3)	0.25	−0.3059(5)	8.7(1)$^{b)}$
O1a	0.847(1)	0.25	0.216(2)	12(1)$^{c)}$
O1b	0.721(2)	0.25	0.388(2)	10.3(9)$^{c)}$
O2	0.9820(6)	0.155(1)	0.254(1)	18.1(4)
O3	1.019(1)	0.25	0.384(2)	16.3(7)$^{b)}$
O4	1.0821(8)	0.25	0.230(1)	15.2(5)$^{c)}$
O5	0.7627(9)	0.25	−0.230(1)	17.6(6)$^{b)}$
O6	0.6777(7)	0.344(1)	−0.297(1)	15.2(4)
O7	0.747(1)	0.25	−0.404(2)	19.0(8)$^{b)}$
N1	0.6727(4)	0.3859(7)	0.0378(7)	5.3(2)
N2	0.7451(5)	0.3669(8)	0.2100(7)	7.2(2)
N3	0.8331(4)	0.3649(7)	0.0006(6)	5.0(2)
C1	0.6397(6)	0.399(1)	−0.051(1)	7.3(3)
C2	0.5917(7)	0.483(1)	−0.071(1)	9.5(4)
C3	0.5825(6)	0.558(1)	0.012(1)	10.5(4)
C4	0.6150(6)	0.549(1)	0.102(1)	7.3(3)
C5	0.6621(5)	0.4601(9)	0.1110(9)	5.6(3)
C6	0.7028(7)	0.446(1)	0.205(1)	7.7(4)
C7	0.7874(9)	0.354(1)	0.304(1)	11.4(5)
C8	0.806(1)	0.25	0.328(2)	12.8(7)$^{b)}$
C9	0.8343(6)	0.4784(9)	0.004(1)	6.1(3)
C10	0.8870(7)	0.542(1)	−0.041(1)	8.2(4)
C11	0.9388(6)	0.486(1)	−0.088(1)	8.9(4)
C12	0.9926(6)	0.305(1)	−0.144(1)	8.7(5)
C13	0.9399(6)	0.368(1)	−0.093(1)	7.0(3)
C14	0.8852(5)	0.3118(9)	−0.0465(7)	4.7(2)
$[Mn_2(L^1)(CH_3COO)(phen)_2](ClO_4)_2\cdot H_2O$ (**4**$\cdot H_2O$)				
Mn1	0.1641(2)	0.3174(2)	0.3395(1)	3.14(5)
Mn2	0.2884(2)	0.0404(2)	0.3046(1)	3.09(5)
Cl1	0.6409(4)	0.3453(5)	0.3691(3)	6.3(1)
Cl2	0.9102(7)	0.2492(6)	−0.0968(3)	15.1(2)
O1	0.2886(8)	0.1846(7)	0.3655(5)	2.8(2)
O2	0.0292(8)	0.2112(8)	0.3854(6)	3.8(2)
O3	0.1042(9)	0.0356(9)	0.3527(6)	4.4(3)^{a}
O4	0.731(1)	0.352(2)	0.4050(8)	10.6(5)
O5	0.660(1)	0.385(2)	0.2880(8)	13.0(6)
O6	0.535(1)	0.394(2)	0.414(1)	14.2(7)
O7	0.624(2)	0.230(2)	0.376(1)	15.6(7)
O8	0.973(2)	0.335(2)	−0.117(1)	11.3(5)$^{a)}$
O9	0.926(2)	0.191(2)	−0.026(1)	13.8(6)$^{a)}$
O10	0.851(2)	0.196(2)	−0.126(2)	7.2(7)$^{a,b)}$
O11	0.982(3)	0.157(3)	−0.160(2)	12(1)$^{a,b)}$
O12	0.789(3)	0.294(3)	−0.102(2)	12(1)$^{a,b)}$
O13	0.821(4)	0.289(4)	−0.008(3)	16(2)$^{a,b)}$
Ow	1.278(3)	0.281(3)	−0.245(2)	25(1)$^{a)}$
N1	0.098(1)	0.5078(9)	0.3686(7)	3.5(3)
N2	0.213(1)	0.3586(9)	0.4543(6)	3.1(3)
N3	0.363(1)	−0.022(1)	0.4137(7)	3.5(3)
N4	0.328(1)	−0.1535(9)	0.3074(7)	3.5(3)
N5	0.078(1)	0.348(1)	0.2275(7)	3.9(3)
N6	0.305(1)	0.3553(9)	0.2273(7)	3.2(3)
N7	0.256(1)	0.069(1)	0.1756(7)	3.9(3)

Table 2. (Continued)

