Synthesis and Characterization of a Series of Mononuclear Manganese(IV) Complexes with *o*-(Salicylideneaminomethyl)phenol and Its Substituted Derivatives

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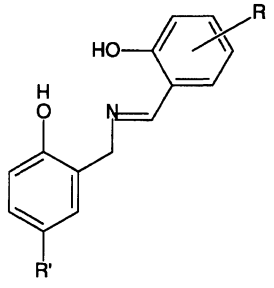
A series of manganese(IV) complexes, $[Mn(R, R'\text{-}L)_2]\cdot nS$ (R or R′=H, Cl, Br, CH_3O; $n=1/2$, 1, 3/2, 2; S=H_2O, THF (THF=tetrahydrofuran)) where H_2(R, R′-L) denotes *o*-(salicylideneaminomethyl)phenol with the substituent R on the salicylideneamino ring and the R′ on the aminomethylphenol ring, have been prepared and characterized by infrared and electronic spectra, magnetic moments, cyclic voltammetry, and spectroelectrochemical experiment. The molecular structure of $[Mn(5\text{-}Cl'\text{-}L)_2]\cdot 2THF$ has been determined by X-ray crystallography. The ligands act as meridional tridentate ONO donors and the complex has an MnO_4N_2 coordination sphere. The spectral, magnetic, and electrochemical properties are discussed in relation to the molecular structure.

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. Higher valent manganese complexes have attracted considerable attention, since Mn(IV) and Mn(III) are thought to play important roles in the oxygen evolution center (OEC) of the photosystem II of green plants.[1—9] Biological studies show that the manganese ions in the OEC are bound to O and/or N donor atoms from the amino-acid residues. Therefore, Mn(IV) complexes with organic ligands containing O and/or N donor atoms are of much interest as possible models for the manganese center in the OEC. However, relatively few Mn(IV) complexes with such organic ligands have been isolated and structurally characterized.[10—17] This may be due to the fact that few ligands are known to be able to bind a high-valent ion without being oxidized by it. In fact, the Mn(IV) complexes tend to be stabilized by strong donor ligands, such as O-donor ligands and a great bulk of Mn(IV) chemistry involves compounds having O-donor ligands.[18] Of the O-donor ligands, it has been recognized that phenolic oxygen is a potential donor group which can stabilize high oxidation states.[10,19] Some dichloromanganese(IV) complexes with Schiff-bases containing phenolic oxygen have been described by Matsushita et al.[20—23] Ōkawa et al. have reported that manganese(IV) complexes formed by the oxidation of manganese(II) complexes of 2-(salicylideneamino)phenol with tetrachloro-*o*-benzoquinone.[24] They have also developed a tridentate chelating ligand having phenolic oxygens and deprotonated amide nitrogen to obtain stable Mn(IV) and Mn(V) complexes.[19] However, no direct proof of the molecular structures has been given for these Mn(IV) complexes until very recently.[16] One ligand which we have found to have great utility is *o*-(salicylideneaminomethyl)phenol, which contains two phenolic oxygen donor atoms.[17] The manganes(IV) complex with this Schiff-base ligand was first recognized by Yamaguchi, who isolated a dark-purple species and commented on its solubility for organic solvents, although the complex has not yet been characterized.[25] By using this Schiff-base and its substituted derivatives, we have synthesized a series of manganese(IV) complexes and have determined the X-ray crystal sturucture of one of the complexes. We herein report on the synthesis, structure, and electrochemical, spectral, and magnetic properties of this series of manganese(IV) complexes.

Experimental

Ligand Synthesis. *o*-Hydroxybenzylamine was prepared by a published procedure.[26] Substituted *o*-hydroxybenzylamines were synthesized according to a method of Yamaguchi.[27] The Schiff-base ligands used in this study were prepared by condensation of *o*-hydroxybenzylamine and salicylaldehyde or a substituted salicylaldehyde.[25] The ligands are abbreviated as H_2(R, R′-L), in which R and R′ are the substituents on salicylaldehyde and *o*-hydroxybenzylamine, respectively, as shown in Fig. 1. The following abbreviations are used throughout the text: H_2L=*o*-(salicylideneaminomethyl)phenol,



H_2(R,R'-L)

Fig. 1. Schiff base ligands used in this study. H_2L: R=R′=H; H_2(3,5-Cl-L): R=3, 5-Cl, R′=H; H_2(3,5-Br-L): R=3, 5-Br, R′=H; H_2(3-MeO-L): R=3-MeO, R′=H; H_2(4,6-MeO-L): R=4,6-MeO, R′=H; H_2(5-Cl-L): R=5-Cl, R′=H; H_2(5-Br-L): R=5-Br, R′=H; H_2(5-Cl′-L): R=H, R′=5-Cl; H_2(5-Br′-L): R=H, R′=5-Br.

