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The Preparation and Characterization of Dichloromanganese(IV) Schiff Base Complexes

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Some chloromanganese(III) Schiff base complexes react with hydrogen chloride to give deep green complexes with the empirical formula of $MnLCl_2$ or MnL'_2Cl_2, where H_2L denotes quadridentate ligands such as *N,N'*-disalicylideneethylenediamine and its analogs, and where HL′ denotes bidentate ligands such as *N*-butylsalicylideneamine and its analogs. These complexes are nonelectrolytes in acetonitrile. Their magnetic moments at room temperature fall within the range of 3.9 to 4.1 BM, and the magnetic susceptibilities obey the Curie-Weiss law with small θ values over the temperature range of 77 to 300 K, indicating that the oxidation state of the manganese ions in these complexes is +IV. The electronic spectra show an intense band around 16000 cm^{-1} which can be assigned to a charge-transfer transition. In the cyclic voltammograms, two cathodic waves are observed at half-peak potentials around +0.9 V and −0.2 V(*vs.* SCE); they can be assigned to the reductions of Mn(IV) to Mn(III) and of Mn(III) to Mn(II) respectively. The probable configurations of the complexes are discussed on the basis of the infrared spectra.

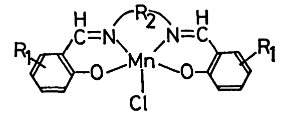
The manganese ion plays an important role in biological redox systems, which are comprised of the oxygen-evolution process of the photosystem II in green plants and the disproportionation of the superoxide ion, O_2^-, by manganese-containing superoxide dismutases. In these systems, the oxidation states of manganese(II), (III), and/or (IV) are believed to be involved.[1)] In relation to its function, manganese complexes with higher oxidation states, such as +III and +IV, have been investigated.[2–6)] Although manganese(III) complexes with various ligands have thus been synthesized and characterized, few manganese(IV) complexes have been isolated so far, for the manganese(IV) ion is a strong oxidant and its complexes are very unstable.[7,8)]

We have found that some chloromanganese(III) Schiff base complexes react with hydrogen chloride to give the corresponding manganese(IV) complexes as deep green crystals. In this paper we will describe the preparation and characterization of a series of novel dichloromanganese(IV) Schiff base complexes.

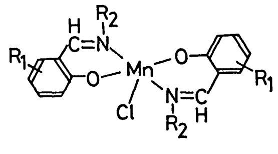
Experimental

Preparation of Manganese(III) Complexes. The quadridentate Schiff base ligands were prepared by a condensation of the salicylaldehydes with diamines. They were recrystallized from ethanol or appropriate organic solvents. The bidentate Schiff base ligands were prepared by a condensation of the salicylaldehydes with butylamine. The 5-nitro-, 5-bromo-, and 5,6-benzo derivatives were recrystallized from ethanol. All the chloromanganese(III) Schiff base complexes (shown in Fig. 1) were prepared by a modification of the method described in the literature.[9–12)] To a methanol solution of a quadridentate Schiff base ligand, an equimolar amount of manganese(III) acetate dihydrate, $Mn(CH_3COO)_3 \cdot 2H_2O$ (a half molar of it when the Schiff-bases were bidentate ligands) was added. The solution was warmed at 60 °C for 1 h, and then a 1.5-molar-fold quantity of lithium chloride over the manganese acetate was added to this solution, which was subsequently further warmed at 60 °C for 1 h. The solution was then concentrated under reduced pressure and cooled. The resulting precipitates were collected on a glass filter, washed with a small volume of water and methanol, and then with ether, and dried *in vacuo*. They were recrystallized from methanol or dichloromethane. The yields were 60—80%. The elemental analyses of the manganese(III) complexes are given in Table 1, along with their magnetic moments measured at room temperature. The magnetic moment of $Mn(N\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl$ was found to be lower than those of the other manganese(III) complexes. This may be caused by the magnetic-exchange interaction in this complex.