Atom	x	y	z	B/Å^2
N8	0.463(1)	0.070(1)	0.2161(7)	4.1(3)
C1	0.047(2)	0.585(1)	0.323(1)	5.1(5)
C2	0.024(2)	0.698(1)	0.342(1)	5.6(5)
C3	0.054(2)	0.729(1)	0.411(1)	5.1(5)
C4	0.104(1)	0.651(1)	0.4572(9)	3.9(4)
C5	0.125(1)	0.542(1)	0.4344(8)	3.3(3)
C6	0.189(1)	0.455(1)	0.4787(8)	3.6(4)
C7	0.282(1)	0.268(1)	0.4885(9)	4.3(4)
C8	0.275(1)	0.161(1)	0.4508(8)	3.2(4)
C9	0.364(1)	0.067(1)	0.4670(8)	3.7(4)
C10	0.383(1)	−0.126(1)	0.4305(9)	4.2(4)
C11	0.374(1)	−0.203(1)	0.3720(9)	4.0(4)
C12	0.407(1)	−0.314(1)	0.381(1)	4.5(4)
C13	0.396(2)	−0.381(1)	0.321(1)	5.8(5)
C14	0.347(2)	−0.336(1)	0.256(1)	5.5(5)
C15	0.315(1)	−0.219(1)	0.2517(9)	4.1(4)
C16	0.022(1)	0.109(1)	0.3817(8)	3.6(4)
C17	−0.095(2)	0.069(1)	0.415(1)	6.1(5)
C18	−0.034(1)	0.343(1)	0.2288(9)	4.5(4)
C19	−0.076(1)	0.357(1)	0.157(1)	5.7(5)
C20	0.001(2)	0.378(1)	0.0842(9)	5.3(5)
C21	0.203(2)	0.406(1)	0.0049(9)	5.3(5)
C22	0.317(2)	0.410(1)	0.0031(9)	5.6(5)
C23	0.474(1)	0.392(1)	0.082(1)	4.7(4)
C24	0.505(1)	0.375(1)	0.1549(9)	4.2(4)
C25	0.417(1)	0.355(1)	0.2258(9)	3.9(4)
C26	0.119(1)	0.385(1)	0.0793(9)	4.3(4)
C27	0.155(1)	0.370(1)	0.1537(8)	3.4(3)
C28	0.275(1)	0.375(1)	0.1526(8)	3.2(3)
C29	0.357(1)	0.393(1)	0.0790(9)	4.2(4)
C30	0.156(1)	0.064(1)	0.1573(9)	4.6(4)
C31	0.136(2)	0.087(2)	0.078(1)	6.0(5)
C32	0.226(2)	0.115(1)	0.0181(9)	6.0(5)
C33	0.441(2)	0.147(1)	−0.0257(9)	6.3(5)
C34	0.542(2)	0.143(1)	−0.007(1)	5.9(5)
C35	0.661(2)	0.120(2)	0.098(1)	6.6(6)
C36	0.665(2)	0.093(2)	0.180(1)	7.1(6)
C37	0.562(1)	0.071(2)	0.235(1)	5.4(5)
C38	0.338(2)	0.118(1)	0.0336(9)	5.2(5)
C39	0.349(1)	0.094(1)	0.1158(8)	3.7(4)
C40	0.459(1)	0.096(1)	0.1351(9)	4.1(4)
C41	0.557(1)	0.122(1)	0.074(1)	4.9(4)
$[\mathrm{Mn(L^2)(NO_3)_2}]$ (**5**)				
Mn	0.37511(6)	0.2218(1)	0.25691(8)	2.89(2)
O1	0.3947(3)	0.0679(7)	0.4143(4)	4.9(1)
O2	0.2831(3)	0.1106(8)	0.3369(4)	5.8(1)
O3	0.3119(3)	−0.0032(9)	0.4893(4)	7.4(2)
O4	0.3345(3)	−0.0448(7)	0.1704(4)	5.2(1)
O5	0.4499(3)	−0.0555(8)	0.2297(4)	5.6(1)
O6	0.3942(3)	−0.2661(8)	0.1282(4)	8.2(2)
N1	0.4884(3)	0.3497(7)	0.3319(4)	3.1(1)
N2	0.3586(3)	0.4889(8)	0.3373(4)	3.3(1)
N3	0.2767(3)	0.3626(8)	0.1458(4)	3.4(1)
N4	0.4014(3)	0.2831(8)	0.0978(4)	3.7(1)
N5	0.3293(3)	0.0568(8)	0.4151(4)	4.0(1)
N6	0.3931(3)	−0.1274(8)	0.1744(4)	4.1(1)
C1	0.5537(4)	0.281(1)	0.3358(5)	4.3(2)
C2	0.6171(4)	0.380(1)	0.3687(6)	4.7(2)
C3	0.6142(4)	0.558(1)	0.3959(6)	4.6(2)
C4	0.5480(4)	0.633(1)	0.3953(5)	4.1(2)
C5	0.4854(3)	0.526(1)	0.3635(5)	3.2(2)
C6	0.4144(4)	0.591(1)	0.3687(5)	3.5(2)
C7	0.2881(4)	0.555(1)	0.3495(5)	4.3(2)
C8	0.2333(4)	0.591(1)	0.2477(6)	4.9(2)
C9	0.2127(4)	0.427(1)	0.1768(6)	4.6(2)
C10	0.2835(4)	0.415(1)	0.0605(5)	3.6(2)
C11	0.3480(4)	0.369(1)	0.0274(5)	3.9(2)
C12	0.3534(4)	0.413(1)	−0.0687(5)	4.6(2)
C13	0.4148(5)	0.364(1)	−0.0959(5)	5.5(2)
C14	0.4689(4)	0.274(1)	−0.0257(6)	5.6(2)
C15	0.4607(4)	0.236(1)	0.0694(5)	4.6(2)
$[\mathrm{Mn(L^2)(bipy)(CH_3OH)](ClO_4)_2}$ (**6**)				
Mn	0.38326(3)	0.23172(7)	0.74857(4)	3.73(1)
Cl1	0.42366(8)	0.2668(1)	1.06561(7)	5.61(3)
Cl2	0.15395(9)	−0.2827(1)	0.64363(8)	6.55(4)
O1	0.3913(2)	0.3805(3)	0.8480(2)	5.12(8)
O2	0.4520(4)	0.2618(7)	1.0037(3)	13.6(2)
O3	0.3570(4)	0.1859(6)	1.0478(5)	14.0(2)
O4	0.4858(4)	0.2316(7)	1.1376(3)	13.5(2)
O5	0.3996(4)	0.3880(5)	1.0742(5)	14.1(2)
O6	0.1477(3)	−0.3167(5)	0.7180(3)	9.8(1)
O7	0.0866(3)	−0.3285(5)	0.5744(3)	10.1(2)
O8	0.2238(3)	−0.3375(5)	0.6401(3)	9.6(1)
O9	0.1568(3)	−0.1467(4)	0.6373(3)	8.1(1)
N1	0.4123(2)	0.4130(4)	0.6850(2)	4.16(8)
N2	0.3329(2)	0.2030(4)	0.6056(2)	5.3(1)
N3	0.4322(2)	0.0348(4)	0.7242(2)	5.2(1)
N4	0.5219(2)	0.2168(4)	0.8287(2)	4.29(9)
N5	0.2449(2)	0.2599(4)	0.7061(2)	4.39(8)
N6	0.3366(2)	0.0929(4)	0.8190(2)	4.26(9)
C1	0.4557(3)	0.5156(5)	0.7233(3)	4.6(1)
C2	0.4810(3)	0.6085(5)	0.6834(3)	5.4(1)
C3	0.4588(3)	0.5982(5)	0.5999(3)	6.0(1)
C4	0.4128(3)	0.4953(6)	0.5584(3)	5.6(1)
C5	0.3909(2)	0.4044(5)	0.6029(3)	4.4(1)
C6	0.3451(3)	0.2911(6)	0.5630(3)	5.4(1)
C7	0.2899(3)	0.0871(7)	0.5633(4)	7.5(2)
C8	0.3457(4)	−0.0252(6)	0.5814(4)	8.5(2)
C9	0.3815(4)	−0.0667(6)	0.6700(4)	7.6(2)
C10	0.5066(3)	0.0156(5)	0.7597(3)	5.5(1)
C11	0.5585(3)	0.1112(5)	0.8158(3)	4.6(1)
C12	0.6403(3)	0.0927(6)	0.8530(3)	6.2(1)
C13	0.6871(3)	0.1845(7)	0.9055(4)	6.8(2)
C14	0.6522(3)	0.2919(6)	0.9200(3)	5.9(1)
C15	0.5688(3)	0.3048(5)	0.8812(3)	4.9(1)
C16	0.2062(2)	0.1671(4)	0.7277(2)	3.84(9)
C17	0.1230(3)	0.1616(5)	0.6916(3)	5.6(1)
C18	0.0802(3)	0.2527(6)	0.6350(4)	6.4(1)
C19	0.1202(3)	0.3485(5)	0.6148(3)	5.7(1)
C20	0.2024(3)	0.3483(5)	0.6514(3)	5.6(1)
C21	0.2562(2)	0.0761(4)	0.7912(2)	3.85(9)
C22	0.2244(3)	−0.0209(5)	0.8224(3)	5.2(1)
C23	0.2747(3)	−0.1011(5)	0.8818(3)	6.5(1)
C24	0.3559(3)	−0.0844(5)	0.9100(3)	5.9(1)
C25	0.3843(3)	0.0137(5)	0.8769(3)	5.2(1)
C26	0.3450(4)	0.4999(8)	0.8458(4)	10.6(2)
$[\mathrm{Mn(L^2)(NCS)_2}]$ (**7**)				
Mn	0.62331(3)	0.14667(8)	0.71458(7)	3.25(1)
N1	0.6768(1)	0.0937(4)	0.9342(4)	3.31(8)
N2	0.6920(2)	−0.0190(5)	0.6764(4)	3.58(8)
N3	0.5767(2)	−0.0821(5)	0.6517(4)	4.15(9)

Table 2. (Continued)

Atom	x	y	z	B/Å^2
N4	0.5408(1)	0.1518(4)	0.8042(4)	3.62(8)
N5	0.6078(2)	0.2294(5)	0.4996(4)	5.3(1)
N6	0.6423(2)	0.3809(5)	0.7861(5)	5.0(1)
S1	0.58446(7)	0.4274(2)	0.2719(2)	6.13(4)
S2	0.67178(7)	0.6358(2)	0.9559(2)	5.51(3)
C1	0.6722(2)	0.1596(6)	1.0601(5)	4.1(1)
C2	0.7113(2)	0.1346(6)	1.1784(5)	5.2(1)
C3	0.7559(2)	0.0428(6)	1.1662(5)	5.2(1)
C4	0.7616(2)	−0.0240(6)	1.0376(5)	4.4(1)
C5	0.7210(2)	0.0037(5)	0.9245(4)	3.19(9)
C6	0.7238(2)	−0.0656(6)	0.7837(5)	3.6(1)
C7	0.6930(2)	−0.1042(7)	0.5423(5)	5.2(1)
C8	0.6396(3)	−0.166(1)	0.4871(8)	11.7(2)
C9	0.5970(3)	−0.2067(7)	0.5635(7)	8.0(2)
C10	0.5304(2)	−0.0965(6)	0.6942(5)	4.1(1)
C11	0.5084(2)	0.0256(5)	0.7787(5)	3.5(1)
C12	0.4572(2)	0.0120(6)	0.8271(5)	4.3(1)
C13	0.4387(2)	0.1324(7)	0.9035(5)	4.7(1)
C14	0.4712(2)	0.2604(6)	0.9309(6)	4.9(1)
C15	0.5221(2)	0.2667(6)	0.8784(6)	4.5(1)
C16	0.5981(2)	0.3127(5)	0.4068(5)	3.7(1)
C17	0.6541(2)	0.4870(5)	0.8571(5)	3.6(1)
[Mn(L^2)(phen)](ClO$_4$)$_2$ (**8**)				
Mn	0.74939(7)	0.25	0.09052(9)	3.83(2)$^{b)}$
N1	0.8303(2)	0.3885(4)	0.0494(3)	4.9(1)
N2	0.7556(2)	0.3717(4)	0.2194(3)	4.8(1)
N3	0.6666(2)	0.3657(4)	0.0171(3)	4.1(1)
Cl1	0.7874(1)	0.25	−0.2871(2)	5.84(6)$^{b)}$
Cl2	0.5075(1)	0.75	−0.2609(2)	6.72(6)$^{b)}$
O1	0.8305(3)	0.3479(5)	−0.2741(4)	10.5(2)
O2	0.7612(5)	0.25	−0.3824(6)	13.8(4)$^{b)}$
O3	0.7348(4)	0.25	−0.2164(7)	12.1(3)$^{b)}$
O4	0.4708(4)	0.6517(6)	−0.2467(6)	17.3(2)
O5	0.5137(7)	0.75	−0.3639(8)	17.6(5)$^{b)}$
O6	0.5730(4)	0.75	−0.2154(7)	11.6(2)$^{b)}$
C1	0.8639(3)	0.4023(7)	−0.0374(5)	6.7(2)
C2	0.9088(4)	0.4954(8)	−0.0547(6)	9.0(2)
C3	0.9203(4)	0.5728(7)	0.0177(7)	10.2(2)
C4	0.8854(4)	0.5606(6)	0.1071(7)	8.3(2)
C5	0.8406(3)	0.4669(5)	0.1200(5)	5.5(2)
C6	0.8003(3)	0.4516(6)	0.2116(5)	5.8(2)
C7	0.7165(4)	0.3592(7)	0.3120(5)	7.1(2)
C8	0.7357(5)	0.25	0.3657(7)	7.3(3)$^{b)}$
C9	0.6650(3)	0.4798(6)	0.0208(5)	5.1(1)
C10	0.6140(3)	0.5450(6)	−0.0293(5)	6.4(2)
C11	0.5636(3)	0.4914(6)	−0.0849(5)	6.3(2)
C12	0.5111(3)	0.3072(6)	−0.1439(4)	6.8(2)
C13	0.5632(3)	0.3716(6)	−0.0899(4)	5.1(1)
C14	0.6156(3)	0.3116(5)	−0.0369(4)	3.9(1)