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Table 1. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Mn	0.74994(5)	0.24997(3)	0.80283(6)	3.19(1)
Cl1	1.1343(1)	0.19966(7)	1.5852(1)	7.29(3)
Cl2	0.3656(1)	0.30030(8)	1.2511(1)	7.32(3)
O1	0.8342(2)	0.3149(1)	1.0332(3)	3.73(6)
O2	0.6696(2)	0.1822(1)	0.5736(3)	4.00(6)
O3	0.6658(2)	0.1850(1)	0.8840(3)	3.70(5)
O4	0.8303(2)	0.3177(1)	0.7216(3)	4.00(6)
O5	1.1139(4)	0.0562(2)	0.9108(8)	14.4(2)
O6	0.3858(4)	0.4437(2)	0.7406(8)	14.5(2)
N1	0.8809(2)	0.1916(2)	0.8280(3)	3.39(7)
N2	0.6190(2)	0.3083(2)	0.7555(3)	3.40(6)
C1	0.9020(3)	0.2882(2)	1.1605(4)	3.48(8)
C2	0.8878(3)	0.2999(2)	1.3188(4)	4.12(9)
C3	0.9595(3)	0.2727(2)	1.4482(5)	4.6(1)
C4	1.0451(3)	0.2348(2)	1.4213(5)	4.5(1)
C5	1.0624(3)	0.2228(2)	1.2670(5)	4.18(9)
C6	0.9903(3)	0.2496(2)	1.1363(4)	3.51(8)
C7	0.9984(3)	0.2342(2)	0.9614(4)	4.03(9)
C8	0.8693(3)	0.1211(2)	0.7420(4)	4.05(9)
C9	0.7614(3)	0.0743(2)	0.6048(4)	4.10(9)
C10	0.7551(4)	−0.0054(2)	0.5405(5)	5.5(1)
C11	0.6550(4)	−0.0515(2)	0.4053(6)	6.0(1)
C12	0.5610(4)	−0.0190(2)	0.3299(5)	5.7(1)
C13	0.5648(4)	0.0588(2)	0.3867(5)	4.7(1)
C14	0.6660(3)	0.1072(2)	0.5265(4)	3.75(8)
C15	0.5980(3)	0.2115(2)	0.9699(4)	3.44(8)
C16	0.6119(3)	0.2002(2)	1.1310(4)	4.11(9)
C17	0.5401(3)	0.2270(2)	1.2152(4)	4.58(9)
C18	0.4545(3)	0.2650(2)	1.1414(5)	4.60(9)
C19	0.4379(3)	0.2771(2)	0.9818(5)	4.21(9)
C20	0.5095(3)	0.2504(2)	0.8966(4)	3.54(8)
C21	0.5013(3)	0.2655(2)	0.7284(4)	4.03(9)
C22	0.6307(3)	0.3788(2)	0.7514(4)	4.09(9)
C23	0.7384(3)	0.4255(2)	0.7689(4)	4.09(9)
C24	0.7449(4)	0.5054(2)	0.7915(6)	5.5(1)
C25	0.8451(4)	0.5514(2)	0.8017(6)	5.9(1)
C26	0.9390(4)	0.5190(2)	0.7879(5)	5.7(1)
C27	0.9352(3)	0.4411(2)	0.7631(5)	4.7(1)
C28	0.8339(3)	0.3929(2)	0.7532(4)	3.77(8)
C29	1.2297(7)	0.0782(4)	0.990(1)	16.1(4)
C30	1.2800(6)	0.0082(4)	0.9941(9)	11.1(2)
C31	1.1892(6)	−0.0516(4)	0.858(1)	11.9(3)
C32	1.0860(7)	−0.0194(5)	0.824(1)	17.3(4)
C33	0.4140(6)	0.5197(4)	0.756(1)	17.2(4)
C34	0.3112(5)	0.5519(4)	0.720(1)	11.9(3)
C35	0.2204(5)	0.4917(4)	0.7068(9)	11.2(2)
C36	0.2705(7)	0.4219(4)	0.683(1)	16.4(4)

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

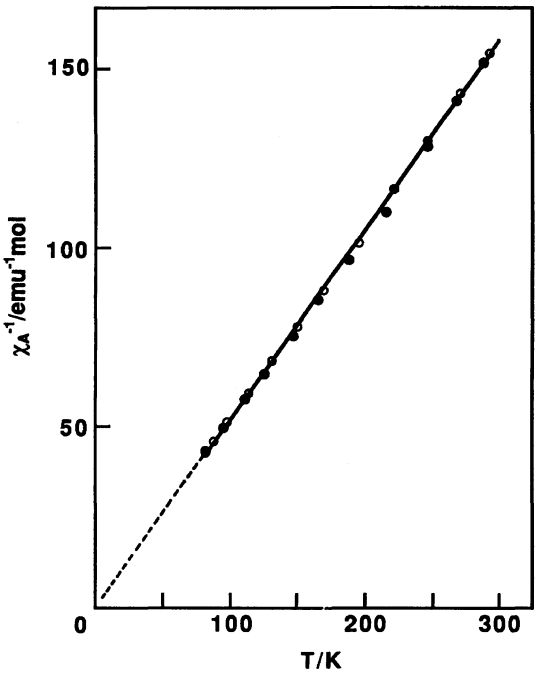

Fig. 2. Temperature dependence of the magnetic susceptibities of [Mn(5-Cl′-L)$_2$]·2THF (**8**) (○) and [Mn(5-Br′-L)$_2$]·2THF (**9**) (●).

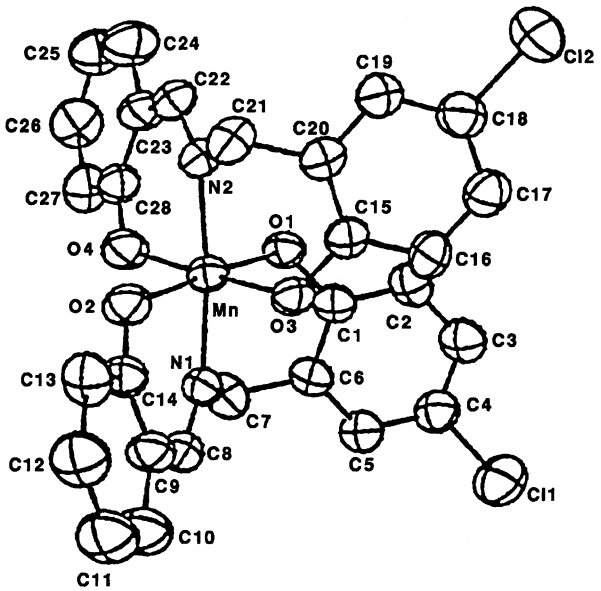

Fig. 3. ORTEP view of the structure of [Mn(5-Cl′-L)$_2$]·2THF (**8**).

