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Preparation and Characterization of Dichlorobis(*N*-alkylsalicylideneaminato)manganese(IV) Complexes

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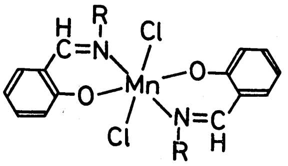
The chlorobis(*N*-alkylsalicylideneaminato)manganese(III) complexes, $Mn^{III}(N\text{-Rsai})_2Cl$, react with hydrogen chloride to give the corresponding dichloromanganese(IV) complexes, $Mn^{IV}(N\text{-Rsai})_2Cl_2$, as deep green crystals; R can be $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$, $n\text{-}C_6H_{13}$, $c\text{-}C_6H_{11}$, $n\text{-}C_8H_{17}$, $n\text{-}C_{12}H_{25}$, $n\text{-}C_{18}H_{37}$, $CH_2C_6H_5$, or $CH_2CH_2C_6H_5$. These complexes were characterized by the magnetic susceptibilities, electronic spectra, infrared spectra, and cyclic voltammograms. The complexes ($R=n\text{-}C_{12}H_{25}$ and $n\text{-}C_{18}H_{37}$) are found to be stable toward water in the solid state. A *trans*, six-coordinate configuration is proposed for these Mn(IV) complexes on the basis of the infrared spectra.

Manganese-(III) and -(IV) complexes are of interest in connection with the biological redox systems involving manganese ions, such as the oxygen evolution process of photosystem II in green plants and the disproportionation of superoxide ion, O_2^-, by the manganese-containing superoxide dismutases.[1] In these systems the involvement of various oxidation states: Mn(II), Mn(III), and/or Mn(IV) have been proposed.[2–5] However, very few Mn(IV) complexes have been isolated and characterized so far, because Mn(IV) ion is very unstable toward water.[6,7] We have previously reported on the dichloromanganese(IV) complexes with the Schiff bases derived from substituted salicylaldehydes with diamines or butylamine.[7] These Mn(IV) complexes are unstable toward moisture even in the solid state and decompose to the reduced manganese complexes. This may be caused because the coordinated chlorine atoms are displaced by water molecules. Thus we have aimed to obtain Mn(IV) complexes which are stable toward water.

In this paper we describe the preparation and characterization of a series of dichloromanganese(IV) complexes with the bidentate Schiff bases derived from salicylaldehyde and primary monoamines (Fig. 1). The reactivity of the Mn(IV) complexes toward water decreased as the chain length of the alkyl groups increased.



R	L	R	L
$n\text{-}C_3H_7$	*N*-Prsai	$n\text{-}C_8H_{17}$	*N*-Octsai
$n\text{-}C_4H_9$	*N*-Busai	$n\text{-}C_{12}H_{25}$	*N*-Dodsai
$i\text{-}C_4H_9$	*N*-*i*-Busai	$n\text{-}C_{18}H_{37}$	*N*-Octdsai
$n\text{-}C_6H_{13}$	*N*-Hxsai	$CH_2C_6H_5$	*N*-Bzsai
$c\text{-}C_6H_{11}$	*N*-*c*-Hxsai	$CH_2CH_2C_6H_5$	*N*-PEsai

Fig. 1. Manganese(IV) Schiff base complexes, $Mn(N\text{-Rsai})_2Cl_2$.

Experimental

*Preparation of Mn(III) Complexes, Mn(*N*-Rsai)$_2$Cl.* All the Mn(III) Schiff base complexes were obtained by a modification of the method described previously.[7]

*Chlorobis(*N*-hexylsalicylideneaminato)manganese(III), Mn(*N*-Hxsai)$_2$Cl.* The tetrahydrofuran (THF) solution (50 cm^3) containing salicylaldehyde (2.44 g) and hexylamine (2.02 g) was refluxed for 1 h. The solvent was evaporated under reduced pressure. The resulting yellow oily residue was dissolved in a mixture of dichloromethane (30 cm^3) and methanol (30 cm^3). Manganese(III) acetate dihydrate (2.68 g) and lithium chloride (0.63 g) were added to the solution. The mixture was refluxed for 1 h. The solvent was evaporated under reduced pressure to yield olive-green solids. They were collected on a glass filter, washed with 2-propanol and ether, and then dried *in vacuo*. They were recrystallized from dichloromethane. The yield was 3.2 g.