*Preparation of Dichloromanganese(IV) Schiff Base Complexes. Dichloro(*N,N′*-disalicylideneethylenediaminato)manganese(IV) Dichloromethane Adduct, $Mn(salen)Cl_2 \cdot (CH_2Cl_2)_{0.5}$:* Into an acetone solution (200 cm^3) of $Mn(salen)Cl \cdot H_2O$ (0.5 g), a two-molar-fold portion of a methanol solution of HCl over the complex was stirred, drop by drop, at room temperature. The solution turned brown to deep green. After the solution had been filtered, the filtrate was concentrated to about 20 cm^3 under reduced pressure. Anhydrous ether (200 cm^3) was then added to this solution. The resulting green precipitates were collected on a glass filter, washed with ether,



R_1	R_2	L
H	CH_2CH_2	salen
H	C_6H_{10}	salchxn
5-NO_2	CH_2CH_2	5-NO_2salen
5-CH_3	CH_2CH_2	5-Mesalen
5-Br	CH_2CH_2	5-Brsalen
5-Br	$CH(CH_3)CH_2$	5-Brsalpln
5-Br	$CH_2CH_2CH_2$	5-Brsalpn



R_1	R_2	L′
H	C_4H_9	*N*-Busai
5-NO_2	C_4H_9	*N*-Bu-5-NO_2sai
5-Br	C_4H_9	*N*-Bu-5-Brsai
5,6-Benzo	C_4H_9	*N*-Bu-5,6-Benzosai

Fig. 1. Manganese(III) Schiff base complexes.

TABLE 1. ELEMENTAL ANALYSES AND MAGNETIC MOMENTS OF MANGANESE(III) COMPLEXES

Complex	Found (%)				Calcd (%)				μ_{eff}[a)]
	C	H	N	Mn	C	H	N	Mn	BM
Mn(salen)Cl·H_2O	50.61	3.96	7.35	14.28	51.29	4.30	7.48	14.66	4.90
Mn(5-Brsalen)Cl	36.30	2.61	5.20	10.60	37.21	2.73	5.42	10.64	4.88
Mn(5-NO_2salen)Cl	41.00	2.96	11.74	11.60	41.18	3.46	12.00	12.24	5.01
Mn(5-Mesalen)Cl	56.68	4.76	7.28	14.26	56.19	4.72	7.28	14.28	5.02
Mn(salchxn)Cl	57.98	4.82	6.90	13.60	58.48	4.91	6.82	13.37	4.96
Mn(5-Brsalpln)Cl	38.64	2.76	5.59	10.37	38.63	2.67	5.30	10.39	4.88
Mn(5-Brsalpn)Cl·H_2O	37.01	2.91	5.08	9.51	37.36	2.95	5.12	10.05	5.04
Mn(*N*-Busai)$_2$Cl	58.80	6.32	6.21	12.53	59.67	6.37	6.33	12.40	5.03
Mn(*N*-Bu-5-NO_2sai)$_2$Cl	49.53	5.11	10.23	10.37	49.59	4.92	10.51	10.31	4.37
Mn(*N*-Bu-5,6-Benzosai)$_2$Cl	66.33	6.13	4.85	10.10	66.36	5.94	5.16	10.12	4.92
Mn(*N*-Bu-5-Brsai)$_2$Cl	43.77	4.52	4.80	9.17	43.97	4.36	4.66	9.15	5.01

a) Measured at room temperature.

TABLE 2. ELEMENTAL ANALYSES AND MAGNETIC MOMENTS OF MANGANESE(IV) COMPLEXES

Complex	Found (%)					Calcd (%)					μ_{eff}[a)]
	C	H	N	X	Mn	C	H	N	X	Mn	BM
Mn(salen)Cl_2·$(CH_2Cl_2)_{0.5}$	45.17	3.55	6.49	24.86	12.80	45.60	3.48	6.45	24.47	12.68	3.91
Mn(5-Brsalen)Cl_2	34.82	2.28	5.00	41.99	9.77	34.82	2.56	5.08	41.80	9.95	3.94
Mn(5-NO_2salen)Cl_2	39.97	2.52	11.54	14.26	11.05	39.69	2.91	11.57	14.65	11.35	3.98
Mn(5-Mesalen)Cl_2·$(CH_2Cl_2)_{0.25}$	49.70	4.25	6.28	20.58	12.67	49.66	4.22	6.35	20.08	12.45	3.97
Mn(salchxn)Cl_2·$(CH_2Cl_2)_{0.6}$	49.96	4.21	5.66	22.84	10.90	49.76	4.30	5.69	22.82	11.05	4.04
Mn(5-Brsalpln)Cl_2·$(CH_2Cl_2)_{0.5}$	34.34	2.54	4.66	42.97	9.09	34.66	2.49	4.62	43.88	9.06	4.00
Mn(5-Brsalpn)Cl_2	35.77	2.52	4.82	41.63	9.96	36.21	2.59	4.97	40.91	9.74	4.02
Mn(*N*-Busal)$_2Cl_2$	54.79	5.76	5.70	15.47	12.03	55.24	5.90	5.86	14.87	11.49	4.10
Mn(*N*-Bu-5-NO_2sai)$_2Cl_2$	46.32	4.56	9.85	12.33	9.72	46.49	4.61	9.86	12.48	9.67	3.90
Mn(*N*-Bu-5,6-Benzosai)$_2Cl_2$	62.03	5.60	4.67	12.87	9.39	62.29	5.58	4.87	12.26	9.50	4.07
Mn(*N*-Bu-5-Brsai)$_2Cl_2$	40.95	4.00	4.19	35.22	8.54	41.54	4.12	4.40	36.30	8.64	4.09

