Synthesis and Characterization of Manganese(III) Complexes with 2-{*N*-[2-(4-Imidazolyl)ethyl]iminomethyl}phenol or 2-{*N*-[2-(2-Pyridyl)ethyl]iminomethyl}phenol

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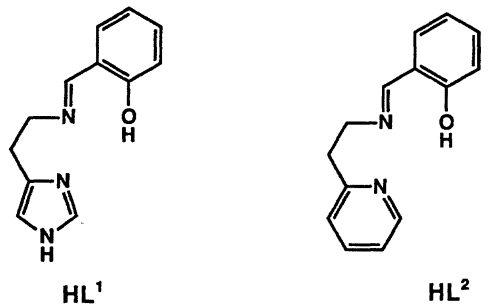
(Received December 13, 1995)

Manganese(III) complexes with 2-{*N*-[2-(4-imidazolyl)ethyl]iminomethyl}phenol (HL^1) or 2-{*N*-[2-(2-pyridyl)ethyl]iminomethyl}phenol (HL^2), $[MnL^1{}_2]ClO_4 \cdot CH_3OH$ (**1**) and $[MnL^2{}_2]ClO_4$ (**2**), have been synthesized and characterized by infrared and electronic spectra, cyclic voltammetry, and temperature dependence of magnetic susceptibilities (80—300 K). The molecular structures of **1** and **2** were determined by single-crystal X-ray structure analysis. The manganese atom adopts an elongated octahedral geometry with two phenolic oxygen atoms, two imine nitrogen atoms, and two imidazolyl or pyridyl nitrogen atoms.

As part of a continuing project on manganese complexes, we have reported on the synthesis and characterization of several manganese complexes with organic ligands.[1—7] These manganese complexes are of interest because of the significant involvement of manganese in various biological systems.[8] In the natural systems, some manganese proteins have been shown by X-ray crystallography to include imidazole nitrogens from histidine residues coordinated to the manganese atom.[8a,8b] It is therefore more interesting to synthesize manganese complexes with organic ligands containing imidazole-nitrogen, which may be expected to have similar structural and electronic effects to those of the active sites in the manganese proteins. However, the examples of such manganese compounds are very few,[9—12] in spite of the existence of a great number of manganese complexes with analogous pyridine-containing ligands.[1a,1b,1c,13—21] Therefore, we have also set out studying about structures and some properties of manganese complexes with imidazole-containing Schiff-base ligands.[6] Herein we report our findings on a manganese complex of 2-{*N*-[2-(4-imidazolyl)ethyl]iminomethyl}phenol (HL^1) together with that of 2-{*N*-[2-(2-pyridyl)ethyl]iminomethyl}phenol (HL^2) (Chart 1).



HL^1 HL^2

Chart 1.

Experimental

Synthesis of the Complexes. **$[MnL^1{}_2]ClO_4 \cdot CH_3OH$ (1).** Salicylaldehyde (52 mg, 0.40 mmol) and histamine (44 mg, 0.40 mmol) were dissolved in 5 ml of methanol. The solution was stirred and heated at ca. 70 °C for 30 min. To the resulting yellow solution were successively added manganese(II) acetate tetrahydrate (98 mg, 0.40 mmol) and sodium perchlorate (98 mg, 0.80 mmol). The solution was filtered while hot after the reaction mixture had been stirred. Dark brown plates were deposited; they were collected by filtration and dried in vacuo over P_2O_5 (yield 80 mg, 34%). Found: C, 48.45; H, 4.56; N, 13.58%. Calcd for $C_{25}H_{28}ClMnN_6O_7$: C, 48.83; H, 4.59; N, 13.67%. IR (KBr) ν/cm^{-1} ν(C=N) 1614(s), $\nu(ClO_4)$ 1150(s), 1115(s), 1110(s), 1089(m). λ_M (CH_3CN)/S mol^{-1} cm^2 169 (lit, range for 1 : 1 electrolytes,[22] 120—160 S mol^{-1} cm^2). Diffuse reflectance spectrum: λ_{max}/nm 275, 325, 394, 465, 650, 785. Electronic spectrum in CH_3CN: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 218 (44600), 265 (21300), 320 (8590), 380 (5320), 610 (348), 1150 (92).