The other Mn(III) complexes were prepared in a similar manner. These complexes are soluble in dichloromethane, acetone, and acetonitrile. The analytical data are given in Table 1, together with the magnetic moments determined at room temperature.

Preparation of Mn(IV) Complexes. *Dichlorobis(*N*-hexylsalicylideneaminato)manganese(IV), Mn(*N*-Hxsai)$_2$Cl$_2$.* To a mixed solution of dichloromethane (20 cm^3) and 2-propanol (50 cm^3) containing $Mn^{III}(N\text{-Hxsai})_2Cl$ (1.0 g), a 2-propanol solution of HCl (1.5 molar folds over the complex) was added drop by drop with stirring at room temperature. The solution changed from greenish-brown to deep green with precipitation of deep green crystals. The mixture was cooled to 0 °C and allowed to stand for 3 h. The crystals precipitated were collected on a glass filter, washed with 2-propanol and ether, and then dried *in vacuo*. The yield was *ca.* 0.4 g. Further purification was not carried out.

The other Mn(IV) complexes (Fig. 1) were obtained in a similar manner. The analytical data are given in Table 2, together with the magnetic moments determined at room temperature. All the complexes are soluble in dichloromethane and the solutions show no noticeable change for an hour if kept isolated from contact with moisture. The complexes with R=Pr, Bu, *i*-Bu, Hx, *c*-Hx, Oct, Dod, Bz, and PE are soluble in acetone and acetonitrile; the complex with R=Octd is slightly soluble in the above solvents. All the complexes are soluble in coordinating solvents such as dimethyl sulfoxide and pyridine, but the solutions change rapidly from deep green to yellow-brown. The complexes with R=Dod and Octd have been found to be unreactive toward water in the solid state.

Reagents. All reagents were of reagent grade. Solvents were purified by refluxing over sodium (ether), calcium oxide (2-propanol), and calcium chloride (dichloromethane, acetone), and then distilled. Acetonitrile was distilled twice

Table 1. Elemental analyses and magnetic moments of manganeses(III) complexes

Complex	Found (%)				Calcd (%)				μ_{eff} a)
	C	H	N	Mn	C	H	N	Mn	BM
Mn(N-Prsai)$_2$Cl	57.68	5.84	6.41	13.12	57.91	5.85	6.75	13.24	4.86
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-i-Busai)$_2$Cl	59.39	6.28	6.28	12.63	59.67	6.37	6.33	12.40	4.87
Mn(N-Hxsai)$_2$Cl	63.21	7.28	5.47	10.82	62.59	7.27	5.61	11.01	5.00
Mn(N-c-Hxsai)$_2$Cl·(H$_2$O)$_{0.5}$	61.50	6.59	5.61	11.28	61.96	6.60	5.55	10.90	4.89
Mn(N-Octsai)$_2$Cl	64.59	8.15	4.98	9·89	64.91	7.99	5.05	9.90	4.93
Mn(N-Dodsai)$_2$Cl	67.84	9.52	4.14	7.96	68.40	9.06	4.20	8.23	4.98
Mn(N-Octdsai)$_2$Cl	71.04	10.50	3.27	6.38	71.82	10.13	3.35	6.57	4.92
Mn(N-Bzsai)$_2$Cl	65.33	5.16	5.38	10.73	65.83	4.73	5.48	10.75	4.26
Mn(N-PEsai)$_2$Cl	66.88	5.21	5.20	10.20	66.86	5.24	5.20	10.19	4.85