a) Measured at room temperature.

and dried *in vacuo*. The solids were recrystallized from dichloromethane to give the above complex as deep green crystals. The yield was *ca.* 30%.

The other dichloromanganese(IV) Schiff base complexes were obtained in a similar manner. The elemental analyses of the manganese(IV) complexes obtained are given in Table 2, together with their magnetic moments measured at room temperature. These deep green complexes are soluble in dichloromethane, acetone, and acetonitrile. The solutions were stable in these solvents if kept without contact with to moisture. They were soluble in donating solvents, such as pyridine, *N,N*-dimethylformamide, and methanol, but these solutions gradually turned brown.

Reagents. All the reagents were of a reagent grade. The solvents were purified by refluxing over sodium (ether), calcium chloride (dichloromethane, acetone), or magnesium (methanol), and then distilled. The acetonitrile was distilled twice from diphosphorus pentaoxide prior to use.

Measurements. The UV, VIS, and NIR spectra were obtained from Hitachi EPS-3 and 340 spectrophotometers. The IR spectra were recorded on a Hitachi EPI-215 grating spectrophotometer in the 700 to 4000 cm^{-1} regions and on a Hitachi EPI-L grating spectrophotometer in the 200 to 700 cm^{-1} regions. All the spectra were measured in Nujol mulls or in a KBr disc. The magnetic susceptibilities were measured by the Gouy method at room temperature and by the Faraday method, using a Shimadzu MB 11 apparatus for the temperature range from 77 to 300 K. The conductivities were determined on a Yanagimoto MY-7 conductivity outfit. The cyclic voltammetry was performed with a Yanagimoto P8 polarograph connected with a Yanagimoto P8-PT potentiostat. The working electrode was a platinum-inlay electrode, while the auxiliary electrode was a platinum wire. The reference electrode was a saturated calomel electrode which was inserted in an aqueous solution of 1 M (1 M=1 mol dm^{-3}) KCl in a 100-cm^3 beaker connected with a conventional brown H-type cell by means of a 4% agar-saturated KCl gel bridge. Tetrabutylammonium perchlorate, Bu_4NClO_4, was used as the supporting electrolyte. The dissolved oxygen was removed by passing nitrogen gas through a sample solution for 20 min.

Results and Discussion

Figure 2 shows the spectral changes on the addition of HCl to an acetone solution of Mn(salen)Cl·H_2O in different molar ratios. The spectra change remarkably on the addition of HCl, and a new absorption band appears around 630 nm. Its intensity increases as the molar ratio of HCl to the complex increases to 4. The further addition of HCl leads to the decolorization of the solution, with the formation of white precipitates, which may consist of hydrogen chloride salts of the ligand. This was confirmed by a comparison of the IR spectra of the white

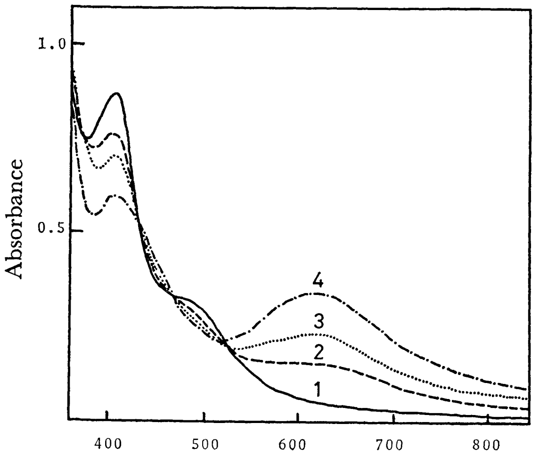


Fig. 2. Spectral changes on the addition of HCl to an acetone solution of 2×10^{-4} M Mn(salen)Cl·H_2O in different molar ratios.
(1): [HCl]/[complex]=0, (2): 1, (3): 2, (4): 4.

precipitates and of the authentic compound obtained by the reaction between salenH_2 and HCl in ether.