H_2(3,5-Cl-L)=*o*-(3,5-dichlorosalicylideneaminomethyl)phenol, H_2(3,5-Br-L)=*o*-(3,5-dibromosalicylideneaminomethyl)phenol, H_2(3-MeO-L)=*o*-(3-methoxysalicylideneaminomethyl)phenol, H_2(4,6-MeO-L)=*o*-(4,6-dimethoxysalicylideneaminomethyl)phenol, H_2(5-Cl-L)=*o*-(5-chlorosalicylideneaminomethyl)phenol, H_2(5-Br-L)=*o*-(5-bromosalicylideneaminomethyl)phenol, H_2(5-Cl′-L)=*o*-(salicylideneaminomethyl)-5-chlorophenol, H_2(5-Br′-L)=*o*-(salicylideneaminomethyl)-5-bromophenol.

Preparation of Complexes. **[Mn(L)$_2$]·3/2H$_2$O (1).** After manganese(II) acetate tetrahydrate (49 mg, 0.20 mmol) and H_2L (91 mg, 0.40 mmol) were dissolved in methanol, the mixture was refluxed for 30 min and filtered. The filtrate was allowed to stand for several days to give black crystals. They were collected by filtration, washed

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

Mn–O1	1.891(2)	Mn–O2	1.897(2)
Mn–O3	1.891(3)	Mn–O4	1.897(3)
Mn–N1	1.996(3)	Mn–N2	1.996(3)
O1–C1	1.349(4)	C1–C6	1.401(5)
C6–C7	1.498(5)	N1–C7	1.476(3)
N1–C8	1.286(4)	C8–C9	1.436(4)
C9–C14	1.403(5)	O2–C14	1.321(4)
O3–C15	1.346(5)	C15–C20	1.405(5)
C20–C21	1.501(6)	N2–C21	1.479(5)
N2–C22	1.285(5)	C22–C23	1.433(5)
C23–C28	1.401(6)	O4–C28	1.325(4)
O1–Mn–O2	177.8(1)	O1–Mn–O3	90.2(1)
O1–Mn–O4	89.5(1)	O1–Mn–N1	90.1(1)
O1–Mn–N2	93.8(1)	O2–Mn–O3	89.4(1)
O2–Mn–O4	91.0(1)	O2–Mn–N1	87.7(1)
O2–Mn–N2	88.4(1)	O3–Mn–O4	177.9(1)
O3–Mn–N1	93.8(1)	O3–Mn–N2	90.1(1)
O4–Mn–N1	88.4(1)	O4–Mn–N2	87.8(1)
N1–Mn–N2	174.5(1)	Mn–O1–C1	121.8(2)
O1–C1–C6	119.8(3)	C1–C6–C7	117.5(3)
N1–C7–C6	108.2(3)	Mn–N1–C7	115.5(2)
Mn–N1–C8	125.3(2)	N1–C8–C9	124.7(3)
C8–C9–C14	121.3(3)	O2–C14–C9	122.5(2)
Mn–O2–C14	125.4(2)	Mn–O3–C15	121.8(2)
O3–C15–C20	120.1(3)	C15–C20–C21	117.1(3)
N2–C21–C20	107.9(2)	Mn–N2–C21	115.4(2)
Mn–N2–C22	125.2(2)	N2–C22–C23	124.8(4)
C22–C23–C28	121.5(3)	O4–C28–C23	122.4(3)
Mn–O4–C28	125.4(3)		

with methanol, and dried in vacuo over P_2O_5. Yield: 34 mg (32%). Anal. Calcd for $C_{28}H_{25}MnN_2O_{5.5}$: C, 63.16; H, 4.73; N, 5.26%. Found: C, 63.26; H, 4.64; N, 5.19%. IR (KBr, cm^{-1}) ν (C=N) 1618. μ_{eff} (298 K, B.M.) 3.82. Λ_M (acetonitrile, S mol^{-1} cm^2) 4.

[Mn(3,5-Cl-L)$_2$]·1/2H$_2$O (2). This complex was prepared in the same way as that for **1** except for using H_2(3,5-Cl-L) instead of H_2L. Yield: 31%. Anal. Calcd for $C_{28}H_{19}Cl_4MnN_2O_{4.5}$: C, 51.56; H, 2.94; N, 4.30%. Found: C, 51.64; H, 3.08; N, 4.07%. IR (KBr, cm^{-1}) ν (C=N) 1617. μ_{eff} (293 K, B.M.) 3.94. Λ_M (acetonitrile, S mol^{-1} cm^2) 5.

[Mn(3,5-Br-L)$_2$]·1/2H$_2$O (3). This complex was prepared in the same way as that for **1** except for using H_2(3,5-Br-L) instead of H_2L. Yield: 28%. Anal. Calcd for $C_{28}H_{19}Br_4MnN_2O_{4.5}$: C, 40.52; H, 2.31; N, 3.38%. Found: C, 40.84; H, 2.32; N, 3.20%. IR (KBr, cm^{-1}) ν (C=N) 1612. μ_{eff} (290 K, B.M.) 3.94. Λ_M (acetonitrile, S mol^{-1} cm^2) 4.

