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Redox Properties for Pentacoordinated Manganese(III) Complexes with Bis(salicylideneamino)alkanes

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Synopsis. The oxidation potentials of Mn(III/IV) for pentacoordinated chloromanganese(III) complexes with bis(salicylideneamino)alkanes shifted cathodically in the presence of excess chloride ions in their solution. The formation of dichloromanganese(IV) complexes with Schiff bases was spectrophotometrically detected by addition of chloride and hydrogen ions to acetonitrile solutions of the corresponding chloromanganese(III) complexes under aerobic conditions.

The chemistry of manganese(III) and (IV) complexes has been of interest in relation to the catalytic activity of manganese enzymes, such as the oxygen evolution process of photosystem II.[1–3] Previously, Matsushita et al. described a unique synthetic method for manganese(IV) complexes, in which dichloromanganese(IV) complexes with tetradentate or bidentate Schiff bases were prepared by treating the corresponding chloromanganese(III) complexes with hydrochloric acid.[4,5] We have also prepared a tetrachlorodimanganese(IV) complex with an octadentate binucleating Schiff base from the corresponding dichlorodimanganese(III) complex by applying the same synthetic method.[6] This is of interest because hydrochloric acid is not able to oxidize manganese(III) to (IV) as an oxidizing agent.

In this study, the electrochemical properties of pentacoordinated manganese(III) complexes with tetradentate Schiff base, 1,2-bis(salicylideneamino)ethane (H_2salen) and 1,3-bis(salicylideneamino)propane (H_2saltn), were investigated; the role of hydrochloric acid is discussed here.

Experimental

Syntheses. All of the pentacoordinated manganese(III) complexes were prepared in an identical manner, employing a modified method from the literature.[7–9] This may be illustrated for Mn(saltn)Cl.

Mn(saltn)Cl: 1,3-Propanediamine (10 mmol) and salicylaldehyde (20 mmol) were dissolved in ethanol (30 cm^3) and then refluxed for 3 h. Manganese(II) chloride tetrahydrate (10 mmol) was added to the reaction mixture; it was then refluxed for 1 h under aerobic conditions. The obtained dark-green solution was filtered and the filtrate was allowed to stand over night. Dark-green fine crystals were deposited; they were then filtered off, washed with ethanol, and dried in vacuo. The yield was ca. 55%. Found: C, 54.38; H, 5.21; N, 6.65%. Calcd for $C_{17}H_{16}N_2O_2MnCl\cdot C_2H_5OH$: C, 54.75, H, 5.32, N, 6.72%.

[Mn(saltn)H$_2$O]ClO$_4$: Found: C, 44.87; H, 4.08; N, 6.13%. Calcd for $C_{17}H_{18}N_2O_7MnCl$: C, 45.10; H, 4.00; N, 6.19%.

Mn(salen)Cl: Found: C, 48.81; H, 4.60; N, 7.14%. Calcd for $C_{16}H_{14}N_2O_2MnCl\cdot 2H_2O$: C, 48.93; H, 4.62; N, 7.13%.

[Mn(salen)H$_2$O]ClO$_4$: Found: C, 43.63; H, 3.69; N, 6.36%. Calcd for $C_{16}H_{16}N_2O_7MnCl$: C, 43.81; H, 3.68; N, 6.39%.

Measurements. The electronic spectra were obtained using a Hitachi 220A or U3210 recording spectrophotometer. The electric conductivities were determined by a Horiba Conductivity Meter (Model DS-14). Polarograms were recorded on a Yanagimoto Polarographic Analyzer (Model P-1100) by the use of a three-electrode cell equipped with glassy carbon as a working electrode, a platinum coil as a auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. In practice, all of the potentials were normalized by using ferrocene as an internal standard.

Results and Discussion

In methanol solutions, all of the perchlorate and chloro complexes, $[Mn(SB)H_2O]ClO_4$ and Mn(SB)Cl (where SB is salen^{2-} or saltn^{2-}) showed almost identical spectral features, indicating the formation of a solvated complex, such as $[Mn(SB)(CH_3OH)_2]^+$. This result is supported by their molar conductivities in methanol at 25 °C (Table 1), whose values are consistent with a 1:1 electrolyte.[10] When tetrabutylammonium chloride (TBACl) was added to the methanol solutions up to a molar ratio of [TBACl]/[complex]=200, the electronic spectra of the complexes were little affected and the specific conductivity was linearly increased with an increase in the concentration of TABCl. It is concluded that monocationic complexes can exist in a methanol solution even with excess chloride ions.

On the other hand, molar conductivity data for the chloro complexes demonstrate essentially nonelectrolyte in acetonitrile (Table 1).[10] Each of the observed spectra of the four complexes in acetonitrile and of the two chloro complexes in dichloromethane can be interpreted as being the spectrum of a pentacoordinated manganese(III) complex.[8,9,11] From optical measurements, the perchlorate complexes are changed to the corresponding chloro complexes by the addition of excess TBACl in acetonitrile, respectively. The absorption spectra of Mn(saltn)Cl and $[Mn(saltn)H_2O]ClO_4$ are shown in Fig. 1 as an example. A plot of the specific conductivity of the perchlorate complex vs. [TBACl]/[complex] in acetonitrile is almost constant within the TBACl concentration range below 1 in molar ratio. The above-mentioned results suggest that an apical ligand substitution occurs in the presence of the chloride ion as follow:

$$[Mn(SB)H_2O]^+ + ClO_4^- + TBA^+ + Cl^- \longrightarrow \\ Mn(SB)Cl + H_2O + TBA^+ + ClO_4^-.$$