The deep green complexes isolated by the reactions between chloromanganese(III) Schiff base complexes and HCl are given in Table 2. Their analytical data are consistent with the empirical formula of $MnLCl_2$ or MnL'_2Cl_2, where L denotes a dianion of quadridentate Schiff base ligands, and L′, a monoanion of bidentate Schiff base ligands. Some of them include dichloromethane as a crystalline solvent.

Magnetic Properties. The room-temperature magnetic moments for these complexes (given in Table 2) fall within the range of 3.9 to 4.1 BM, consistent with a calculated spin-only value expected for a complex with a d^3 high-spin configuration. Figure 3 shows the Curie-Weiss plot for Mn(salen)Cl_2·$(CH_2Cl_2)_{0.5}$ over the temperature range from 77 to 300 K. The magnetic susceptibilities obey the Curie-Weiss law, $\chi_A=C/(T+\theta)$. The same behavior was observed for the complexes of Mn(5-Mesalen)Cl_2·$(CH_2Cl_2)_{0.25}$ and Mn(*N*-Bu-5-NO_2sai)$_2Cl_2$. Their Weiss constants are given in Table 3. These values were obtained from an extrapolation of the plot of the reciprocal of the molar susceptibilities, χ_A, against the absolute temperature. These small θ values indicate that there are very small magnetic interactions in these complexes. These results suggest that the oxidation state of the central manganese ion in the complexes is +IV.

Conductivities. The molar conductivities for several manganese(III) and manganese(IV) complexes are summarized in Table 4. These values indicate that they are essentially nonelectrolytes in acetonitrile. The slightly large value observed for the Mn(*N*-Busai)$_2Cl_2$, complex may be caused by its lower solubility in acetonitrile. On the other hand, in methanol the molar conductivity for Mn(salen)Cl·H_2O was found to be 71 S cm^2 mol^{-1}, and that for Mn(salen)Cl_2·$(CH_2Cl_2)_{0.5}$, to be 191 S cm^2 mol^{-1}. These values indicate that both complexes undergo considerable dissociation in methanol.

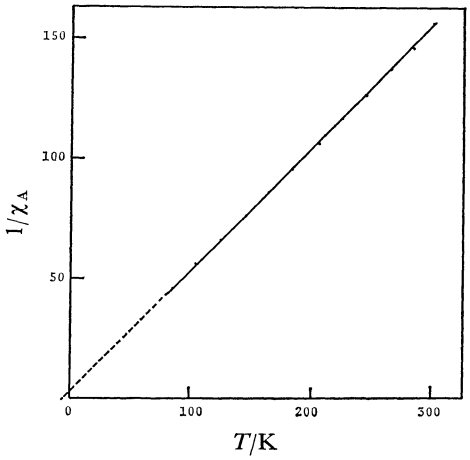


Fig. 3. Curie-Weiss plot for Mn(salen)Cl_2·$(CH_2Cl_2)_{0.5}$.

TABLE 3. WEISS CONSTANTS OF MANGANESE(IV) COMPLEXES

Complex	Weiss constant θ/K
Mn(salen)Cl_2·$(CH_2Cl_2)_{0.5}$	6
Mn(5-Mesalen)Cl_2·$(CH_2Cl_2)_{0.25}$	3
Mn(*N*-Bu-5-NO_2sai)$_2Cl_2$	9

Table 4. MOLAR CONDUCTIVITIES OF MANGANESE(III) AND MANGANESE(IV) COMPLEXES IN ACETONITRILE

Complex	$\Lambda$$^{a)}$ S cm^2 mol^{-1}
Mn^{III}(salen)Cl·H_2O	2.38
Mn^{IV}(salen)Cl_2·$(CH_2Cl_2)_{0.5}$	3.48
Mn^{III}(*N*-Busai)$_2$Cl	8.35
Mn^{IV}(*N*-Busai)$_2Cl_2$	25.28$^{b)}$
Mn^{III}(*N*-Bu-5-NO_2sai)$_2$Cl	10.22
Mn^{IV}(*N*-Bu-5-NO_2sai)$_2Cl_2$	3.70

a) Measured at 25 °C. The concentration of the complexes was 10^{-3} M. b) The concentration of the complex was 5×10^{-4} M.