a) Atom was refined isotropically. b) Atom was refined with occupancy factor of 0.5. c) Atom was refined with occupancy factor of 0.25. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$.

$R_w=[w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are listed in Table 1. The weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. All of the calculations were carried out on a VAX station 4000 90A computer using a MolEN program package.[17] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of the nonhydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the F_o-F_c tables were deposited as Document No. 70037 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion.

Reaction of *N*,*N*′-bis(2-pyridylmethylene)-1,3-diaminopropan-2-ol (HL^1) with manganese(II) nitrate hexahydrate in ethanol gave pale yellow plates of [Mn(HL^1)(NO$_3$)$_2$]·C$_2$H$_5$OH (**1**·C$_2$H$_5$OH). The X-ray crystallography of **1**·C$_2$H$_5$OH reveals a novel eight-coordinate Mn atom which has a distorted square antiprism with four N atoms of HL^1 and four O atoms of two bidenetate NO$_3$ ions. A perspective view of the molecule is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The HL^1 ligand is not deprotonated and forms an N$_4$ basal plane for the metal atom by folding the two pyridylmethylene moieties. The Mn atom is situated upon this N$_4$ plane by 1.13 Å. The four Mn–N bond lengths [Mn–N1 2.284(4), Mn–N4 2.354(4) Å; Mn–N2 2.327(4), Mn–N3 2.273(4) Å] are comparable to those commonly observed in six-coordinate octahedral manganese(II) complexes [Mn–N(pyridyl) 2.203(14)—2.411(3) Å, Mn–N(imine) 2.150(5)—2.308(2) Å].[3] The two nitrate ions are coordinated to the manganese atom in an unsymmetrical bidentate manner in the opposite site to the N$_4$ plane [Mn–O2 2.354(5), Mn–O3 2.547(5) Å; Mn–O5 2.292(4), Mn–O6 2.502(5) Å]. Such an unsymmetrical bidentate manner is observed in the eight-coordinate Mn-

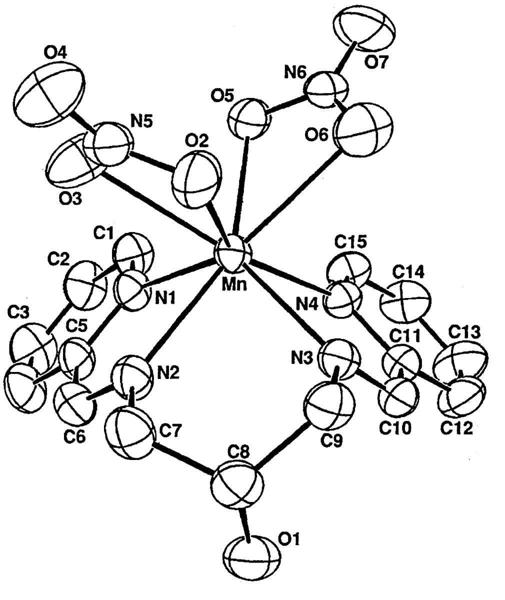

Fig. 1. View of the structure of [Mn(HL^1)(NO$_3$)$_2$]·C$_2$H$_5$OH (**1**·C$_2$H$_5$OH), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