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	Cl	Mn	C	H	N	Cl	Mn	BM
Mn(N-Prsai)$_2$Cl$_2$	53.15	5.34	6.17	15.76	12.50	53.35	5.37	6.22	15.75	12.20	3.96
Mn(N-Busai)$_2$Cl$_2$	55.12	5.95	5.80	15.35	11.32	55.24	5.90	5.86	14.82	11.49	4.06
Mn(N-i-Busai)$_2$Cl$_2$	55.18	5.89	5.83	14.50	11.70	55.24	5.90	5.86	14.82	11.49	3.84
Mn(N-Hxsai)$_2$Cl$_2$	58.33	6.93	5.21	13.50	10.15	58.43	6.79	5.24	13.27	10.28	4.09
Mn(N-c-Hxsai)$_2$Cl$_2$	59.28	6.36	5.14	12.48	10.05	58.88	6.08	5.28	13.37	10.36	4.07
Mn(N-Octsai)$_2$Cl$_2$	60.90	7.53	4.64	11.20	9.31	61.02	7.51	4.74	12.01	9.30	3.92
Mn(N-Dodsai)$_2$Cl$_2$	64.90	8.70	3.95	9.90	8.02	64.95	8.61	3.99	10.09	7.82	3.93
Mn(N-Octdsai)$_2$Cl$_2$	68.75	9.55	3.19	8.90	6.07	68.94	9.72	3.22	8.14	6.31	4.08
Mn(N-Bzsai)$_2$Cl$_2$·CH$_2$Cl$_2$	55.35	4.25	4.39	21.01	8.53	55.18	4.87	4.82	22.46	8.70	3.99
Mn(N-PEsai)$_2$Cl$_2$	62.85	4.87	4.82	12.13	9.19	62.73	4.91	4.88	12.34	9.56	3.95

a) Measured at room temperature.

from diphosphorus pentaoxide before use.

Measurements. The UV and VIS absorption spectra were obtained from a Hitachi 340 recording spectrophotometer. The IR spectra were recorded on a Hitachi EPI-215 and a Hitachi EPI-L grating spectrophotometer for the 4000 to 650 cm^{-1} and the 700 to 250 cm^{-1} regions, respectively. The magnetic susceptibilities were measured by the Gouy method at room temperature. The cyclic voltammograms were made with a Yanagimoto P-8 polarograph connected with a Yanagimoto P8-PT potentiostat. A platinum wire and a platinum spiral were used as a working and an auxiliary electrode, respectively. An aqueous saturated calomel electrode was used as a reference electrode; this was inserted in an aqueous solution of 1 M (1 M= 1 mol dm^{-3}) KCl, which was connected with an agar salt bridge to a solution under investigation *via* an acetonitrile solution containing 0.1 M electrolyte. Tetrabutylammonium perchlorate was used as a supporting electrolyte.

Results and Discussion

The analytical data for the Mn(III) and Mn(IV) complexes are in agreement with the empirical formulas of MnL$_2$Cl and MnL$_2$Cl$_2$, respectively; here L denotes monoanion of N-alkylsalicylideneamines (Tables 1 and 2).

In general, most of the Mn(IV) compounds are not stable and are thus readily hydrolysed and reduced. The dichloromanganese(IV) complexes such as Mn^{IV}(salen)Cl$_2$ obtained previously are unstable in a moist air even in the solid state, where salen denotes dianion of N,N'-disalicylideneethylenediamine. Therefore many difficulties arose in the syntheses of these complexes. In this study we prepared a series of dichloromanganese(IV) Schiff base complexes (Fig. 1) in order to obtain water-resistant Mn(IV) complexes. This idea is based on the hope that the long chain alkyl groups such as n-C$_{12}$H$_{25}$ and n-C$_{18}$H$_{37}$ may protect against the attack of water molecules on the central manganese atom of the complex. Figure 2 shows the absorption spectral changes on the addition of water to an acetone solution of Mn(N-c-Hxsai)$_2$Cl$_2$. The intensity of the characteristic absorption band at 600 nm for the Mn(IV) complex decreased with time. The final absorption spectrum is almost the same as that of Mn^{III}(N-c-Hxsai)$_2$Cl in a mixture of acetone and water, indicating that water resulted in the reduction of the Mn(IV) complex. Figure 3 shows the time courses of the absorbances in the characteristic absorption bands for the complexes: Mn(N-Prsai)$_2$Cl$_2$, Mn(N-c-Hxsai)$_2$Cl$_2$, Mn(N-Octsai)$_2$Cl$_2$, and Mn(N-Dodsai)$_2$Cl$_2$, when water was added to these acetone solutions. It is apparent that their reactivity with water depends on the alkyl groups and decreases in the order of R= Dod<Oct<Pr<c-Hx. The most rapid change in absorbance observed for Mn(N-c-Hxsai)$_2$Cl$_2$ may be