$[MnL^2{}_2]ClO_4$ (2). To a hot solution of salicylaldehyde (52 mg, 0.40 mmol), 2-(2-aminoethyl)pyridine (47 mg, 0.40 mmol) in 5 ml of ethanol was added manganese(II) perchlorate hexahydrate (111 mg, 0.40 mmol). The solution was filtered while hot. Black crystals were obtained by vapor diffusion of diethyl ether into the filtrate (yield 51 mg, 21%). Found: C, 55.30; H, 4.45; N, 9.14%. Calcd for $C_{28}H_{26}ClMnN_4O_6$: C, 55.59; H, 4.33; N, 9.26%. IR (KBr) ν/cm^{-1} ν(C=N) 1610(s), $\nu(ClO_4)$ 1110(s), 1083(s), 1068(s). λ_M (CH_3CN)/S mol^{-1} cm^2 157. Diffuse reflectance spectrum: λ_{max}/nm 250, 284, 324, 400, 478. Electronic spectrum in CH_3CN: λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 261 (27000), 281 (20700), 310 (13000), 385(3790), 450 (1350), 635 (169).

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer model IR700 in the 4000—400 cm^{-1} region on a KBr disk. Electronic 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. Cyclic voltammetric measurements were carried out on a BAS 100B Electrochemical Analyzer. A three-electrode cell comprising a glassy carbon electrode, a platinum-wire counter electrode, and a nonaqueous Ag/Ag^+ electrode was used. The magnetic susceptibilities were measured 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.[23] The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analysis. The unit-cell parameters and intensities of **1** and **2** were measured on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1 °C. The unit-cell parameters were determined by a least-squares refinement based on 25 reflections with $20 \leq 2\theta \leq 30°$. Intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data for $[MnL^1{}_2]ClO_4 \cdot CH_3OH$ (**1**): $C_{25}H_{28}ClMnN_6O_7$, F.W. = 614.9, orthorhombic, *Pnma*, $a = 8.391(2)$, $b = 24.436(5)$ $c = 13.543(5)$ Å, $V = 2777(1)$ Å^3, $D_m = 1.48$, $D_c = 1.47$ g cm^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 6.05 cm^{-1}. Specimen: dark brown crystal 0.53×0.28×0.06 mm. A total of 5389 reflections were measured in the range $2 \leq 2\theta \leq 64°$; 1107 reflections with $I \geq 3\sigma(I)$ were assumed as observed. $R = 0.064$, $R_w = 0.069$.

For $[MnL^2{}_2]ClO_4$ (**2**): $C_{28}H_{26}ClMnN_4O_6$, F.W.=604.9, triclinic, $P\bar{1}$, $a = 11.405(9)$, $b = 13.174(9)$, $c = 11.292(9)$ Å, $\alpha = 111.56(4)$, $\beta = 110.04(4)$, $\gamma = 102.08(4)°$, $V = 1369(2)$ Å^3, $D_m = 1.47$, $D_c = 1.47$