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

$[\mathrm{Mn(HL^1)(NO_3)_2]\cdot C_2H_5OH}$ (**1**·$\mathrm{C_2H_5OH}$)			
Mn–N1	2.284(4)	Mn–O2	2.354(5)
Mn–N2	2.327(4)	Mn–O3	2.547(5)
Mn–N3	2.273(4)	Mn–O5	2.292(4)
Mn–N4	2.354(4)	Mn–O6	2.502(5)
N1–Mn–N2	71.8(2)	N3–Mn–O2	87.6(2)
N1–Mn–N3	126.4(1)	N3–Mn–O3	132.6(2)
N1–Mn–N4	86.4(2)	N3–Mn–O5	134.5(2)
N1–Mn–O2	126.9(2)	N3–Mn–O6	85.4(2)
N1–Mn–O3	78.4(2)	N4–Mn–O2	146.7(2)
N1–Mn–O5	86.1(2)	N4–Mn–O3	156.1(2)
N1–Mn–O6	136.6(2)	N4–Mn–O5	81.7(2)
N2–Mn–N3	75.4(2)	N4–Mn–O6	76.4(2)
N2–Mn–N4	115.7(1)	O2–Mn–O3	50.7(2)
N2–Mn–O2	81.7(2)	O2–Mn–O5	96.6(2)
N2–Mn–O3	77.0(2)	O2–Mn–O6	76.4(2)
N2–Mn–O5	150.1(2)	O3–Mn–O5	79.0(2)
N2–Mn–O6	151.4(2)	O3–Mn–O6	102.3(2)
N3–Mn–N4	71.3(2)	O5–Mn–O6	52.4(2)
$[\mathrm{Mn(HL^1)(NCS)_2}]$ (**2**)			
Mn–N1	2.341(2)	Mn–N4	2.296(3)
Mn–N2	2.275(3)	Mn–N5	2.158(3)
Mn–N3	2.318(3)	Mn–N6	2.185(3)
N1–Mn–N2	70.9(1)	N3–Mn–N5	82.8(1)
N1–Mn–N3	118.6(1)	N3–Mn–N6	153.0(1)
N1–Mn–N4	91.4(1)	N4–Mn–N5	119.0(1)
N1–Mn–N5	148.2(1)	N4–Mn–N6	91.6(1)
N1–Mn–N6	81.6(1)	N5–Mn–N6	87.8(1)
N2–Mn–N3	77.8(1)	N2–Mn–N4	131.0(1)
N2–Mn–N4	131.0(1)	N2–Mn–N5	93.2(1)
N2–Mn–N5	93.2(1)	N2–Mn–N6	128.1(1)
N2–Mn–N6	128.1(1)	N4–Mn–N5	119.0(1)
N3–Mn–N4	71.4(1)	N4–Mn–N6	91.6(1)
N5–Mn–N6	87.8(1)		
$[\mathrm{Mn(HL^1)(phen)](ClO_4)_2}$ (**3**)			
Mn–N1	2.316(9)	Mn–N3	2.286(8)
Mn–N2	2.221(9)	Mn–O1a	2.57(2)
O1a–Mn–N1	129.8(3)	N1–Mn–N3	88.1(3)
O1a–Mn–N2	60.4(5)	N1–Mn–N3′	142.1(3)
O1a–Mn–N3	79.5(5)	N2–Mn–N2′	76.9(4)
N1–Mn–N1′[a]	87.7(3)	N2–Mn–N3	91.0(3)
N1–Mn–N2	71.5(3)	N2–Mn–N3′	139.0(4)
N1–Mn–N2′	123.0(4)	N3–Mn–N3′	72.8(3)
$[\mathrm{Mn_2(L^1)(CH_3COO)(phen)_2](ClO_4)_2\cdot H_2O}$ (**4**·$\mathrm{H_2O}$)			
Mn1–Mn2	3.518(3)	Mn2–O1	2.103(9)
Mn1–O1	2.122(9)	Mn2–O3	2.141(10)
Mn1–O2	2.130(10)	Mn2–N3	2.252(12)
Mn1–N1	2.385(11)	Mn2–N4	2.324(11)
Mn1–N2	2.261(12)	Mn2–N7	2.284(12)
Mn1–N5	2.329(13)	Mn2–N8	2.283(11)
Mn1–N6	2.251(10)		
Mn1–O1–Mn2	112.7(5)	O1–Mn2–O3	92.3(4)
O1–Mn1–O2	89.3(4)	O1–Mn2–N3	74.9(4)
O1–Mn1–N1	140.5(4)	O1–Mn2–N4	145.4(4)
O1–Mn1–N2	73.6(4)	O1–Mn2–N7	116.5(4)
O1–Mn1–N5	129.0(4)	O1–Mn2–N8	91.6(4)
O1–Mn1–N6	84.6(4)	O3–Mn2–N3	102.7(4)
O2–Mn1–N1	111.9(4)	O3–Mn2–N4	93.5(4)
O2–Mn1 –N2	103.3(4)	O3–Mn2–N7	89.0(4)
O2–Mn1 –N5	83.3(4)	O3–Mn2–N8	160.9(4)
O2–Mn1 –N6	141.9(4)	N3–Mn2–N4	70.6(4)
N1–Mn1–N2	69.3(4)	N3–Mn2 –N7	163.6(4)
N1–Mn1–N5	87.8(4)	N3–Mn2–N8	96.3(4)
N1–Mn1–N6	96.0(4)	N4–Mn2–N7	97.7(4)
N2–Mn1–N5	157.0(4)	N4–Mn2–N8	93.8(4)
N2–Mn1–N6	110.8(4)	N7–Mn2–N8	72.5(5)
N5–Mn1–N6	72.0(4)		
$[\mathrm{Mn(L^2)(NO_3)_2}]$ (**5**)			
Mn–O1	2.350(5)	Mn–N1	2.317(5)
Mn–O2	2.445(6)	Mn–N2	2.294(6)
Mn–O4	2.289(5)	Mn–N3	2.301(5)
Mn–O5	2.557(6)	Mn–N4	2.392(6)
O1–Mn–O2	52.5(2)	O4–Mn–N1	135.1(2)
O1–Mn–O4	90.5(2)	O4–Mn–N2	153.0(2)
O1–Mn–O5	78.5(2)	O4–Mn–N3	86.7(2)
O1–Mn–N1	84.1(2)	O4–Mn–N4	79.6(2)
O1–Mn–N2	88.8(2)	O5–Mn–N1	83.7(2)
O1–Mn–N3	134.8(2)	O5–Mn–N2	153.3(2)
O1–Mn–N4	152.9(2)	O5–Mn–N3	130.1(2)
O2–Mn–O4	76.4(2)	O5–Mn–N4	75.6(2)
O2–Mn–O5	107.6(2)	N1–Mn–N2	71.6(2)
O2–Mn–N1	129.5(2)	N1–Mn–N3	127.1(2)
O2–Mn–N2	81.8(2)	N1–Mn–N4	85.3(2)
O2–Mn–N3	83.2(2)	N2–Mn–N3	74.9(2)
O2–Mn–N4	145.0(2)	N2–Mn–N4	111.3(2)
O4–Mn–O5	51.7(2)	N3–Mn–N4	70.2(2)
$[\mathrm{Mn(L^2)(bipy)(CH_3OH)](ClO_4)_2}$ (**6**)			
Mn–O1	2.304(3)	Mn–N4	2.347(3)
Mn–N1	2.363(4)	Mn–N5	2.335(3)
Mn–N2	2.337(4)	Mn–N6	2.283(4)
Mn–N3	2.344(4)		
O1–Mn–N1	82.4(1)	N2–Mn–N3	72.6(1)
O1–Mn–N2	142.1(1)	N2–Mn–N4	120.3(2)
O1–Mn–N3	144.7(1)	N2–Mn–N5	76.4(1)
O1–Mn–N4	81.9(1)	N2–Mn–N6	116.1(1)
O1–Mn–N5	83.8(1)	N3–Mn–N4	70.0(1)
O1–Mn–N6	86.2(1)	N3–Mn–N5	119.4(1)
N1–Mn–N2	69.7(1)	N3–Mn–N6	78.3(2)
N1–Mn–N3	116.0(2)	N4–Mn–N5	163.4(1)
N1–Mn–N4	87.1(1)	N4–Mn–N6	99.9(1)
N1–Mn–N5	99.4(1)	N5–Mn–N6	70.6(1)
N1–Mn–N6	165.6(1)		
$[\mathrm{Mn(L^2)(NCS)_2}]$ (**7**)			
Mn–N1	2.355(3)	Mn–N4	2.274(4)
Mn–N2	2.262(4)	Mn–N5	2.148(4)
Mn–N3	2.319(4)	Mn–N6	2.166(4)
N1–Mn–N2	71.5(1)	N2–Mn–N6	120.6(2)
N1–Mn–N3	105.0(1)	N3–Mn–N4	71.9(1)
N1–Mn–N4	95.0(1)	N3–Mn–N5	91.1(2)
N1–Mn–N5	156.1(2)	N3–Mn–N6	162.9(2)
N1–Mn–N6	80.4(1)	N4–Mn–N5	107.0(2)
N2–Mn–N3	76.4(1)	N4–Mn–N6	91.6(2)
N2–Mn–N4	140.8(1)	N5–Mn–N6	89.5(2)
N2–Mn–N5	95.9(2)		
$[\mathrm{Mn(L^2)(phen)](ClO_4)_2}$ (**8**)			
Mn–N1	2.286(5)	Mn–N3	2.285(4)
Mn–N2	2.240(5)		
N1–Mn–N1′[a]	89.6(2)	N2–Mn–N2′	78.4(2)
N1–Mn–N2	73.0(2)	N2–Mn–N3	89.9(2)
N1–Mn–N2′	126.7(2)	N2–Mn–N3′	137.9(2)
N1–Mn–N3	86.4(2)	N3–Mn–N3′	72.2(2)
N1–Mn–N3′	140.0(2)		

a) Primes refer to the equivalent positions (x, $1/2-y$, z).

(II) complex [Mn(dppn)$_2$(NO$_3$)$_2$] (dppn = 3,4-di-2-pyridylpyridazine) [Mn–N 2.29(1)—2.33(1) Å, Mn–O 2.30(2)—2.47(1) Å].[18] The infrared spectrum of **1** shows absorptions [ν(NO$_3$) 1459(s), 1326(s), 1301(s) cm^{-1}] indicative of the asymmetric bidentate nature of the NO$_3$ groups.[18] As shown in Fig. 2, the N$_4$ and O$_4$ equilateral squares which parallel each other, are mutually staggered so as to give a square-antiprismatic geometry rather than cube. Thus, the geometry around the Mn atom can be described as a distorted square antiprism. This example of square-antiprismatic coordination geometry is very rare,[19] although other eight-coordinate geometries such as dodecahedron,[20] cube,[21] and bicapped trigonal antiprism[22] have been found for Mn(II). The uncoordinated hydroxy group of HL^1 is located in the vicinity of the nitrate ion of the neighbor molecule by hydrogen bonding [O1···O3 (x, y, $1+z$) 2.805(6) Å].

A similar reaction of a related Schiff-base ligand, *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine (L^2) with manganese(II) nitrate afforded an analogous complex, [Mn(L^2)(NO$_3$)$_2$] (**5**). The infrared spectral feature of the NO$_3$ group region is similar to that of **1**, suggesting that the coordination geometry is square-antiprismatic. The X-ray structure analysis shows that the manganese atom in **5** is eight-coordinated by the four N atoms of the L^2 ligand and the four O atoms of the two nitrate groups (Fig. 3) arranged at the corners of a square antiprism. The Mn–N and Mn–O bond distances range from 2.294(6) to 2.392(6) Å and from 2.289(5) to 2.557(6) Å, respectively. These bond lengths are comparable to those of **1**.