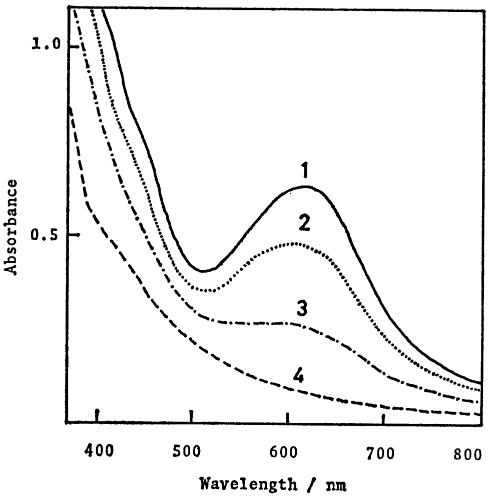


Fig. 2. Spectral changes on the addition of water (0.05 cm^3) to an acetone solution of 1.6×10^{-4} M Mn^{IV}(*N*-*c*-Hxsai)$_2$Cl$_2$ (5 cm^3).
1: No addition, 2: 7.5 min after addition of water, 3: 17.5 min, 4: 42.5 min. Cell length: 1 cm.

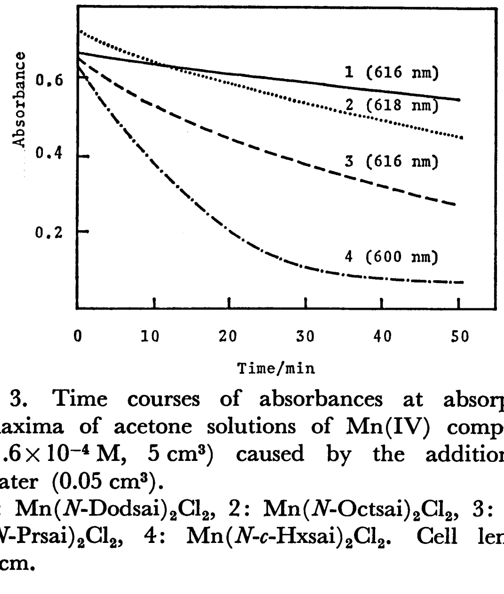


Fig. 3. Time courses of absorbances at absorption maxima of acetone solutions of Mn(IV) complexes (1.6×10^{-4} M, 5 cm^3) caused by the addition of water (0.05 cm^3).
1: Mn(*N*-Dodsai)$_2$Cl$_2$, 2: Mn(*N*-Octsai)$_2$Cl$_2$, 3: Mn(*N*-Prsai)$_2$Cl$_2$, 4: Mn(*N*-*c*-Hxsai)$_2$Cl$_2$. Cell length: 1 cm.

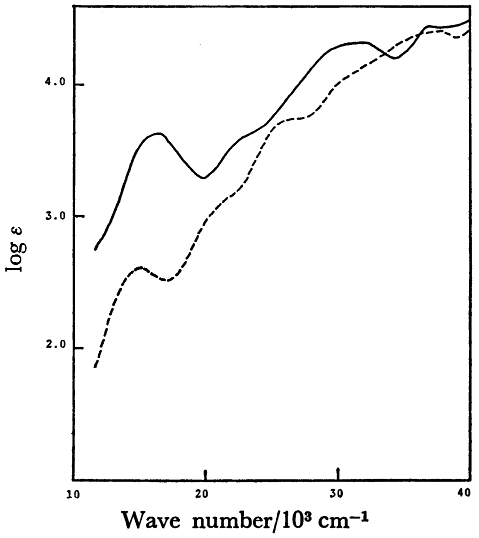


Fig. 4. Electronic spectra in dichloromethane.
——: Mn^{IV}(*N*-Octsai)$_2$Cl$_2$, ----: Mn^{III}(*N*-Octsai)$_2$Cl.

caused by the instability of the complex due to steric hindrance of the cyclohexyl group. In the case of Mn(*N*-Octdsai)$_2$Cl$_2$, such spectral changes could not be measured owing to its solubility restriction in acetone. However, this complex may be more water-resistant than the others investigated here, because that it showed no significant change on washing with water.