Electronic Spectra. Figure 4 shows the electronic spectra of Mn(salen)Cl·H_2O and Mn(salen)Cl_2·$(CH_2Cl_2)_{0.5}$ in dichloromethane. In the visible region, the spectrum of the manganese(III) complex shows three absorption bands, at 15600, 20800, and 23800 cm^{-1}. They have been previously assigned to the ligand-field transitions of $d_{xy}\rightarrow d_{x^2-y^2}$ and of d_{yz}, $d_{xz}\rightarrow d_{x^2-y^2}$, and to the charge-transfer transition of $d\pi$(Mn) to π^* (azomethine), respectively.[12,13] On the other hand, the spectrum of the manganese(IV) complex shows two absorption bands, at 15400 and 23000 cm^{-1}. The lower-energy band is very intense compared with that of the manganese(III) complex. Therefore, it seems to be due to a charge-transfer transition.

Moews has reported on the absorption spectrum of $K_2Mn^{IV}Cl_6$ in fluorocarbon grease mulls; it shows two absorption bands, at 15400 (very strong) and 27400 cm^{-1} (strong) in the visible region.[8d] The lower-energy band has been assigned to a charge-transfer

Table 5. Spectroscopic data for manganese(IV) complexes

Complex	$\frac{\tilde{\nu}_{\max}}{10^3\ \mathrm{cm}^{-1}}$ (log ε)[a]		$\frac{\nu(\mathrm{Mn–Cl})}{\mathrm{cm}^{-1}}$
$\mathrm{Mn(5\text{-}Mesalen)Cl_2\cdot(CH_2Cl_2)_{0.25}}$	14.9 (3.60)	22.8 (3.81)	323
$\mathrm{Mn(5\text{-}Brsalen)Cl_2}$	15.3 (3.59)	23.1 (3.69)	337
$\mathrm{Mn(salchxn)Cl_2\cdot(CH_2Cl_2)_{0.6}}$	15.6 (3.62)	23.7 (3.74)	350
$\mathrm{Mn(salen)Cl_2\cdot(CH_2Cl_2)_{0.5}}$	15.4 (3.60)	23.0 (3.78)	341
$\mathrm{Mn(5\text{-}NO_2salen)Cl_2}$	16.7 (3.40)	24.4 sh	356
$\mathrm{Mn(5\text{-}Brsalpln)Cl_2\cdot(CH_2Cl_2)_{0.5}}$	15.3 (3.60)	24.1 (3.78)	339
$\mathrm{Mn(5\text{-}Brsalpn)Cl_2}$	14.8 (3.63)	24.1 (3.83)	367
$\mathrm{Mn(\mathit{N}\text{-}Busai)_2Cl_2}$	16.0 (3.52)	22.0 sh	346
$\mathrm{Mn(\mathit{N}\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl_2}$	17.2 (3.80)	23.4 sh	359, 342
$\mathrm{Mn(\mathit{N}\text{-}Bu\text{-}5\text{-}Brsai)_2Cl_2}$	15.5 (3.76)	22.7 sh	333
$\mathrm{Mn(\mathit{N}\text{-}Bu\text{-}5,6\text{-}Benzosai)_2Cl_2}$	14.6 (3.71)	23.0 sh	334

a) Measured in dichloromethane.

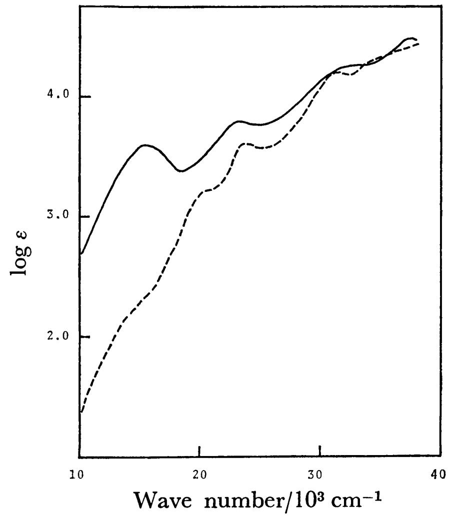


Fig. 4. Electronic spectra in dichloromethane. (——): $\mathrm{Mn^{IV}(salen)Cl_2\cdot(CH_2Cl_2)_{0.5}}$, (– – –): $\mathrm{Mn^{III}(salen)Cl\cdot H_2O}$.