[Mn(3-MeO-L)$_2$]·1/2H$_2$O (4). This complex was prepared in the same way as that for **1**, except for using H_2(3-MeO-L) instead of H_2L. Yield: 29%. Anal. Calcd for $C_{30}H_{27}MnN_2O_{6.5}$: C, 62.72; H, 4.74; N, 4.88%. Found: C, 62.87; H, 4.73; N, 4.87%. IR (KBr, cm^{-1}) ν (C=N) 1614. μ_{eff} (291 K, B.M.) 3.97. Λ_M (acetonitrile, S mol^{-1} cm^2) 3.

[Mn(4,6-MeO-L)$_2$]·H$_2$O (5). After manganese(II) acetate tetrahydrate (24 mg, 0.10 mmol) and H_2(4,6-MeO-L) (58 mg, 0.20 mmol) were dissolved in ethanol, the mixture was refluxed for 30 min and filtered. The filtrate was allowed to stand for several days to give a black precipitate. This was collected by filtration, washed with ethanol, and dried in vacuo over P_2O_5. Yield: 31 mg (43%). Anal. Calcd for $C_{32}H_{32}MnN_2O_9$: C, 59.72; H, 5.01; N, 4.35%. Found: C, 59.93; H, 5.22; N, 4.16%. IR (KBr, cm^{-1}) ν (C=N) 1589. μ_{eff} (292 K, B.M.) 4.02. Λ_M (acetonitrile, S mol^{-1} cm^2) 3.

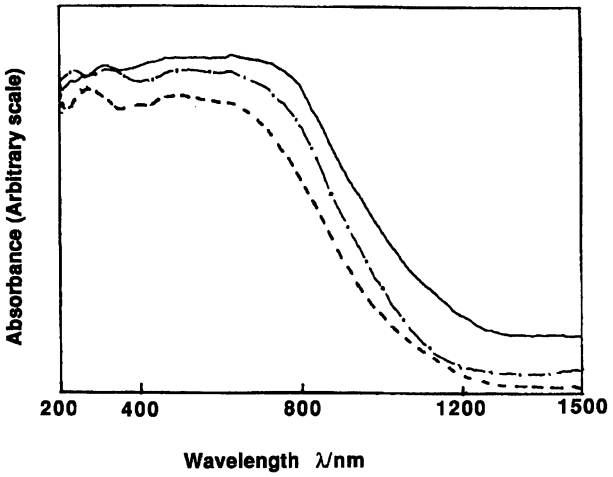

Fig. 4. Diffuse reflectance spectra of [Mn(L)$_2$]·3/2H$_2$O (**1**). (—), [Mn(4-6-MeO-L)$_2$]·H$_2$O (**5**) (- - -), and [Mn(5-Cl′-L)$_2$]·2THF (**8**) (–·–).

[Mn(5-Cl-L)$_2$]·THF (6). After manganese(II) acetate tetrahydrate (24 mg, 0.10 mmol) and H_2(5-Cl-L) (52 mg, 0.20 mmol) were dissolved in tetrahydrofuran, the mixture was refluxed for 30 min and filtered. Cyclohexane was layered onto the filtrate and the mixture was placed in a refrigerator overnight. The dark-purple precipitate that deposited was collected by filtration and dried in vacuo over P_2O_5. Yield: 20 mg (31%). Anal. Calcd for $C_{32}H_{28}Cl_2MnN_2O_5$: C, 59.46; H, 4.37; N, 4.33%. Found: C, 59.15; H, 4.20; N, 4.33%. IR (KBr, cm^{-1}) ν (C=N) 1619. μ_{eff} (290 K, B.M.) 4.10. Λ_M (acetonitrile, S mol^{-1} cm^2) 5.

[Mn(5-Br-L)$_2$]·THF (7). This complex was prepared in the same way as that for **6**, except for using H_2(5-Br-L) instead of H_2(5-Cl-L). Yield: 30%. Anal. Calcd for $C_{32}H_{28}Br_2MnN_2O_5$: C, 52.27; H, 3.84; N, 3.81%. Found: C, 52.39; H, 3.74; N, 3.82%. IR (KBr, cm^{-1}) ν (C=N) 1619. μ_{eff} (299 K, B.M.) 3.85. Λ_M (acetonitrile, S mol^{-1} cm^2) 5.

[Mn(5-Cl′-L)$_2$]·2THF (8). 2-Hydroxy-5-chlorobenzylamine (95 mg, 0.60 mmol) and salicylaldehyde (73 mg, 0.60 mmol) were dissolved in 3 ml of THF. Manganese(II) acetate tetrahydrate (147 mg, 0.60 mmol) was then added. The mixture was refluxed for 0.5 h and filtered; slow evaporation gave black crystals. They were collected by filtration, washed with THF, and dried in vacuo over P_2O_5. Yield: 58 mg (27%). Anal. Calcd for $C_{36}H_{36}Cl_2MnN_2O_6$: C, 60.18; H, 5.05; N, 3.90%. Found: C, 60.33; H, 5.05; N, 3.83%. IR (KBr, cm^{-1}) ν (C=N) 1616. μ_{eff} (293 K, B.M.) 3.89. Λ_M (acetonitrile, S mol^{-1} cm^2) 5.