Magnetic Properties. The magnetic moments of the Mn(III) complexes fall within the range of 4.85 to 5.03 BM, with the exception of Mn(*N*-Bzsai)$_2$Cl (Table 1). This indicates that these complexes may have a d^4 high-spin electron configuration. The low value (4.26 BM) observed for the above complex may be caused by magnetic exchange interactions due to the formation of a binuclear complex in the solid state like Fe(salen)Cl.[8] Further investigation on the complex was not made in this work. On the other hand, the magnetic moments of the Mn(IV) complexes fall within the range of 3.84 to 4.08 BM; such moments are consistent with the spin-only value expected for a complex with a d^3 high-spin electron configuration.

Electionic Spectra. Figure 4 shows the electronic spectra of the complexes Mn^{III}(*N*-Octsai)$_2$Cl and Mn^{IV}(*N*-Octsai)$_2$Cl$_2$ in dichloromethane. In the Mn(III) complex, three absorption bands were observed in the visible region: at 15200, 21300 sh, and 26300 cm^{-1}. On the other hand, the electronic spectrum of the Mn(IV) complex shows an intense absorption band at 16000 cm^{-1} ($\log\varepsilon=3.62$). The frequencies of the absorption maxima for the Mn(III) and Mn(IV) complexes are summarized in Table 3. It is apparent from the Table that the alkyl groups of the Schiff base ligands have little effect on the frequencies for either Mn(III) or Mn(IV) complexes. These results suggest that the Mn(III) and Mn(IV) complex pairs may have similar configurations.

Recently, Boucher *et al.* have reported the absorption spectra of Mn^{III}(X-salen)Cl[9] and Mn^{III}(acacen)Cl[10] in noncoordinating solvents; here X-salen and acacen denote dianions of *N*,*N*′-di(substituted salicylidene)ethylenediamine and *N*,*N*′-bis(2-acetyl-1-methylethylidene)ethylenediamine, respectively. The X-ray structural analysis of the latter complex has revealed that its coordination polyhedron approximates an idealized C_{4v} symmetry.[10] They have assigned the three absorption bands observed for Mn(acacen)Cl in chloroform as follows; the band at 16400 cm^{-1} ($\log\varepsilon=2.31$) to $d_{xy}\rightarrow d_{x^2-y^2}$, the band at 22400 cm^{-1} (3.23) to $d_{xy}\rightarrow\pi^*$ (azomethine) involving $d_{yz},d_{zx}\rightarrow d_{x^2-y^2}$ as a lower energy shoulder, and the band at 26200 cm^{-1} (3.81) to $d_{yz},d_{xz}\rightarrow\pi^*$ (azomethine). The absorption spectra of the present Mn(III) complexes are similar to that of the above complex, suggesting that these Mn(III) complexes may have a five-coordinate structure ($\approx C_{4v}$) in dichloromethane. Therefore, the absorption bands near 15200 cm^{-1} can be safely assigned to the ligand field transition due to $d_{xy}\rightarrow d_{x^2-y^2}$.