Table 1. Atomic Coordinates and Equivalent Isotropic Temperature Factors of Non-hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 [a]	Atom	x	y	z	B_{eq}/Å^2 [a]
$[MnL^1{}_2]ClO_4 \cdot CH_3OH$ (**1**)					$[MnL_2{}^2]ClO_4$(**2**)				
Mn	0.000	0.000	0.000	2.48(3)	Mn1	0.000	0.000	0.000	3.26(3)
Cl	0.1486(5)	−0.250	0.0200(4)	5.6(1)	Mn2	0.000	0.500	1.000	3.88(3)
O1	0.2146(7)	0.0173(2)	−0.0219(4)	2.9(1)	Cl	−0.3041(1)	0.2256(1)	0.3705(1)	5.09(4)
O2	0.148(2)	−0.2023(4)	0.0781(8)	10.4(3)	O1	0.0335(3)	0.1459(3)	0.1481(3)	3.81(9)
O3	0.024(2)	−0.250	−0.045(1)	17.7(6)	O2	0.0971(4)	0.4095(3)	0.9474(4)	5.1(1)
O4	0.285(2)	−0.250	−0.028(2)	19.7(8)	O3	−0.3857(6)	0.1754(6)	0.2237(5)	10.6(2)
O5	−0.010(1)	−0.250	−0.3061(8)	5.8(3)	O4	−0.3655(7)	0.1653(7)	0.4238(6)	13.7(2)
N1	−0.0552(9)	0.0513(3)	−0.1113(5)	3.1(2)	O5	−0.1811(6)	0.231(1)	0.4001(8)	18.7(4)
N2	−0.028(1)	−0.1464(3)	−0.1888(7)	5.8(2)	O6	−0.311(1)	0.3290(7)	0.434(1)	22.9(5)
N3	−0.008(1)	−0.0657(3)	−0.1206(5)	3.1(1)	N1	0.2007(4)	0.0435(3)	0.0756(4)	3.8(1)
C1	0.276(1)	0.0655(4)	−0.0447(6)	3.2(2)	N2	0.0321(4)	0.0800(4)	−0.1491(4)	4.2(1)
C2	0.428(1)	0.0791(4)	−0.0190(8)	4.2(2)	N3	0.0502(5)	0.4824(4)	1.1791(4)	4.9(1)
C3	0.502(2)	0.1266(5)	−0.0459(9)	5.9(3)	N4	−0.1972(5)	0.3361(4)	0.9187(4)	4.3(1)
C4	0.413(1)	0.1647(4)	−0.0978(9)	5.8(3)	C1	0.1297(5)	0.1937(4)	0.2832(5)	3.8(1)
C5	0.261(1)	0.1543(4)	−0.1264(8)	4.7(3)	C2	0.1060(6)	0.2590(5)	0.3932(6)	4.8(2)
C6	0.185(1)	0.1051(4)	−0.0995(7)	3.4(2)	C3	0.2061(7)	0.3126(6)	0.5351(6)	6.1(2)
C7	0.032(1)	0.0919(3)	−0.1372(6)	3.6(2)	C4	0.3296(7)	0.3013(6)	0.5676(7)	6.6(2)
C8	−0.194(1)	0.0362(4)	−0.1732(8)	4.0(2)	C5	0.3555(6)	0.2404(6)	0.4604(6)	5.8(2)
C9	−0.142(1)	−0.0066(4)	−0.2500(7)	4.2(2)	C6	0.2557(5)	0.1820(5)	0.3160(6)	4.4(2)
C10	−0.088(1)	−0.0598(4)	−0.2095(7)	4.0(2)	C7	0.2877(5)	0.1199(5)	0.2074(6)	4.7(2)
C11	−0.098(2)	−0.1100(5)	−0.2502(9)	6.1(3)	C8	0.2512(5)	0.0011(5)	−0.0274(6)	4.8(2)
C12	0.024(1)	−0.1183(4)	−0.1112(7)	4.0(2)	C9	0.2595(6)	0.0758(6)	−0.1021(6)	5.7(2)
C13	0.134(3)	−0.250	−0.353(2)	10.3(8)	C10	0.1304(6)	0.0865(5)	−0.1858(5)	4.4(1)
					C11	0.1225(7)	0.1107(6)	−0.2986(6)	6.2(2)
					C12	0.0105(8)	0.1277(5)	−0.3720(6)	6.5(2)
					C13	−0.0884(7)	0.1215(5)	−0.3338(6)	5.9(2)
					C14	−0.0764(6)	0.0991(5)	−0.2219(6)	5.1(2)
					C15	0.2152(6)	0.4160(4)	1.0336(7)	5.2(2)
					C16	0.3072(7)	0.3962(6)	0.9847(8)	6.9(2)
					C17	0.4263(8)	0.3948(7)	1.069(1)	9.6(3)
					C18	0.4522(8)	0.4085(6)	1.204(1)	9.8(3)
					C19	0.3656(8)	0.4291(6)	1.2563(9)	8.1(3)
					C20	0.2453(6)	0.4364(5)	1.1739(7)	5.6(2)
					C21	0.1556(7)	0.4562(5)	1.2322(6)	5.9(2)
					C22	−0.0423(7)	0.4818(6)	1.2380(6)	6.2(2)
					C23	−0.1529(8)	0.3600(6)	1.1607(7)	7.1(2)
					C24	−0.2410(5)	0.3030(5)	0.9989(6)	4.5(1)
					C25	−0.3621(6)	0.2104(5)	0.9409(6)	5.4(2)
					C26	−0.4386(7)	0.1464(6)	0.7944(7)	6.3(2)
					C27	−0.3928(7)	0.1791(6)	0.7108(6)	5.7(2)
					C28	−0.2744(6)	0.2744(5)	0.7758(6)	4.7(2)