transition of chlorine to manganese. Later, Jeżowska-Trzbiatowska *et al.*[14] claimed that the absorption spectrum of the same complex in 12 mol dm^{-3} HCl does not agree with that observed by Moews in the intensities of these bands. However, as was pointed out by Moews, hexachloromanganate(IV) salts are rapidly converted to the corresponding aquapentachloromanganate(III) salts on standing in moist air. Therefore, it is uncertain as to whether or not $\mathrm{K_2Mn^{IV}Cl_6}$ exists as the $\mathrm{Mn^{IV}Cl_6^{2-}}$ ion in 12 mol dm^{-3} HCl.

The spectral data for the manganese(IV) complexes are summarized in Table 5. All the complexes show two intense bands around 16000 and 23000 cm^{-1} in the visible region. It can be seen that the absorption maxima of the lower-energy bands are affected by the Schiff base ligands. In the complexes of the salen type, the absorption maxima are shifted to higher energies in the order of the substituents of 5-Me<5-Br<H<5-$\mathrm{NO_2}$. In the complexes of the *N*-butylsalicylideneamine type, similar shifts are observed in the order of the substituents of 5,6-Benzo<5-Br<H<5-$\mathrm{NO_2}$. Furthermore, the absorption maxima of the former complexes are observed at lower energies than those of the latter complexes. These results imply that the lower-energy bands may be assigned to a charge-transfer transition of Cl(pπ) to Mn(dπ). The absorption bands due to the ligand-field transitions expected for the manganese(IV) complexes may be obscured by these intense bands.

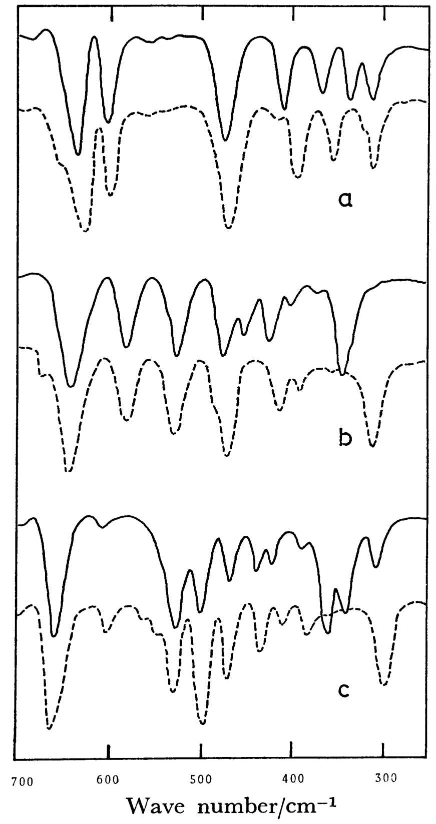


Fig. 5. Infrared spectra (in Nujol mulls). a) (——): $\mathrm{Mn^{IV}(salen)Cl_2\cdot(CH_2Cl_2)_{0.5}}$; (– – –): $\mathrm{Mn^{III}(salen)Cl\cdot H_2O}$, b) (——): $\mathrm{Mn^{IV}(\mathit{N}\text{-}Busai)_2Cl_2}$; (– – –): $\mathrm{Mn^{III}(\mathit{N}\text{-}Busai)_2Cl}$, c) (——): $\mathrm{Mn^{IV}(\mathit{N}\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl_2}$; (– – –): $\mathrm{Mn^{III}(\mathit{N}\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl}$.

Infrared Spectra. In the region from 4000 to 500 cm^{-1} the infrared spectra of the manganese(IV) complexes are almost the same as those of the cor-

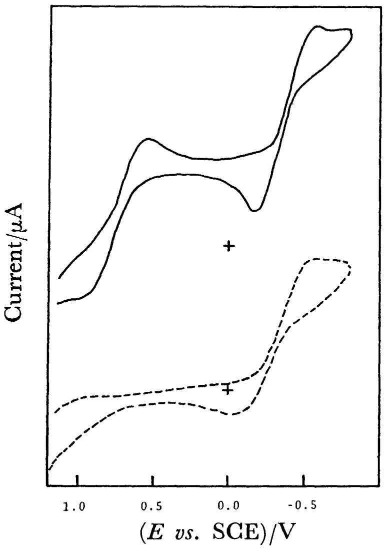


Fig. 6. Current potential curves in acetonitrile. (——): $\mathrm{Mn^{IV}(salen)Cl_2 \cdot (CH_2Cl_2)_{0.5}}$; (– – –): $\mathrm{Mn^{III}(salen)Cl \cdot H_2O}$.