[Mn(5-Br′-L)$_2$]·2THF (9). This complex was prepared in the same way as that for **8**, except for using 2-hydroxy-5-bromobenzylamine instead of 2-hydroxy-5-chlorobenzylamine. Yield: 31%. Anal. Calcd for $C_{36}H_{36}Br_2MnN_2O_6$: C, 53.55; H, 4.49; N, 3.47%. Found: C, 53.88; H, 4.65; N, 3.33%. IR (KBr, cm^{-1}) ν (C=N) 1617.

Table 3. Electronic Spectral Data

Complex	Reflectance λ_{max}/nm		Acetonitrile solution λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})				
1	307	470—650(br)	313(20840)	410sh(6670)	490(7290)	600sh(4950)	
2	308	555(br)	309(17280)	350sh(13290)	440sh(5860)	491(6640)	600sh(4890)
3	312	556(br)	311(16770)	350sh(13160)	430sh(5780)	491(6530)	600sh(4810)
4	300	500—700(br)	275(24230)	310(14830)	443(5650)	520(5370)	
5	272	479 616(sh)	300(35710)	370sh(7980)	480(8400)	600sh(5390)	
6	321	553 629	309(19620)	350sh(14030)	440sh(5940)	496(6970)	600sh(4960)
7	369	558 629	310(18990)	350sh(13230)	430sh(5620)	495(6820)	600sh(4850)
8	320	484 619	313(20720)	409sh(6090)	505(7340)	600sh(5490)	
9	319	481 623	313(18600)	410sh(5550)	507(6680)	600sh(4920)	

a) sh=shoulder, b) br=broad.

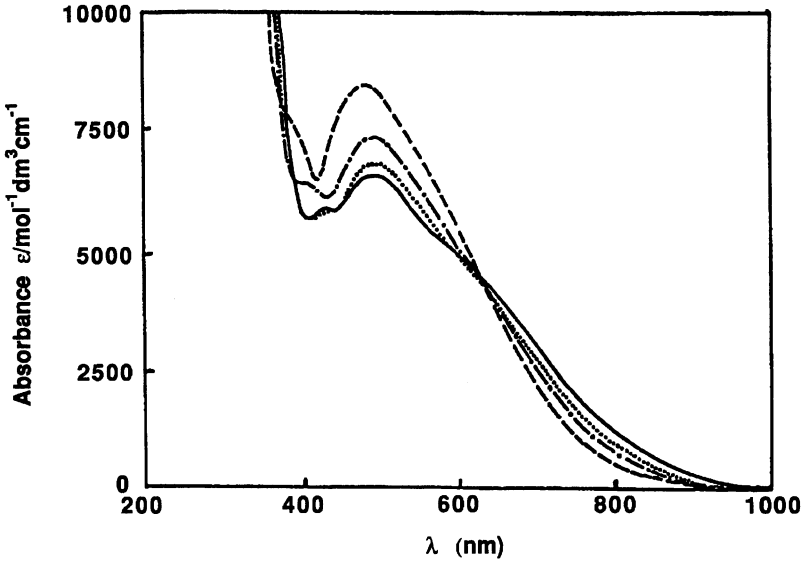

Fig. 5. Electronic spectra of [Mn(3,5-Br-L)$_2$]·1/2H$_2$O (**3**) (—), [Mn(5-Br-L)$_2$]·THF (**7**) (····), [Mn(L)$_2$]·3/2H$_2$O (**1**) (–·–), and [Mn(4,6-MeO-L)$_2$]·H$_2$O (**5**) (- - -).

μ_{eff} (288 K, B.M.) 3.90. Λ_M (acetonitrile, S mol^{-1} cm^2) 5.

Measurements. A Perkin–Elmer 2400 Series II CHNS/O Analyzer was used to collect microanalytical data (C, H, N). 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 in ca. 10^{-3} mol dm^{-3} acetonitrile solutions of the complexes. Electronic spectra were measured using a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. Magnetic susceptibilities were measured by the Faraday method over the temperature range 80—300 K. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[28] 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. Cyclic voltammetric measurements were carried out on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HB-104 function generator and a Yokogawa 3086 X–Y recorder. A three-electrode cell comprising a glassy carbon electrode, a platinum-wire counter electrode, and a nonaqueous Ag/Ag$^+$ electrode was used. Spectroelectrochemistry was performed in a cell constructed from a quartz cuvette with a quartz compartment separating the working and counter electrodes, which were Pt-mesh minigrids.[29] The potential of the cell was controlled by a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HB-104 function generator and a Hokuto Denko HF-201 digital coulometer.

X-Ray Crystal Structure Analysis. Single crystals of **8** grew from tetrahydrofuran. A plate with dimensions of 0.30×0.41×0.52 mm^3 was used for the X-ray work. The lattice constants and intensities were measured on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å) at 25±1°C. 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 collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption.

Crystal Data: $C_{36}H_{36}Cl_2MnN_2O_6$, F.W.=718.5, triclinic, space group $P\bar{1}$, a=12.271(4), b=18.196(5), c=8.568(2) Å, α=103.61(2), β=110.42(1), γ=96.13(2)°, V=1704.7(9) Å^3, D_c=1.40, D_m=1.42 g cm^{-3}, Z=2, μ (Mo $K\alpha$)=5.75 cm^{-1}.