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

$g\,cm^{-3}$, $Z=2$, $\mu(Mo\,K\alpha)=6.08\ cm^{-1}$. Specimen: dark brown crystal $0.52\times0.49\times0.20$ mm. A total of 4257 reflections were measured in the range $2\leq2\theta\leq48°$; 2880 reflections with $I\geq3\sigma(I)$ were assumed as observed. $R=0.058$, $R_w=0.067$.

The structures were solved by the direct methods and refined by the full-matrix least-squares method. 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 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.[24] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, the bond distances and angles, and the F_o-F_c tables were deposited as Document No. 69038 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

In the recent reports, we described the synthesis and characterization of related manganese complexes with dinucleating ligands containing imidazole-nitrogen or pyridine-nitrogen, 2,6-bis{*N*-[2-(4-imidazolyl)ethyl]iminomethyl}-4-methylphenol (HL^3)[6] or 4-methyl-2,6-bis{*N*-[2-(2-pyridyl)-ethyl]iminomethyl}phenol (HL^4).[1a,1b,1c] In these cases, we obtained mononuclear, dinuclear, or tetranuclear manganese complexes. On the other hand, in the case of the present Schiff-base ligands, mononuclear species **1** and **2** could be isolated in methanol or ethanol by using a template reaction. In both cases we could get crystals suitable for a single-crystal X-ray diffraction study.

The X-ray crystal structures of **1** and **2** have been determined. Perspective drawings of the molecular structures of **1** and **2** are given in Figs. 1 and 2, respectively. The crystal structure of **1** consists of mononuclear manganese complex cations $[ML^1{}_2]^+$, perchlorate ions, and methanol molecules. The manganese atom occupies a crystallographic inversion center, adopting an elongated octahedral geometry with two phenolic oxygen atoms, two imine nitrogen atoms, and two imidazolyl nitrogen atoms of the two Schiff-base ligands, L^1, each of which acts as a facial tridentate chelate forming a fused 6-6 membered chelate ring. The atoms O1, $O1^i$, N1, and $N1^i$ form a square plane. The bond distances in the square plane [Mn–O1 1.874(5) Å, Mn–N1 2.014(7) Å] fall in the range of the corresponding bonds in manganese(III) complexes with Schiff-base ligands.[2–5] The axial bonds with imidazolyl nitrogens [Mn–N3 2.291(6) Å] are considerably longer than the in-plane bond distances. This tetragonal elongation may be a consequence of the Jahn-Teller effect expected for a high-spin d^4 ion. The occupation of the imidazolyl nitrogens for the axial positions means that it has poor affinity for Mn(III) compared with those of the phenolic oxygen and imine nitrogen. Very recently Pecoraro et al. have reported on manganese complexes of the nitro-substituted derivative of HL^1, 2-{*N*-[2-(5-nitro-4-imidazolyl)ethyl]iminomethyl}phenol (HL^5).[9] They have isolated manganese(II) species probably due to the electron-withdrawing properties