When the ligand L^2 was treated with Mn(ClO$_4$)$_2$·6H$_2$O and 2,2′-bipyridyl (bpy) in methanol–ethanol, we have isolated a Mn(II) complex, [Mn(L^2)(bpy)(CH$_3$OH)](ClO$_4$)$_2$ (**6**). In the infrared spectrum of **6**, no splitting of the Cl–O band of the perchlorate ion is observed. This shows there is no coordination of the perchlorate ion to the metal in **6**.[23] In the X-ray crystal structure of **6**, novel seven-coordination geometry is formed around the central metal ion (Fig. 4). Six N atoms from the L^2 ligand and bpy form a trigonal prism around Mn, and a methanol oxygen (O1) forms a cap above one of the square faces of the prism. The coordination geometry is described as a distorted monocapped-trigonal prism. The Mn–N and Mn–O distance are 2.283(4)—2.363(4) and 2.304(3) Å, respectively. These bond lengths are in the range of the Mn–N and Mn–O distances of the eight-coordinate Mn(II) complexes, **1** and **5**. Most of reported seven-coordinate Mn(II) complexes have a pentagonal bipyramidal geometry around the metal atom[24] and very few examples are structurally verified as a distorted monocapped trigonal prism.[25]

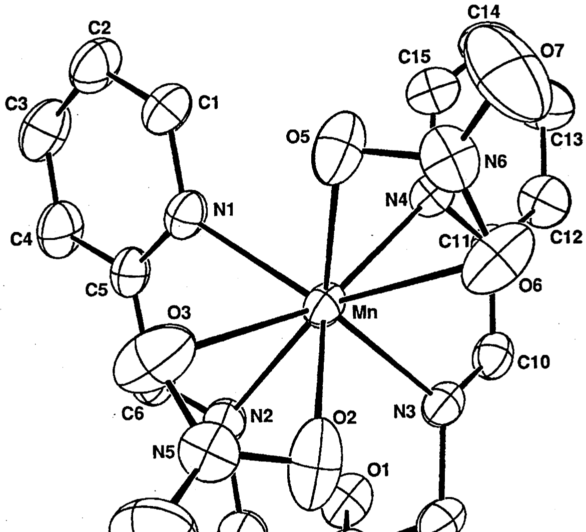

Fig. 2. Another view of the structure of [Mn(HL^1)(NO$_3$)$_2$]·C$_2$H$_5$OH (**1**·C$_2$H$_5$OH), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

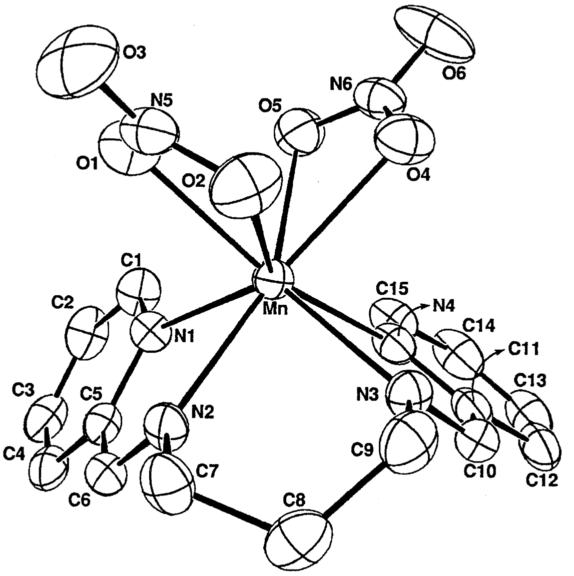

Fig. 3. View of the structure of [Mn(L^2)(NO$_3$)$_2$] (**5**), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

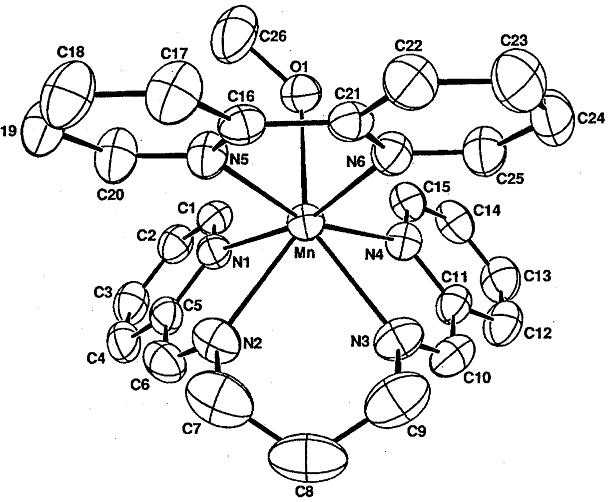

Fig. 4. View of the structure of [Mn(L^2)(bipy)(CH$_3$OH)](ClO$_4$)$_2$ (**6**), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

When the HL^1 ligand was reacted with $Mn(ClO_4)_2 \cdot 6H_2O$ in the presence of 1,10-phenanthroline (phen), a Mn(II) complexes, $[Mn(HL^1)(phen)](ClO_4)_2$ (**3**), was isolated. In the crystal structure of **3** (Fig. 5), the molecule has a mirror plane containing Mn, C8, O1a, and O1b, as required from the crystallographic symmetry. The alkoxy oxygen atom O1 is subjected to disorder and divided into two positions O1a and O1b with an occupancy factor of 0.25. Thus the manganese atom has a disordered geometry of a 1 : 1 mixture of a monocapped trigonal prism made up by four N atoms of HL^1, two N atoms of phen, and one alkoxy O atom (O1a) and a six-coordinate trigonal prism. The Mn–N and Mn–O distances are 2.221(9)—2.316(9) and 2.57(2) Å, respectively.

An analogous Mn(II) complex, $[Mn(L^2)(phen)](ClO_4)_2$ (**8**), was isolated from the reaction of the L^2 ligand with $Mn(ClO_4)_2 \cdot 6H_2O$ in the presence of phen. The infrared spectrum of **8** shows that the perchlorate ion does not participate in coordination to the metal; $\nu(ClO_4^-)$ band appears as a broad band at 1083 cm^{-1} like **3** and **6**. As is shown in Fig. 6, the L^2 ligand forms an N_4 basal plane and the Mn atom is situated upon this N_4 plane by 1.07 Å. The phen molecule occupies the fifth and sixth coordination sites. The molecule has a crystallographic mirror plane along the Mn and C8 atoms. The arrangement of the six nitrogen atoms around the metal is trigonal prismatic, the triangular faces being defined by N1, N2, and N3 and N1′, N2′, and N3′. These two triangular faces are related to each other by the mirror plane. The Mn–N distances range from 2.240(5) to 2.286(5) Å. This type of coordination geometry is rare for Mn(II);[26] octahedral geometry has been found in a vast number of manganese(II) complexes.[2] The trigonal prismatic geometry can be also found in the thiocyanato complexes of HL^1 and L^2. Reaction of the Schiff base ligands with manganese(II) bromide and sodium thiocyanate resulted in the formation of $[Mn(HL^1)(NCS)_2]$ (**2**) and $[Mn(L^2)(NCS)_2]$ (**7**). The X-ray structures of **2** and **7** are shown in Figs. 7 and 8, respectively. In both **2** and **7**, the manganese atoms are six-coordinate and the coordination geometries are distorted trigonal prisms. In each complex, the triangle defined by N1, N4, and N6 is almost parallel to the triangle of N2, and N3, and N5. The Mn–N bond lengths range

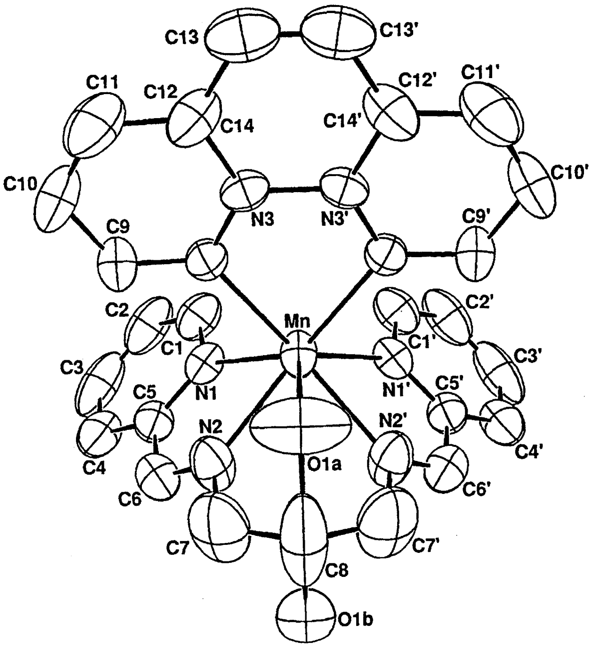

Fig. 5. View of the structure of $[Mn(HL^1)(phen)](ClO_4)_2$ (**3**), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

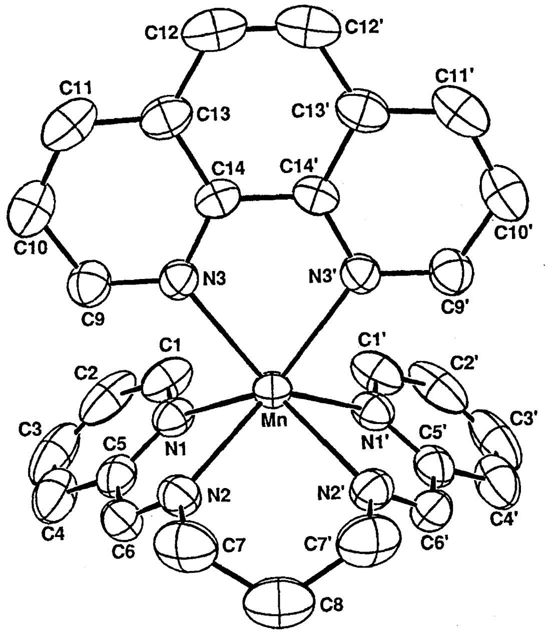

Fig. 6. View of the structure of $[Mn(L^2)(phen)](ClO_4)_2$ (**8**), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