Of the 5099 reflections ($2\theta\leq 46°$) measured, 3762 unique reflections with $I>3\sigma(I)$ were considered as observed. The structures were solved by direct methods. Refinements were carried out by full-matrix least-squares methods. All of

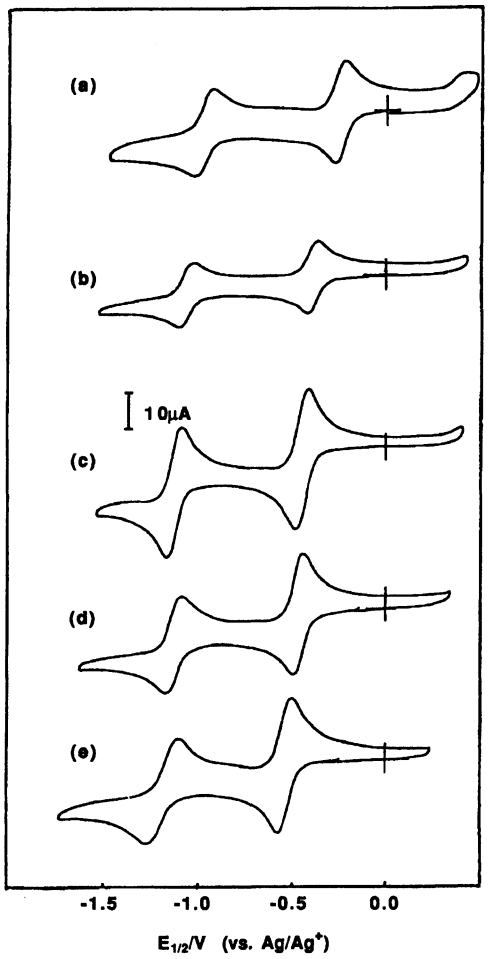

Fig. 6. Cyclic voltammograms of the complexes in CH_3CN. (a) $[Mn(3,5\text{-}Cl\text{-}L)_2]\cdot 1/2H_2O$ (**2**), (b) $[Mn(5\text{-}Cl\text{-}L)_2]\cdot THF$ (**6**), (c) $[Mn(L)_2]\cdot 3/2H_2O$ (**1**), (d) $[Mn(3\text{-}MeO\text{-}L)_2]\cdot 1/2H_2O$ (**4**), (e) $[Mn(4,6\text{-}MeO\text{-}L)_2]\cdot H_2O$ (**5**).

the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included at the calculated positions and fixed at their positions. The final discrepancy factors are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.041$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.040$. A 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 Micro-VAXII computer using the Enraf–Nonius SDP program package.[29] The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and temperature factors of hydrogen atoms, and the F_o–F_c tables are deposited as Document No. 66007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Using *o*-(salicylideneaminomethyl)phenol and its substituted derivatives has proved to be convenient to attain a manganese(IV) state. The synthesis of a series of manganese(IV) complexes, $[Mn(R, R'\text{-}L)_2]$, was readily effected by the reaction of manganese(II) salt with Schiff-base ligands in an organic solvent. These complexes can also be prepared by a template reaction of *o*-hydroxybenzylamine (or its substituted amine) and the appropriate salicylaldehyde in the presence of manganese ion. The complexes were deep-purple to black crystalline solids, which were soluble in common organic solvents such as methylene chloride, acetonitrile, and tetrahydrofuran. The electronic conductance measurements in acetonitrile confirm that the $[Mn(R, R'\text{-}L)_2]$ complexes are essentially non-electrolyte with molar conductances of 3—5 S mol^{-1} cm^2.[31] Further physicochemical data substantiate the formulation of the complexes as formally being Mn(IV) species.

Table 4. Cyclic Voltammetric Data [a]

Complex	Solvent	$E^1_{1/2}$ [b]	ΔE_p/mV [c]	$E^2_{1/2}$ [b]	ΔE_p/mV [c]
1	CH_3CN	−0.45	70	−1.14	90
	CH_2Cl_2	−0.43	135	−0.98	170
2	CH_3CN	−0.25	65	−0.97	105
	CH_2Cl_2	−0.25	110	−0.89	130
3	CH_3CN	−0.24	75	−0.95	95
	CH_2Cl_2	−0.25	120	−0.86	120
4	CH_3CN	−0.47	65	−1.14	115
	CH_2Cl_2	−0.44	130	−0.98	210
5	CH_3CN	−0.54	75	−1.19	165
	CH_2Cl_2	−0.58	110	−1.09	200
6	CH_3CN	−0.35	75	−1.00	200
	CH_2Cl_2	−0.32	135	−0.90	160
7	CH_3CN	−0.34	70	−1.04	270
	CH_2Cl_2	−0.32	100	−0.85	180
8	CH_3CN	−0.37	70	−1.05	80
	CH_2Cl_2	−0.37	110	−0.98	115
9	CH_3CN	−0.36	60	−1.04	80
	CH_2Cl_2	−0.36	120	−0.97	120

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

The effective magnetic moments of $[Mn(R, R'\text{-}L)_2]$ (**1**—**9**) fall in the range 3.82—4.10 B.M./Mn at room temperature. These values are close to the spin-only value (3.87 B.M.) for a d^3 system. The temperature dependence of the magnetic susceptibilities of **8** and **9** was measured on powdered samples in the temperature range 80—300 K; the results are given in Fig. 2. The magnetic data obeys the Curie law. Since there is no evidence for any intermolecular magnetic interaction, the magnetic data support the formulation of these complexes as Mn(IV) complexes. The X-band EPR spectrum of **8** is consistent with a d^3 system, showing a dominating signal at $g\approx 4.0$.[17]