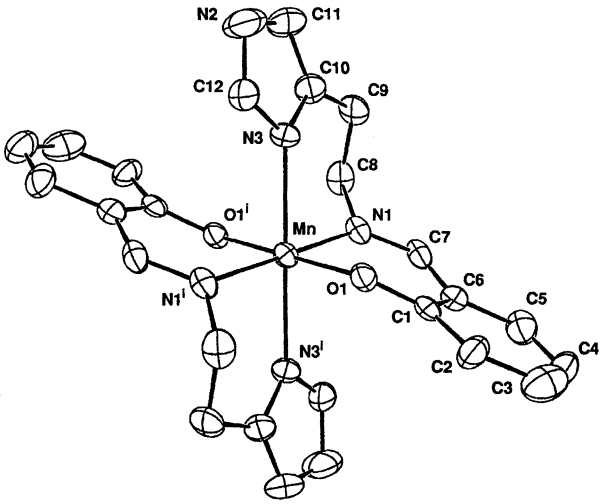


Fig. 1. A perspective view of the structure of $[MnL^1{}_2]ClO_4\cdot CH_3OH$ (**1**), showing the atom-labeling scheme. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn–O1 1.874(5), Mn–N1 2.014(7), Mn–N3 2.291(6), O1–Mn–$O1^i$ 180.0, O1–Mn–N1 87.8(3), O1–Mn–$N1^i$ 92.2(3), O1–Mn–N3 94.2(3), O1–Mn–$N3^i$ 85.8(3), N1–Mn–$N1^i$ 180.0. N1–Mn–N3 84.0(3), N1–Mn–$N3^i$ 96.0(3), N3–Mn–$N3^i$ 180.0. Superscript (i) refers to the equivalent position $(-x, -y, -z)$.

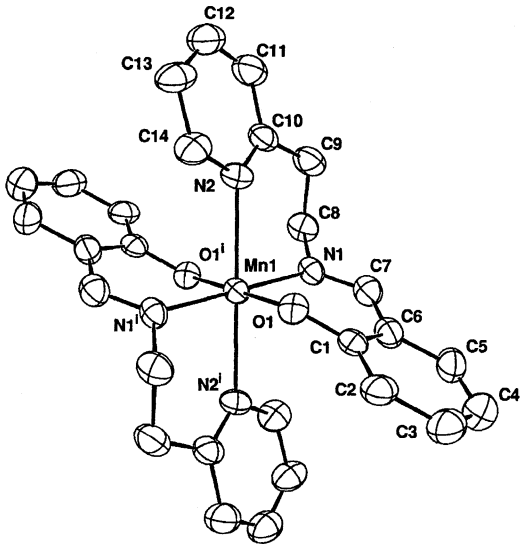


Fig. 2. A perspective view of the structure of $[MnL^2{}_2]ClO_4$ (**2**), showing the atom-labeling scheme. Selected bond distances (l/Å) and angles (ϕ/°) are: Mn1–Ol 1.878(3), Mnl–N1 2.012(4), Mn1–N2 2.376(6), Mn2–O2 1.866(5), Mn2–N3 2.020(5), Mn2–N4 2.378(4); O1–Mn1–$O1^i$ 180.0, O1–Mn1–Nl 89.1(2), O1–Mn1–$N1^i$ 90.9(2), O1–Mn1–N2 94.3(2), O1–Mn1–$N2^i$ 85.7(2), N1–Mn1–Nl^i 180.0, N1–Mn1–N2 81.7(2), N1–Mn1–$N2^i$ 98.3(2), N2–Mn1–$N2^i$ 180.0, O2–Mn2–$O2^{ii}$ 180.0, O2–Mn2–N3 88.7(2), O2–Mn2–$N3^{ii}$ 91.4(2), O2–Mn2–N4 95.4(2), O2–Mn2–$N4^{ii}$ 84.7(2), N3–Mn2–$N3^{ii}$ 180.0, N3–Mn2–N4 80.8(2), N3–Mn2–$N4^{ii}$ 99.2 (2), N4–Mn2–$N4^{ii}$ 180.0 Superscripts (i) and (ii) refer to the equivalent positions $(-x, -y, -z)$ and $(x, 1-y, 2-z)$, respectively.

of the nitro group, which tends to stabilize a lower oxidation state. In their mononuclear Mn(II) compound, $MnL^5{}_2$, which has a distorted octahedral geometry around the metal atom, the Mn–N (imidazolyl) distances [2.199(4), 2.222(5) Å] are significantly shorter than those of the Mn–N (imine) bonds [2.291(4), 2.312(4) Å] contrary to our case. This results suggests that imidazole nitrogen prefers Mn(II) to Mn(III).

The crystal structure of **2** contains two crystallographically independent mononuclear manganese complex cations $[MnL_2{}^2]^+$ and one perchlorate ion. The structures of the two $[MnL_2{}^2]^+$ cations are essentially the same and centrosymmetric about the manganese atom (Fig. 2). The manganese atom is coordinated to the two L^2 ligands in an elongated octahedral arrangement with phenolate oxygen, imine nitrogen, and pyridyl nitrogen of each ligand facially oriented. The axial positions are occupied by the pyridyl nitrogen atoms. The axial Mn–N bonds [Mn1–N2 2.376(6), Mn2–N4 2.378(4) Å] are considerably longer than the in-plane distances [Mn1-O1 1.878(3), Mn1–N1 2.012(4), Mn2–O2 1.866(5), Mn2–N3 2.020(5) Å]. It is noteworthy that the Mn–N (pyridyl) distances are significantly longer than the Mn–N (imidazolyl) distances [2.291(6) Å] in **1**.