TABLE 3. SPECTROSCOPIC DATA FOR MANGNESE(III) AND MANGANESE(IV) COMPLEXES

R	$Mn^{III}(N\text{-}Rsai)_2Cl$			$Mn^{IV}(N\text{-}Rsai)_2Cl$		
	$\frac{\nu_{max}}{10^3\ cm^{-1}}$ (log ε)a)		$\frac{\nu(Mn\text{–}Cl)}{cm^{-1}}$	$\frac{\nu_{max}}{10^3\ cm^{-1}}$ (log ε)a)		$\frac{\nu(Mn\text{–}Cl)}{cm^{-1}}$
Pr	15.1 (2.59)	21.3 sh 26.3 (3.74)	299	16.1 (3.63)	23.7 sh 31.2 (4.33)	351
Bu	15.2 (2.62)	21.3 sh 26.5 (3.74)	315	16.1 (3.66)	23.6 sh 31.3 (4.36)	347
i-Bu	15.2 (2.64)	21.3 sh 26.5 (3.75)	327	15.9 (3.63)	23.5 sh 31.4 (4.33)	354
Hx	15.2 (2.48)	21.3 sh 26.7 (3.67)	314	16.1 (3.62)	23.5 sh 31.6 (4.40)	348
c-Hx	15.2 (2.54)	21.3 sh 25.9 (3.71)	317	16.6 (3.55)	23.5 sh 31.8 (4.31)	351
Oct	15.2 (2.60)	21.3 sh 26.3 (3.73)	317	16.0 (3.62)	23.6 sh 31.3 (4.32)	348
Dod	15.1 (2.62)	21.3 sh 26.5 (3.75)	321	16.1 (3.59)	23.6 sh 31.6 (4.44)	348
Octd	15.2 (2.61)	21.3 sh 26.5 (3.74)	322	16.2 (3.53)	23.6 sh 31.6 (4.35)	348
Bz	15.1 (2.64)	21.3 sh 26.3 (3.73)	318	16.2 (3.55)	22.7 sh 31.6 (4.30)	350
PE	15.1 (2.60)	21.3 sh 26.3 (3.75)	305	16.1 (3.53)	22.4 sh 31.4 (4.26)	347

a) Measured in dichloromethane.

Previously we have observed intense absorption bands around 16000 cm^{-1} (log $\varepsilon \approx 3.5$) for the complexes $Mn^{IV}(X\text{-salen})Cl_2$ and $Mn^{IV}(N\text{-Bu-X-sai})_2Cl_2$ and have assigned them to the charge transfer transition due to Cl to Mn on the basis of the intensity. Thus the intense absorption bands near 16000 cm^{-1} observed for the present Mn(IV) complexes can be assigned to the same transition. The ligand field transitions which are expected for a complex with a d^3 high-spin configuration may be obscured by the intense charge transfer band. Therefore, the absorption bands near 23600 cm^{-1} cannot be easily assigned.

Infrared Spectra. The IR spectra of the Mn(IV) complexes are almost the same as those of the corresponding Mn(III) complexes in the 4000 to 500 cm^{-1} region, indicating that the Schiff base ligands coordinate with manganese ions by the same fashion in both complexes. However, in the 500 to 250 cm^{-1} region, the IR spectra of the Mn(III) and Mn(IV) complexes differ markedly, especially in the region sensitive to the ν(Mn–Cl). The absorption bands observed at 310 cm^{-1} for $Mn(N\text{-Prsai})_2Cl$[11], at 290 cm^{-1} for Mn(acac)Cl,[12] and at 279 cm^{-1} for Mn(acacen)-Cl[10] have been assigned to the ν(Mn–Cl); here acac denotes the monoanion of acetylacetone. In the present Mn(III) complexes, strong bands were observed around 310 cm^{-1}; these may be assigned to the ν(Mn–Cl). The band positions are listed in Table 3. On the other hand, the IR spectra of the Mn(IV) complexes showed strong bands around 350 cm^{-1}. The absorption band observed at 358 cm^{-1} for $K_2Mn^{IV}Cl_6$ has been assigned to the ν(Mn–Cl).[13] It is expected that the band due to the ν(Mn–Cl) may be shifted to higher frequencies on going from Mn(III) to Mn(IV), since the Mn(III) complexes have a five-coordinate structure, while the Mn(IV) complexes have a six-coordinate structure. The absorption bands observed around 350 cm^{-1} for the Mn(IV) complexes are assigned to the ν(Mn–Cl). The band positions are listed in Table 3. In the previous paper we have pointed out that the dichloromanganese(IV) complexes with the bidentate Schiff base ligands may have a *cis*- or *trans*-octahedral configuration; with the com-