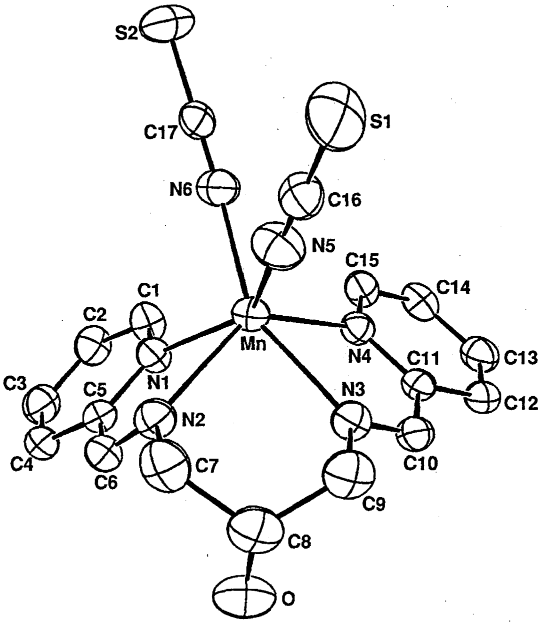

Fig. 7. View of the structure of $[Mn(HL^1)(NCS)_2]$ (**2**), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

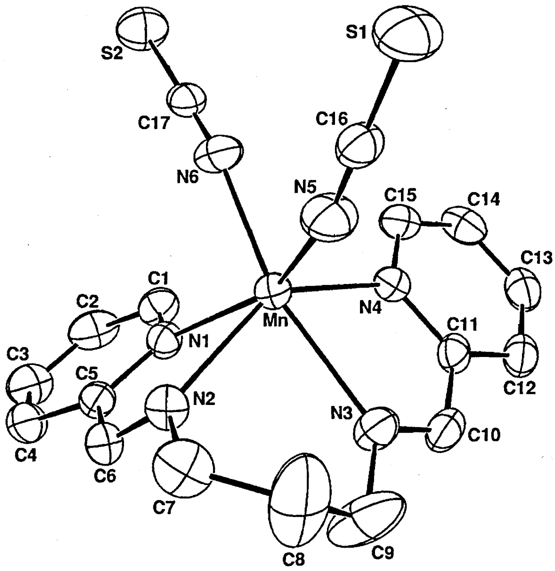

Fig. 8. View of the structure of [Mn(L^2)$(NCS)_2$] (**7**), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

from 2.148(4) to 2.355(3) Å. The Mn-N (thiocyanato) bond lengths [2.148(4)—2.185(3) Å] are significantly shorter than those found for the Mn-N distances to the Schiff-base ligands [2.274(4)—2.355(3) Å]. Shorter Mn–N (NCS) distances are also observed in other manganese(II) complexes such as *cis*-[Mn$(NCS)_2$$(bpy)_2$],[27a)] *cis*-[Mn$(NCS)_2$$(phen)_2$],[27b)] and [Mn(HL)$(NCS)_2$$(H_2O)$] (HL = 4-methyl-2,6-bis{*N*-[2-(2-pyridyl)ethyl]iminomethyl}phenol).[3c)] The infrared spectra of **2** and **7** show two ν_{CN} (NCS) stretching bands at 2052—2069 cm^{-1}. This fact is in harmony with the crystal structures of **2** and **7**, which contain two crystallographically independent N-coordinating NCS groups.

When the HL^1 ligand was reacted with manganese(II) acetate tetrahydrate in a ligand to metal ratio of 1 : 2 in the presence of triethylamine, 1,10-phenanthroline, and sodium perchlorate, a dinuclear species [$Mn_2$$(L)^1$$(CH_3COO)$$(phen)_2$]$(ClO_4)_2$·$H_2O$ (**4**·H_2O), was isolated as dark vermillion columns. A crystal structure determination of **4**·H_2O confirmed that the HL^1 ligand had been deprotonated and that the two Mn(II) atoms are bridged by the endogenous *μ*-alkoxo-oxygen atom and the exogenous *syn–syn*-bridging acetate group (Fig. 9). So far, most of the structurally characterized alkoxo-bridged Mn_2 complexes are $Mn(III)_2$ species[5a,6a—6g)] and only one example is structurally elucidated for alkoxo-bridged $Mn(II)_2$ complexes.[28)] The L^1 ligand is hexadentate, forming a planar backbone, but acts as a meridional tridentate chelate for each Mn atom. The two phen molecules are bidentate and occupy the fifth and sixth coordination sites of each Mn atom in a fashion approximately perpendicular to the L^1 ligand plane. The coordination geometry of each Mn atom is a distorted octahedron, in contrast to those for **1**—**3**, **5**—**8**. The Mn–N and Mn–O distances are 2.251(10)—2.385(11) and 2.103(9)—2.141(10) Å, respectively. The Mn1–M2 distance is 3.518(3) Å and Mn1–O1–Mn2 angle is 112.7(5)°. The acetate group is in a *cis*-arrangement to the L^1 ligand. This doubly-bridge $Mn(II)_2$ structure is quite rare in the general context of dinuclear Mn complexes. As can be seen in Fig. 9, the phen ligands lie approximately parallel to each other with an average interplanar separation of 3.42(12) Å. This observed interplanar separation is suggestive of some π–π attraction between these groups.

Room-temperature magnetic moments of these complexes [**1**, 5.73 B.M. (295 K); **2**, 5.98 B.M. (285 K); **3**, 5.92 B.M.

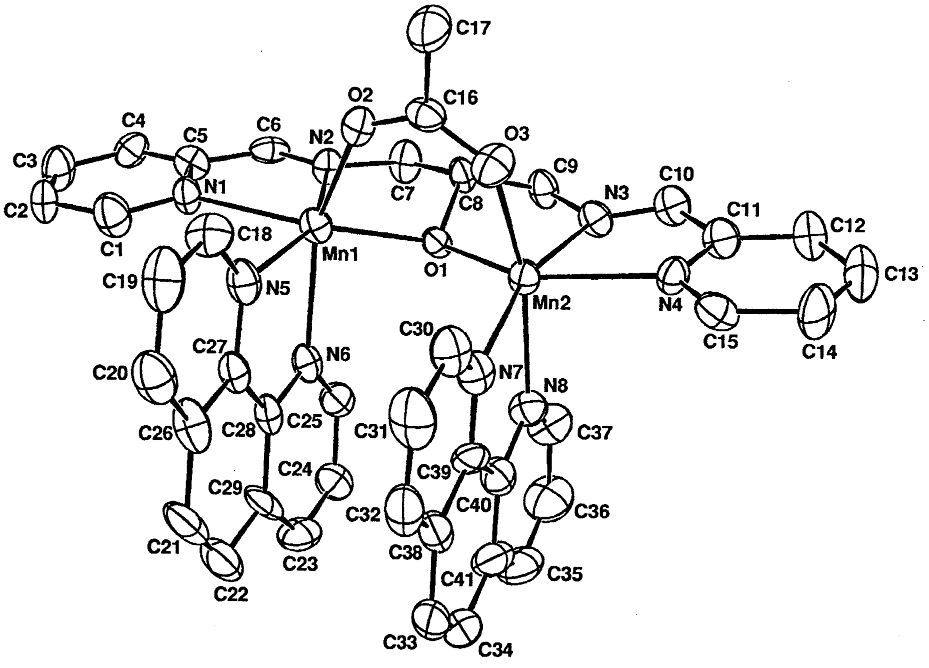

Fig. 9. View of the structure of [$Mn_2$$(L^1)$$(CH_3COO)$$(phen)_2$]$(ClO_4)_2$·$H_2O$ (**4**·H_2O), showing the atom-labeling scheme. Hydrogen atoms are not shown for clarity.