The magnetic moments of **1** and **2** are 4.96 and 4.83 B.M. at room temperature, respectively, which are close to the spin-only value (4.99 B.M.) for a high-spin d^4 system. The temperature dependence of the magnetic susceptibilities of **1** and **2** were measured in the temperature range 80—300 K (Fig. 3). The magnetic data of **1** and **2** obey the Curie–Weiss law, $\chi_A = C/(T-\theta)$, with $\theta = 5.2$ and 3.9 K, respectively, in harmony with the monomeric nature of these complexes.

The complexes **1** and **2** are soluble in acetonitrile. Thus conductivity measurements were performed for both complexes. The conductivity data show that complexes **1** and **2** are 1 : 1 electrolytes in these solutions, in agreement with the formulations as $[MnL^1{}_2]ClO_4$ or $[MnL^2{}_2]ClO_4$.

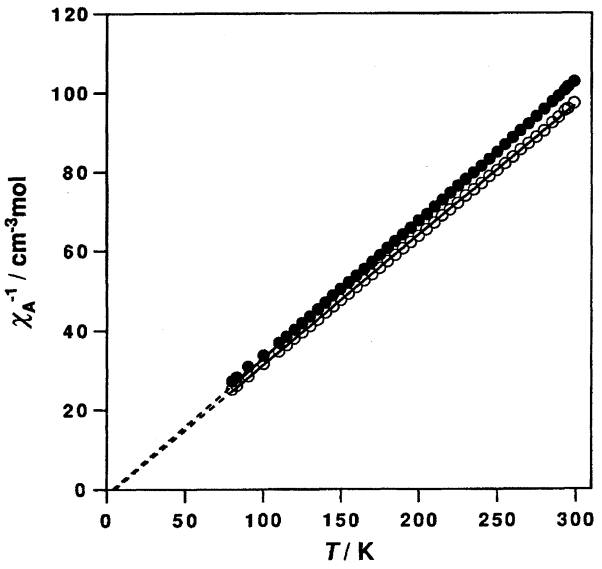


Fig. 3. Plots of magnetic susceptibilities of $[MnL^1{}_2]$-$ClO_4 \cdot CH_3OH$ (**1**) (○) and $[MnL^2{}_2]ClO_4$ (**2**) (●).

Electronic spectra of **1** and **2** in acetonitrile are shown in Fig. 4. The spectra are characterized by three or four intense absorptions in the range 250—450 nm, which are charge-transfer transitions in origin, and a broad absorption with some shoulder peaks in the visible region, which can be associated with d–d transitions, judging from the intensities of the solution specra. The spectral features are consistent with the elongated octahedral manganese(III) ion.[25]