In order to establish the molecular structure of $[Mn(R, R'\text{-}L)_2]$, the crystal structure of **8** was determined by X-ray crystallography. The crystal consists of discrete neutral complexes, $[Mn(5\text{-}Cl'\text{-}L)_2]$ and THF molecules. A perspective drawing of the complex is given in Fig. 3. Selected bond distances and angles are listed in Table 2. The manganese ion adopts a slightly distorted octahedral geometry with four phenolic-oxygen and two imine-

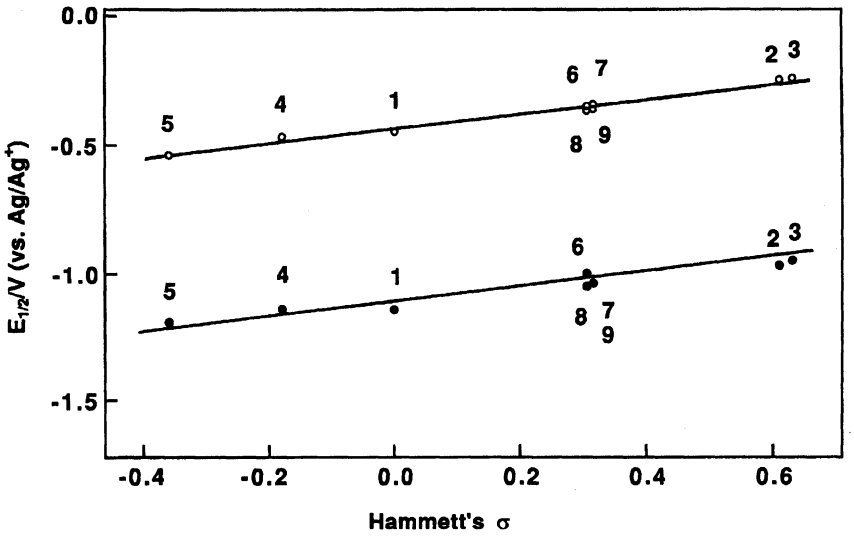

Fig. 7. Correlation between the redox potentials ($E^1_{1/2}$ (○) and $E^2_{1/2}$ (●)) and the Hammett σ value of the substituents for the complexes in CH_3CN.

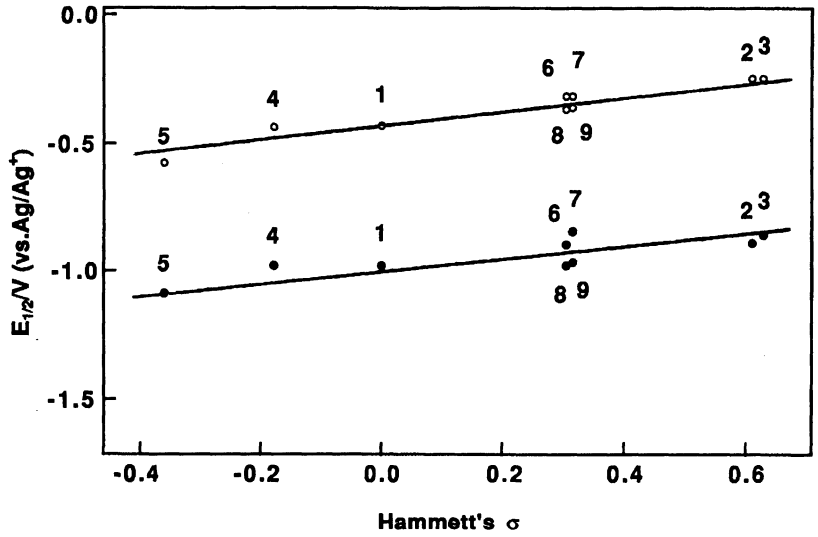

Fig. 8. Correlation between the redox potentials ($E^1_{1/2}$ (○) and $E^2_{1/2}$ (●)) and the Hammett σ value of the substituents for the complexes in CH_2Cl_2.

nitrogen atoms of the two ligands. Each ligand, 5-Cl′-L, acts as a meridional tridentate chelate forming two adjacent six-membered rings. The Mn–O (1.891(2)—1.897(3) Å) and Mn–N (1.996(3) Å) bond lengths fall in the range of the corresponding bonds in the manganese(IV) complexes which have appeared recently (Mn(IV)–O(phenolate)=1.823(5)—1.922(5) Å, Mn(IV)–N(imine)=1.968(8)—2.011(10) Å).[10—17] The angles at the metal center show small deviations (Table 2, 87.7(1)—93.8(1)° and 174.5(1)—177.9(1)°) from the ideal octahedral values of 90° and 180°, in contrast to the cases for the similar Schiff-base Mn(IV) complexes with adjacent five- and six-membered rings: Chakravorty et al. have reported the X-ray crystal structures of mononuclear manganese(IV) complexes of 2-(salicylideneamino)phenol (H_2amp) or 2,2′-dihydroxyazobenzene (H_2azp), Mn(amp)$_2$ and Mn(azp)$_2$ very recently.[15] In these complexes, the MnO_4N_2 coordination spheres are subject to considerable distortions due to the ligand rigidity of the five- and six-membered chelate rings. The corresponding angles are 80.0(3)—95.2(3)° and 168.7(4)—174.3(3)° for these complexes. The THF molecules are in the vicinity of the tridentate ligands as crystal solvents (with the closest contacts of O5(THF)···C8 3.321(6) Å, O6(THF)···C22 3.325(6) Å).