responding manganese(III) complexes, except around 1290 cm^{-1}, where the absorption band due to ν(C–O) should be observed. This indicates that there is no change in the coordination features of the Schiff base ligands in either manganese(III) or manganese(IV) complexes. In the ν(C–O) region, lower-energy shifts of about 10 cm^{-1} were observed on going from the manganese(III) complexes to the manganese(IV) complexes; they may be caused by the change of the oxidation state of the central manganese ion from +III to +IV. In the region from 200 to 500 cm^{-1}, the spectra of the manganese(IV) complexes show the strong absorption bands at about 340 cm^{-1}, unlike those of the corresponding manganese(III) complexes. Figure 5-a shows the spectra of $\mathrm{Mn^{IV}(salen)Cl_2 \cdot (CH_2Cl_2)_{0.5}}$ and $\mathrm{Mn^{III}(salen)Cl \cdot H_2O}$. The band observed at 341 cm^{-1} for the manganese(IV) complex may be assigned to ν(Mn–Cl). Figure 5-b shows the spectra of $\mathrm{Mn^{IV}(\mathit{N}\text{-}Busai)_2Cl_2}$ and $\mathrm{Mn^{III}(\mathit{N}\text{-}Busai)_2Cl}$. The band observed at 348 cm^{-1} for the manganese(IV) complex may be assigned to ν(Mn–Cl). On the other hand, as is shown in Fig. 5-c, the spectrum of $\mathrm{Mn^{IV}(\mathit{N}\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl_2}$ exhibits two strong bands, at 364 and 333 cm^{-1}, which may be assigned to ν(Mn–Cl). The frequencies of the characteristic bands assigned to ν(Mn–Cl) for the manganese(IV) complexes are summarized in Table 5. In the complexes of the salen type, one band assignable to ν(Mn–Cl) was observed, whereas in the $\mathrm{Mn^{IV}(\mathit{N}\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl_2}$ complex, two bands were observed. For the octahedral complexes of the $\mathrm{MA_4Cl_2}$ type (A denotes unidentate ligands such as ammonia), one band due to ν(M–Cl) should be observed in the case of a *trans*-configuration, whereas two strong bands should be observed in the case of a *cis*-configuration.[15] These results suggest that the manganese(IV) complexes of the salen type may have a *trans*-octahedral configuration, while in the manganese(IV) complexes of the bidentate Schiff bases, *trans*- and *cis*-octahedral configurations may be probable.

TABLE 6. REDUCTION POTENTIALS FOR MANGANESE(IV) COMPLEXES

Complex	$E_{p/2}$ *vs.* SCE[a)] / V $\mathrm{Mn^{IV} \to Mn^{III}}$	 $\mathrm{Mn^{III} \to Mn^{II}}$
$\mathrm{Mn(salen)Cl_2 \cdot (CH_2Cl_2)_{0.5}}$	0.76	−0.37 (−0.38)[b)]
$\mathrm{Mn(5\text{-}Brsalen)Cl_2}$	0.85	−0.16 (+0.01)
$\mathrm{Mn(5\text{-}NO_2salen)Cl_2}$	0.90	−0.01 (+0.11)
$\mathrm{Mn(5\text{-}Mesalen)Cl_2 \cdot (CH_2Cl_2)_{0.25}}$	0.85	−0.34 (−0.32)
$\mathrm{Mn(salchxn)Cl_2 \cdot (CH_2Cl_2)_{0.6}}$	0.83	−0.29 (−0.32)
$\mathrm{Mn(5\text{-}Brsalpln)Cl_2 \cdot (CH_2Cl_2)_{0.5}}$	1.00	−0.09 (−0.14)
$\mathrm{Mn(5\text{-}Brsalpn)Cl_2}$	0.88	−0.05 (−0.02)
$\mathrm{Mn(\mathit{N}\text{-}Busai)_2Cl_2}$	0.84	−0.11 (−0.08)
$\mathrm{Mn(\mathit{N}\text{-}Bu\text{-}5\text{-}Brsai)_2Cl_2}$	0.94	+0.01 (−0.12)
$\mathrm{Mn(\mathit{N}\text{-}Bu\text{-}5\text{-}NO_2sai)_2Cl_2}$	0.98	+0.08 (+0.24)

a) Measured in acetonitrile at 25 °C. b) Half-peak potentials observed for the corresponding manganese(III) complexes.