(286 K); **4**, 5.20 B.M./Mn (289 K); **5**, 5.98 B.M. (289 K); **6**, 5.89 B.M. (295 K); **7**, 5.85 B.M. (289 K); **8**, 5.88 B.M. (285 K).] are close to the spin-only value (5.92 B.M.) for a high-spin d^5 configuration except for **4**. The high-spin character of the Mn(II) complexes is confirmed by the electronic spectra. The diffuse reflectance spectra of the present complexes are featureless in the visible region, which can be expected from spin-forbidden d–d transitions for high-spin d^5 system. The magnetic moment of **4** is considerably lower than those of usual high-spin Mn(II) complexes, suggesting antiferromagnetic behavior of this complex. The magnetic susceptibility was measured over the temperature range 80—300 K (Fig. 10). The magnetic susceptibility data were analyzed with Van Vleck equation based on the Heisenberg model ($\mathcal{H}=-2JS_1\cdot S_2$ ($S_1=S_2=5/2$)); the best fitting parameters are $J=-4.0$ cm^{-1} and $g=1.89$. This indicates that the two high-spin Mn(II) ions are antiferromagnetically coupled. The J value is comparable to those of phenoxo-bridged dinuclear Mn(II) complexes which has an analogous bridging mode containing *syn–syn* acetate groups ($J=-2.5$—-5.5 cm^{-1}).[3a—3c,29] The present complexes are soluble in methanol and DMF. However, the conductivities of these solutions suggest that dissociation of the anionic ligands occurs to a greater extent and the solvent molecules may be coordinated to the metal ion in place of the leaving ligands. The frozen solution ESR spectra (X-band) of these complexes are similar to each other, as shown in Fig. 11. This fact suggests that the coordination geometries of the metal ions are similar to each other in solution. Thus, the X-band ESR spectra were measured for polycrystalline samples of the complexes. Some representative examples are shown in Fig. 12. The ESR spectra of both the eight-coordinate Mn(II) complexes, **1** and **5**, are characterized by a broad absorption around $g=2.0$. The seven-coordinate complex, **6**, shows a more complicated spectrum with some absorptions. The ESR spectrum of the trigonal prismatic Mn(II) is different from these spectra, a strong peak being found at $g=4.8$ for **7**. In the case of the dinuclear Mn(II) complex, **4**, the ESR spectrum shows two peaks centered near $g=2.8$ and 4.9 in addition to a signal around $g=2.0$. It can be seen that the ESR spectra of the present complexes reflect their coordination environments. However, these spectra are hard to clearly distinguish by the coordination geometries.

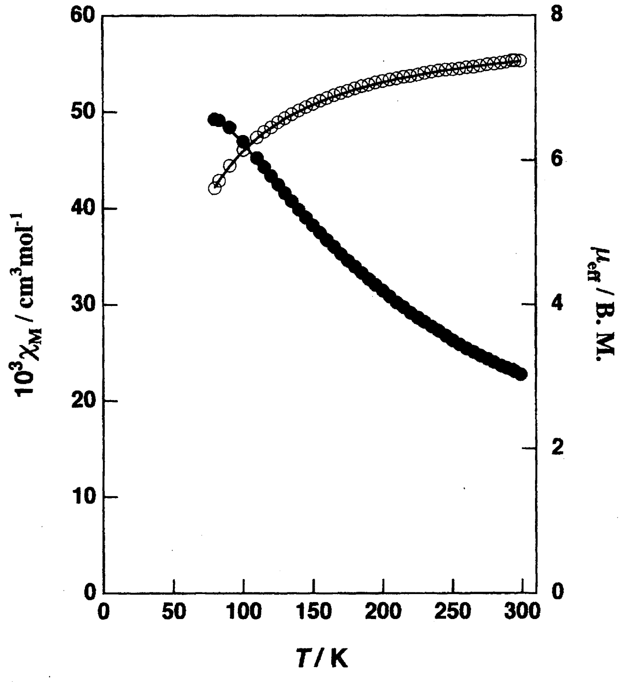

Fig. 10. Magnetic susceptibity data (●) and effective magnetic moments (○) of [$Mn_2(L^1)(CH_3COO)(phen)_2$]($ClO_4$)$_2$ (**4**).

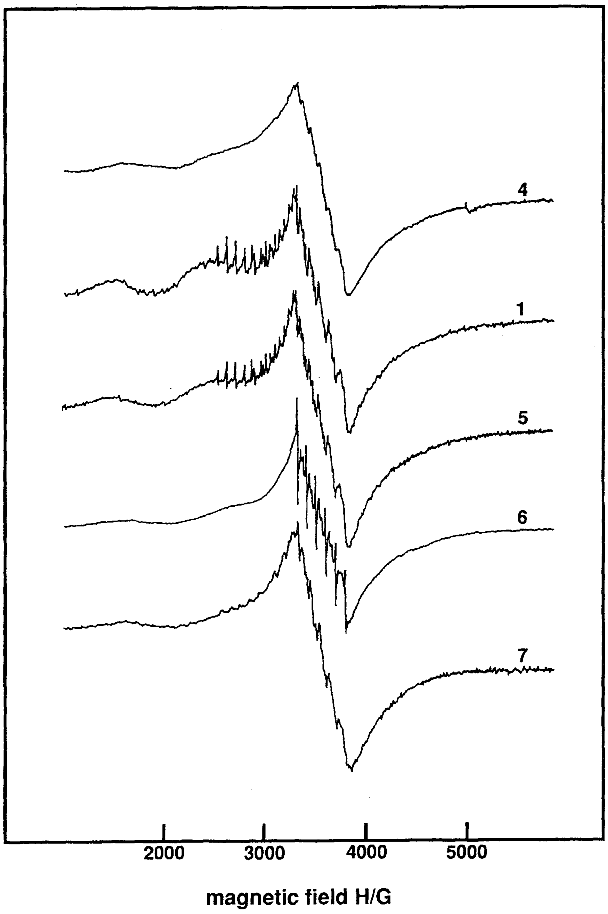

Fig. 11. ESR spectra of [$Mn(HL^1)(NO_3)_2$] (**1**), [$Mn_2(L^1)(CH_3COO)(phen)_2$]($ClO_4$)$_2$ (**4**), [$Mn(L^2)(NO_3)_2$] (**5**), [$Mn(L^2)(bipy)(CH_3OH)$](ClO_4)$_2$ (**6**), and [$Mn(L^2)(NCS)_2$] (**7**) in DMF at 77 K.

Conclusions

The two pyridyl-containing ligands, *N*,*N*′-bis(2-pyridylmethylene)-1,3-diaminopropan-2-ol (HL^1) and *N*,*N*′-bis(2-pyridylmethylene)-1,3-propanediamine (L^2), have proved to be novel ligands that enable us to attain various coordination geometries for Mn(II) in the presence of exogenous ligands such as NO_3^-, phen, bpy, CH_3OH, and NCS^-. The present donor-sets including pyridyl-N and imino-N atoms seem to favor Mn(II) state. In the series of mononuclear Mn(II) complexes, the coordination geometries are quite variable

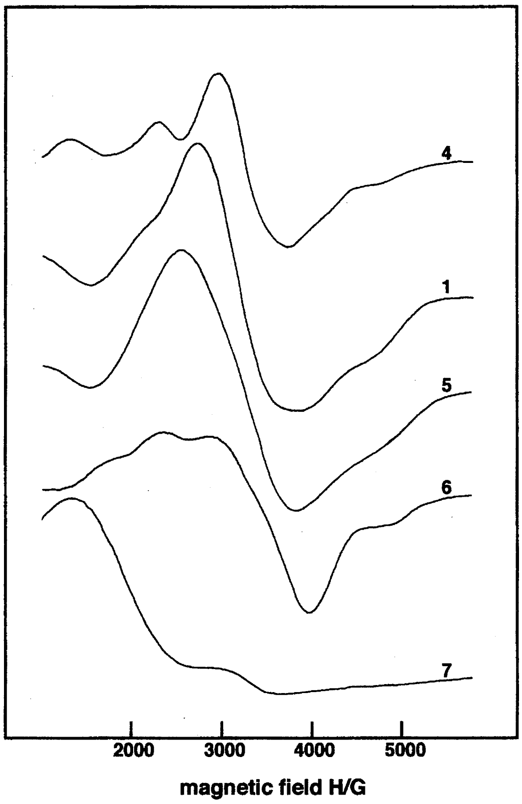

Fig. 12. Polycrystalline ESR spectra of [Mn(HL^1)(NO$_3$)$_2$] (**1**), [Mn$_2$(L^1)(CH$_3$COO)(phen)$_2$](ClO$_4$)$_2$ (**4**), [Mn(L^2)(NO$_3$)$_2$] (**5**), [Mn(L^2)(bipy)(CH$_3$OH)](ClO$_4$)$_2$ (**6**), and [Mn(L^2)(NCS)$_2$] (**7**) at 77 K.

and the basal four N atoms from the HL^1 or L^2 ligand are in a nearly planar-arrangement, leaving ample space for two, three, or four more donor-atoms in the opposite site, where the exogenous ligands determine the coordination number of the metal ion. On the other hand, the deprotonated L^1 ligand does not keep the steric requirement of the basal N$_4$ plane of the Schiff base, but forms an N$_2$ON$_2$ plane bridging the two octahedral Mn atoms. The steric and electronic effects resulting from the combination of the Schiff-base ligands and the exogenous ligands appear to play a major role in defining these geometries, in keeping with the lack of the crystal field stabilization energies for the high-spin d^5 configuration.