The solid state spectra are essentially featureless with strong absorbances in the visible region. The diffuse reflectance spectra of **1**, **5**, and **8** are shown in Fig. 4 as representative examples. The complexes show very broad bands in the 270—800 nm range (Table 3). In acetonitrile, the complexes display three or four distinct absorptions in the visible region (Table 3). Some exam-

ples are given in Fig. 5. The absorption bands at 400—520 nm can be assigned to a LMCT transition from the p_π orbital on the phenolate oxygen to the half-filled d^*_π orbitals on the manganese ion, judgilng from the energies and intensities.[32] The lowest-energy shoulder may include d–d transitions, since the Mn(IV) ion in the octahedral environment is expected to exhibit two absorption bands due to d–d transitions, $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$.[33] The large extinction coefficients for these transitions may be a consequence of the intense tail from the charge-transfer absorptions in the visible region. The visible spectra of the present complexes are in agreement with those reported for other manganese(IV) Schiff base complexes.[13—16]

Cyclic voltammograms of the complexes **1**—**9** were measured in acetonitrile. Representative cyclic voltammograms are shown in Fig. 6 and the voltammetric data are listed in Table 4. The voltammogram was essentially the same for all complexes, showing two well-defined redox waves. The first of these redox processes ($E^1_{1/2}=-0.24$——-0.54 V vs. Ag/Ag^+) has the characteristic of an electrochemically reversible couple, the peak-to-peak separation (ΔE_p) being in the range 60—75 mV. The second redox couple at $E^2_{1/2}=-0.95$——-1.19 V is quasi-reversible with a ΔE_p in the range 80—270 mV. 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.

$$[Mn(IV)L_2] \overset{E^1_{1/2}}{\rightleftharpoons} [Mn(III)L_2]^- \overset{E^2_{1/2}}{\rightleftharpoons} [Mn(II)L_2]^{2-}$$

Constant-potential coulometry confirmed the one-electron nature of these couples (electrolysis of dark purple solution of **4** at -0.70 and -1.50 V gave $n=1.0\pm0.1$ as the number of electron transferred for each step). The $E^1_{1/2}$ values are comparable to those of the Mn(IV)-O_4N_2 complexes with phenolic oxygen donors.[15,16] The low reduction potentials of the Mn(IV)–Mn(III) couple explain the rapid formation of Mn(R, R′-L)$_2$ from the solution of H_2(R, R′-L) and manganese(II) salt in air. The potentials, $E^1_{1/2}$ and $E^2_{1/2}$, are sensitive to the nature of the substituents on the aromatic rings, R and R′, and a correlation with the Hammett constants, σ,[34] is found for this series of complexes. Plots of $E^1_{1/2}$ or $E^2_{1/2}$ versus σ are linear, as shown in Fig. 7. As the electron-donating ability of the substituents increases, the observed potentials shift in the cathodic direction and the higher oxidation states of manganese are stabilized. This implies that the substituent groups directly affect the electron density on the metal atom. The greater is the electron density present on the metal atom as the result of the electronic properties of the substituent groups, the more difficult it should be to perform a reduction. Similar results have been found for other manganese complexes.[19,24] The redox behaviors of the complexes were also examined in dichloromethane. The voltammograms are similar to those in acetonitrile and

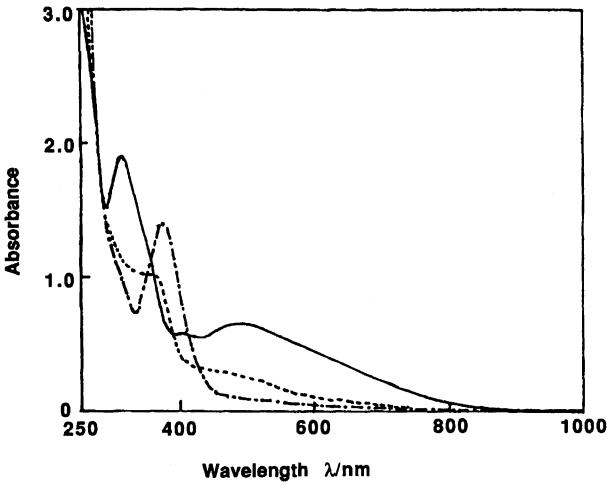

Fig. 9. Spectroelectrochemical results for [Mn(L)$_2$]·3/2H_2O (**1**) (0.9×10^{-4} mol dm^{-3}) in CH_3CN: original spectrum (—), spectrum after reduction with 1 equiv of charge at -0.6 V (Ag/Ag^+) (---), and spectrum after reduction with 2 equiv of charge at -1.8 V (Ag/Ag^+) (-·-).

a good correlation exists between the redox potentials and the σ values (Table 4, Fig. 8). An anodic shift in the $E^2_{1/2}$ values is observed on going from acetonitrile to dichloromethane, although the $E^1_{1/2}$ values in acetonitrile are almost the same as those in dichloromethane. This suggests that the $[Mn(III)L_2]^-$ is suifficiently stabilized by the solvation of CH_3CN, compared with CH_2Cl_2. As the reduction proceeded, the color of the solution changed from dark purple to brown, and then to yellow. Controlled-potential electrolysis of the complex changes their electronic spectra. The electronic spectra of **1** before electrolysis and after electrolyses at -0.6 and -1.8 V are illustrated in Fig. 9. One-electron reduction at -0.6 V in **1** results in a partial loss of the low-energy transitions (between 400—900 nm), and a blue-shift of the phenolate-to-manganese LMCT band. Upon further reduction at -1.8 V, almost a total loss of the lowest energy absorption was observed. This confirms the assignment of the lowest energy absorption as arising from an overlapping of the phenolate-to-manganese LMCT and d–d transition bands.

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