Electrochemical Properties. Figure 6 shows some typical current-potential curves of $\mathrm{Mn^{III}(salen)Cl \cdot H_2O}$ and $\mathrm{Mn^{IV}(salen)Cl_2 \cdot (CH_2Cl_2)_{0.5}}$ measured in acetonitrile. In the manganese(III) complex, one cathodic wave is observed at −0.38 V(*vs.* SCE); it can be assigned to the reduction of Mn(III) to Mn(II). On the other hand, in the manganese(IV) complex, two cathodic waves are observed, at +0.76 and −0.37 V(*vs.* SCE), with similar wave heights; they can be assigned to the reductions of Mn(IV) to Mn(III) and of Mn(III) to Mn(II) respectively. The separations of the peak potentials between the cathodic wave and the corresponding anodic wave for both redox waves are larger than the 57 mV expected for a reversible one-electron redox wave, so these electrode reactions may be irreversible.

All the manganese(IV) complexes show two cathodic waves around +0.85 V and −0.20 V(*vs.* SCE). The half-peak potentials for the reductions of the manganese(IV) complexes are summarized in Table 6, together with those of the corresponding manganese(III) complexes. As has been discussed in connection with the electronic spectra, the potentials for both reductions are also affected by the Schiff base ligands. The reduction potentials are shifted to more positive values upon the introduction of an electron-withdrawing substituent such as the 5-$\mathrm{NO_2}$ group in both types of the complexes. Furthermore, the reduction potentials for the complexes of the *N*-butylsalicylideneamine type are observed at more positive values than those for the complexes of the salen type. These shifts can be explained in terms of the electron density on the central manganese ion in the complexes.

Reactions. These manganese(IV) complexes have reduction potentials high enough to oxidize water. Thus, we have attempted their reactions with water. Figure 7 shows the spectral changes on the addition of water to an acetonitrile solution of $\mathrm{Mn(salen)Cl_2 \cdot (CH_2Cl_2)_{0.5}}$ in different molar ratios. The

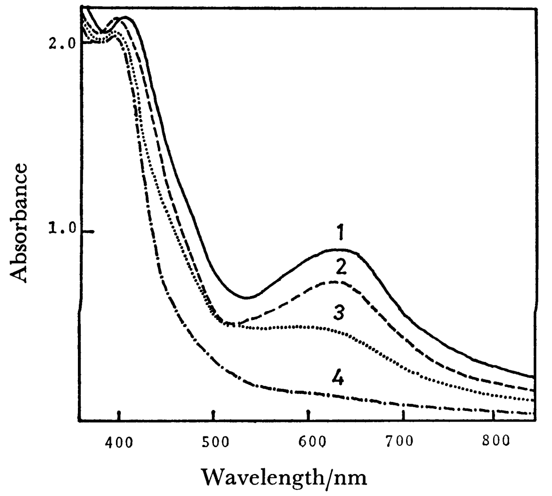


Fig. 7. Spectral changes on the addition of H_2O to an acetonitrile solution of 4×10^{-4} M Mn(salen)$Cl_2\cdot(CH_2Cl_2)_{0.5}$ in different molar ratios.
(1): $[H_2O]/[complex]=0$, (2): 10, (3): 20, (4): 40.

intensity of the characteristic absorption band at 624 nm decreased with an increase in the molar ratio of water to the complex. The final absorption spectrum is almost identical with that of the corresponding manganese(III) complex in the acetonitrile and water mixture, indicating that water reduced the manganese(IV) complex to the manganese(III) complex. We have also succeeded in detecting free "molecular oxygen" liberated during the reactions of the manganese(IV) complexes with water by means of the spectrophotometry of an alkaline pyrogallol solution and a dissolved oxygen probe.[16] The details will be described in the near future.

Some novel dichloromanganese(IV) Schiff base complexes have been prepared and characterized. The higher oxidation state of the manganese ion may be stabilized by charge neutralization with chloride ions. The mechanism for the reaction of the manganese(III) complexes with HCl has not been clarified in this work. However, some experimental evidence suggests that the manganese(IV) complexes may result from a disproportionation of the manganese(III) complexes: manganese(II) compounds are often formed as contaminants in the preparation of the manganese(IV) complexes, and their yields are always 50% or below.

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