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References

1) a) K. Wieghardt, *Agrew. Chem., Int. Ed. Engl.*, **28**, 1153 (1989); b) E. J. Larson and V. L. Pecoraro, in "Manganese Redox Enzymes," ed by V. L. Pecoraro, VCH, New York (1992), Chap. 1; c) K. Sauer, *Acc. Chem. Res.*, **13**, 249 (1980); d) G. Christou, *Acc. Chem. Res.*, **22**, 328 (1989); e) G. W. Brudvig and R. H. Crabtree, *Prog. Inorg. Chem.*, **37**, 99 (1989); f) J. B. Vincent and G. Christou, *Adv. Inorg. Chem.*, **33**, 197 (1989); g) L. Que, Jr., and A. E. True, *Prog. Inorg. Chem.*, **38**, 97 (1990).

2) a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Wiley Interscience, New York (1988), pp. 697—709; b) B. Chiswell, E. D. McKenzie, and L. F. Lindoy, in "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Pergamon, Oxford (1987), Vol. 4, Chap. 41.

3) a) M. Mikuriya, Y. Kawasaki, T. Tokii, S. Yanai, and A. Kawamori, *Inorg. Chim. Acta*, **156**, 21 (1989); b) M. Mikuriya, T. Fujii, S. Kamisawa, Y. Kawasaki, T. Tokii, and H. Oshio, *Chem. Lett.*, **1990**, 1181; c) M. Mikuriya, T. Fujii, T. Tokii, and A. Kawamori, *Bull. Chem. Soc. Jpn.*, **66**, 1675 (1993); d) M. Mikuriya, K. Nakadera, and T. Tokii, *Inorg. Chim. Acta*, **194**, 129 (1992).

4) a) M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, and H. Okawa, *Inorg. Chim. Acta*, **179**, 3 (1991); b) M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, and H. Okawa, *Bull. Chem. Soc. Jpn.*, **67**, 3263 (1994).

5) a) M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **65**, 1466 (1992); b) M. S. Shongwe, M. Mikuriya, E. W. Ainscough, and A. M. Brodie, *J. Chem. Soc., Chem. Commun.*, **1994**, 887; c) M. Mikuriya, H. Takebayashi, and K. Matsunami, *Bull. Chem. Soc. Jpn.*, **67**, 3128 (1994).

6) a) N. Torihara, M. Mikuriya, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **53**, 1610 (1980); b) M. Mikuriya, N. Torihara, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **54**, 1063 (1981); c) M. Mikuriya, S. Kida, and I. Murase, *Chem. Lett.*, **1988**, 35; d) M. Mikuriya, Y. Yamato, and T. Tokii, *Inorg. Chim. Acta*, **118**, 1 (1991); e) M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.*, **1991**, 1429; f) M. Mikuriya, Y. Yamato, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **65**, 2624 (1992); g) M. Mikuriya, Y. Yamato, and T. Tokii, *Chem. Lett.*, **1992**, 1571; h) M. Mikuriya and Y. Yamazaki, *Chem. Lett.*, **1995**, 373.

7) M. Mikuriya, K. Majima, and Y. Yamato, *Chem. Lett.*, **1992**, 1929.

8) M. Mikuriya, K. Nakadera, T. Kotera, T. Tokii, and W. Mori, *Bull. Chem. Soc. Jpn.*, **68**, 3077 (1995).

9) M. Mikuriya, Y. Hashimoto, and A. Kawamori, *Chem. Lett.*, **1995**, 1095.

10) a) M. Mikuriya, S. Shigematsu, K. Kawano, T. Tokii, and H. Oshio, *Chem. Lett.*, **1990**, 729; b) M. Mikuriya, D. Jie, Y. Kakuta, and T. Tokii, *Bull. Chem. Soc. Jpn.*, **66**, 1132 (1993).

11) M. Mikuriya, R. Nukada, W. Tokami, Y. Hashimoto, and T. Fujii, *Bull. Chem. Soc. Jpn.*, **69**, 1573 (1996).

12) a) B. Chiswell, *Inorg. Chim. Acta*, **12**, 195 (1975); b) W. C. Potter and L. T. Taylor, *Inorg. Chem.*, **15**, 1329 (1976).

13) M. Mikuriya, Y. Hatano, and E. Asato, *Chem. Lett.*, **1996**, 849.

14) T. G. Campbell and F. L. Urbach, *Inorg. Chem.*, **12**, 1836 (1973).

15) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

16) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp. 78, 91.

17) C. K. Fair, "MolEN Structure Determination System," Delft Instruments, Delft, The Netherlands (1990).

18) J. E. Andrew, A. B. Black, and L. R. Fraser, *J. Chem. Soc., Dalton Trans.*, **1975**, 800.

19) B. B. Hughes, R. C. Haltiwanger, C. G. Pierpont, M. Hampton, and G. L. Blackmer, *Inorg. Chem.*, **19**, 1801 (1980).

20) a) J. Drummond and J. S. Wood, *J. Chem. Soc. A*, **1970**, 226; b) N. Milinski, B. Ribar, Z. Culum, and S. Djuric, *Acta Crystallogr., Sect. B*, **B33**, 1678 (1977).

21) a) K. S. Hagen, *Angew. Chem., Int. Ed. Engl.*, **31**, 764 (1992); b) M. D. Vaira, F. Mani, and P. Stoppioni, *J. Chem. Soc., Dalton Trans.*, **1992**, 1127.

22) Y. Gultneh, A. Farooq, K. D. Karlin, S. Liu, and J. Zubieta,

Inorg. Chim. Acta, **211**, 171 (1993).

23) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, Wiley Interscience, New York (1986).

24) a) N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, **1974**, 727; b) M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, **1977**, 438; c) M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, **1977**, 1350; d) C. Pelizzi, G. Pelizzi, G. Predieri, and S. Resola, *J. Chem. Soc., Dalton Trans.*, **1982**, 1349; e) C. Lorenzini, C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Chem. Soc., Dalton Trans.*, **1983**, 721; f) C. Pelizzi, G. Pelizzi, and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, **1985**, 215; g) S. Brooker and V. McKee, *J. Chem. Soc., Dalton Trans.*, **1990**, 2397; h) N. A. Bailey, D. E. Fenton, S. J. Kitchen, T. H. Lilley, M. G. Williams, P. A. Tasker, A. J. Leong, and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, **1991**, 2989; i) S. Brooker and V. McKee, *Acta Crystallogr., Sect. C*, **C49**, 441 (1993); j) C.-W. Chan, C.-M. Che, and S.-M. Peng, *Polyhedron*, **12**, 2169 (1993); k) Y. Deng, J. H. Burns, and B. A. Moyer, *Inorg. Chem.*, **34**, 209 (1995); l) Y. Nishida, N. Tanaka, A. Yamazaki, T. Tokii, N. Hashimoto, K. Ide, and K. Iwasawa, *Inorg. Chem.*, **34**, 3616 (1995); m) D. P. Riley, S. L. Henke, P. J. Lennon, R. H. Weiss, W. L. Neumann, W. J. Rivers, K. W. Aston, K. R. Sample, H. Rashman, C.-S. Ling, J.-J. Shieh, D. H. Busch, and W. Szulbinski, *Inorg. Chem.*, **35**, 5213 (1996).

25) a) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964); b) M. B. Inoue, R. E. Navarrro, M. Inoue, and Q. Fernando, *Inorg. Chem.*, **34**, 6074 (1995).

26) a) P. B. Donaldson, P. A. Tasker, and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, **1977**, 1160; b) R. M. Kirchner, C. Mealli, M. Bailey, N. Howe, L. P. Torre, L. J. Wilson, L. C. Andrews, N. J. Rose, and E. C. Lingafelter, *Coord. Chem. Rev.*, **77**, 89 (1987); c) N. Arulsamy, J. Glerup, and D. J. Hodgson, *Inorg. Chem.*, **33**, 3043 (1994); d) M. B. Inoue, P. Oram, G. Andreu-de-Riquer, M. Inoue, P. Borbat, A. Raitsimring, and Q. Fernando, *Inorg. Chem.*, **34**, 3528 (1995).

27) a) M. V. Veidis, B. Dockum, F. F. Charron, Jr., W. M. Reiff, and T. F. Brennan, *Inorg. Chim. Acta*, **53**, L197 (1981); b) S. R. Holleman, O. J. Parker, and G. L. Breneman, *Acta Crystallogr., Sect. C*, **C50**, 867 (1994).

28) P. J. Pessiki, S. V. Khangulov, D. M. Ho, and G. C. Dismukes, *J. Am. Chem. Soc.*, **116**, 891 (1994).

29) M. Suzuki, M. Mikuriya, S. Murata, A. Uehara, H. Oshio, S. Kida, and K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 4305 (1987).