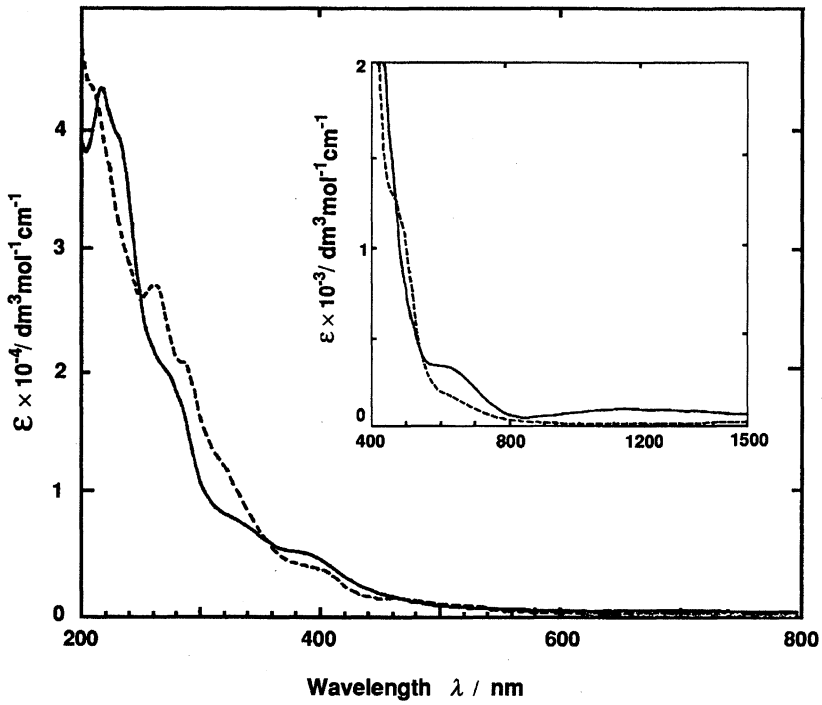


Fig. 4. Electronic spectra of $[MnL^1{}_2]ClO_4 \cdot CH_3OH$ (**1**) (—) and $[MnL^2{}_2]\ ClO_4$ (**2**) (- - -) in acetonitrile.

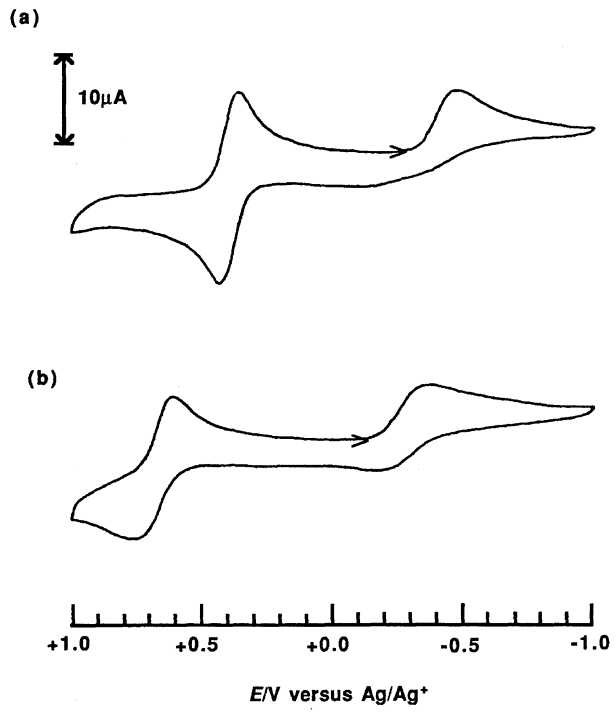


Fig. 5. Cyclic voltammograms of (a) $[MnL^1{}_2]ClO_4 \cdot CH_3OH$ (**1**) and (b) $[MnL^2{}_2]ClO_4$ (**2**).

The electronic spectra in the solid state are similar to those in acetonitrile, suggesting that the solid-state strucutres are maintained in the solutions.

The cyclic voltammograms of **1** and **2** were measured in acetonitrile solutions. The voltammograms are shown in Fig. 5. In the 1.0 to −1.0 V versus Ag/Ag^+ region, two reduction waves are observed. The first of these reduction processes has the characteristic of an electrochemically quasi-reversible couple (E_{pc}=+0.36, E_{pa}=+0.43, $E_{1/2}$=+0.39 V vs. Ag/Ag^+ for **1**; E_{pc}=+0.61, E_{pa}=+0.76, $E_{1/2}$=+0.69 V vs. Ag/Ag^+ for **2**), but the second reduction process appears partially irreversible (E_{pc} = −0.49 V for **1**, E_{pc} = −0.38 V for **2**). The former may be assigned to the Mn(IV)/Mn(III) couple and the latter may be due to the Mn(III)/Mn(II) couple. It is noteworthy that all these reduction processes show a significant cathodic shift upon replacing pyridyl nitrogen by imidazolyl nitrogen. This means that pyridyl nitrogen favors Mn(II) state more strongly than imidazolyl nitrogen. It is known that imidazole is a good σ-donor for Cu(II) and as a π-acceptor, it is also capable of stabilizing Cu(I).[26,27] Therefore the same things may hold for Mn(III) and Mn(II), although imidazole nitrogen seems to favor Mn(II) rather than Mn(III) in the crystal structure.

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