TABLE 4. REDUCTION POTENTIALS FOR MANGANESE(IV) COMPLEXES

Complex	$\frac{E_{p/2}\ vs.\ SCE^{a)}}{V}$	
	$Mn^{IV}\rightarrow Mn^{III}$	$Mn^{III}\rightarrow Mn^{II}$
$Mn(N\text{-Prsai})_2Cl_2$	0.84	−0.12(−0.18)b)
$Mn(N\text{-Busai})_2Cl_2$	0.84	−0.17(−0.13)
$Mn(N\text{-}i\text{-Busai})_2Cl_2$	0.81	−0.18(−0.15)
$Mn(N\text{-Hxsai})_2Cl_2$	0.82	−0.12(−0.15)
$Mn(N\text{-}c\text{-Hxsai})_2Cl_2$	0.75	−0.21(−0.15)
$Mn(N\text{-Octsai})_2Cl_2$	0.83	−0.12(−0.16)
$Mn(N\text{-Dodsai})_2Cl_2$c)	0.79	−0.17(−0.15)
$Mn(N\text{-Octdsai})_2Cl_2$c)	0.75	−0.11(−0.16)
$Mn(N\text{-Bzsai})_2Cl_2 \cdot CH_2Cl_2$	0.87	−0.05(−0.12)
$Mn(N\text{-PEsai})_2Cl_2$	0.84	−0.11(−0.13)

a) Measured in acetonitrile containing 0.1 M Bu_4NClO_4 at 25 °C. b) Half-peak potentials for the corresponding manganese(III) complexes. c) Measured in acetonitrile-dichloromethane (2/1 volume ratio).

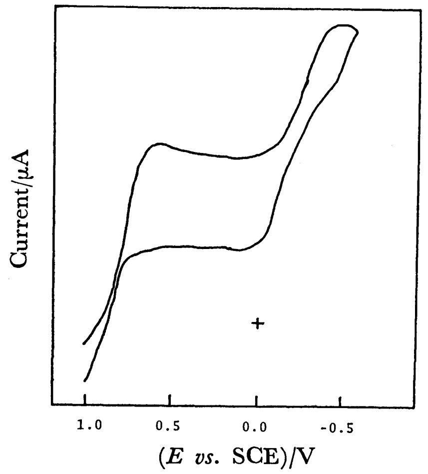


Fig. 5. Current-potential curve of $Mn^{IV}(N\text{-}i\text{-Busai})_2Cl_2$ measured in acetonitrile at 25 °C. Scan rate was 0.06 V s^{-1}.

plexes in which two chlorine atoms coordinate with manganese ion in a *cis*-form two absorption bands due to the ν(Mn–Cl) would be observed, while there is only one band in a *trans*-form. In the present Mn(IV) complexes, one strong band assignable to the ν(Mn–Cl) was observed, suggesting that two chlorine atoms may coordinate with manganese ion in a *trans*-form.

The coordination features of the bidentate Schiff base ligands cannot be determined from the available data. However, the structures of the Ni(II) complexes with the *N*-alkylsalicylideneamines have been investigated extensively and explained as follows. The complexes with *n*-alkyl groups have a *trans*-planar configuration. If the alkyl chain is branched at the β-carbon, as in the Ni(*N*-*i*-Busai)$_2$, the steric situation is very similar to the *n*-alkyl case and no tetrahedral form is observed.[14)] In the present work, attempts to isolate $\mathrm{Mn^{IV}}$(*N*-Rsai)$_2$Cl$_2$ (R=*i*-C_3H_7 and *s*-C_4H_9) were unsuccessful, perhaps because of the instability due to the steric hindrance of these groups. These results suggest that the present Mn(IV) complexes are in a *trans*, six-coordinate configuration, as shown in Fig. 1, but the Schiff base ligands may deviate from planarity to varying degrees.

Electrochemical Properties. The current-potential curve of the complex $\mathrm{Mn^{IV}}$(*N*-*i*-Busai)$_2$Cl$_2$, is shown in Fig. 5. Two-step cathodic waves with a similar wave height were observed at the half-peak potentials of +0.81 and −0.18 V(*vs.* SCE); these can be assigned to the reductions of Mn(IV) to Mn(III) and Mn(III) to Mn(II), respectively. The reduction potentials for the Mn(IV) complexes are given in Table 4, together with those for the Mn(III) complexes. The potentials for both reductions are not much affected by the alkyl groups of the Schiff base ligands. These results are consistent with the spectroscopic data.

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