Each of the four manganese(III) complexes exihibits

Table 1. Molar Conductivities and Electrochemical Data for Manganese(III) Complexes

Complex	Solvent	Λ_{M}[a]	TBAX[b]	E_{pc}	E_{pa}	ΔE_{p}	$E'_{1/2}$[c]	$E_{1/2}$
		S cm² mol⁻¹		V	V	mV	V	V
Mn(salen)Cl	CH_3OH	0.70×10²	ClO_4	−0.635	−0.560	75	−0.598	−0.590
								0.770
			Cl	−0.649	−0.575	74	−0.612	−0.610
								0.653
	CH_3CN	2.69	ClO_4	−0.668	−0.583	85	−0.626	−0.645
				0.423	0.651	228	0.537	0.643
			Cl	−0.728	−0.560	168	−0.644	−0.699
				0.223	0.313	90	0.268	0.264
	CH_2Cl_2		ClO_4	−0.701	−0.595	106	−0.648	−0.651
								0.571
			Cl	−0.741	−0.659	82	−0.700	−0.729
								0.291
$[Mn(salen)H_2O]ClO_4$	CH_3OH	1.08×10²	ClO_4	−0.645	−0.570	75	−0.608	−0.600
								0.740
			Cl	−0.652	−0.574	78	−0.613	−0.601
								0.746
	CH_3CN	1.55×10²	ClO_4	−0.606	−0.540	66	−0.573	−0.574
								1.083
			Cl	−0.755	−0.522	233	−0.639	−0.731
				0.219	0.322	103	0.271	0.268
Mn(saltn)Cl	CH_3OH	1.00×10²	ClO_4	−0.570	−0.490	80	−0.530	−0.522
								0.780
			Cl	−0.575	−0.495	80	−0.535	−0.535
	CH_3CN	3.10	ClO_4	−0.558	−0.463	95	−0.511	−0.503
								0.467
			Cl	−0.640	−0.450	190	−0.545	−0.575
								0.285
	CH_2Cl_2		ClO_4	−0.573	−0.488	85	−0.531	−0.528
								0.597
			Cl	−0.635	−0.550	85	−0.592	−0.595
								0.245
$[Mn(saltn)H_2O]ClO_4$	CH_3OH	1.02×10²	ClO_4	−0.565	−0.485	80	−0.525	−0.512
								0.740
			Cl	−0.565	−0.485	80	−0.525	−0.524
	CH_3CN	1.21×10²	ClO_4	−0.459	−0.394	65	−0.427	−0.429
								1.074
			Cl	−0.617	−0.455	162	−0.536	−0.575
								0.295

a) Measured at 25 °C. The concentration of the complexes was 5.0×10^{-4} mol dm⁻³. b) TBAX means tetrabutylammonium salts used as a supporting electrolyte. c) $E'_{1/2}=(E_{\mathrm{pc}}+E_{\mathrm{pa}})/2$.

two redox waves attributable to the manganese center, since the ligands do not show any redox waves at these potential region (Table 1). The oxidation potentials observed are dependent on the charge of the manganese(III) complexes in solution. Namely, the monocationic complexes show irreversible oxidation waves at 0.74—0.78 V in methanol and 1.1 V in acetonitrile. The neutral chloro complexes, however, are oxidized at 0.47—0.64 V in acetonitrile and dichloromethane. When excess chloride ions exist in the solution, the oxidation potentials of the chloro complexes shift negatively to 0.26—0.30 V (Table 1). Furthermore, in the case of the acetonitrile solutions of Mn(salen)Cl and $[Mn(salen)H_2O]ClO_4$, a cathodic peak is detected in the reverse scan by the addition of excess chloride ions, in which the peak-to-peak separation (ΔE_{p}) is 90—103 mV and the peak ratio ($i_{\mathrm{pc}}/i_{\mathrm{pa}}$) is almost equal to unity. Under the same experimental conditions, the normally reversible one-electron oxidation of ferrocene displays rather large ΔE_{p} values of ca. 60 mV. Accordingly, we have tentatively assigned the oxidation waves to an irreversible one-electron transfer process for Mn(III/IV).

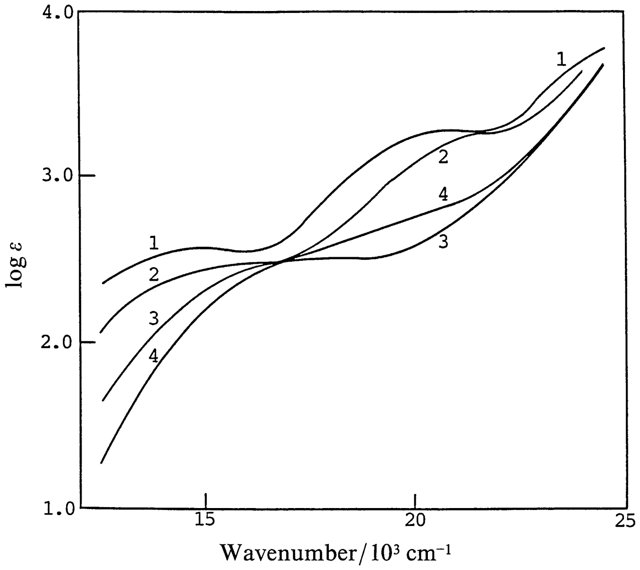

Fig. 1. Electronic spectra of Mn(saltn)Cl in dichloromethane (1), in acetonitrile (2), in methanol (3) and $[Mn(saltn)H_2O]ClO_4$ in acetonitrile (4).

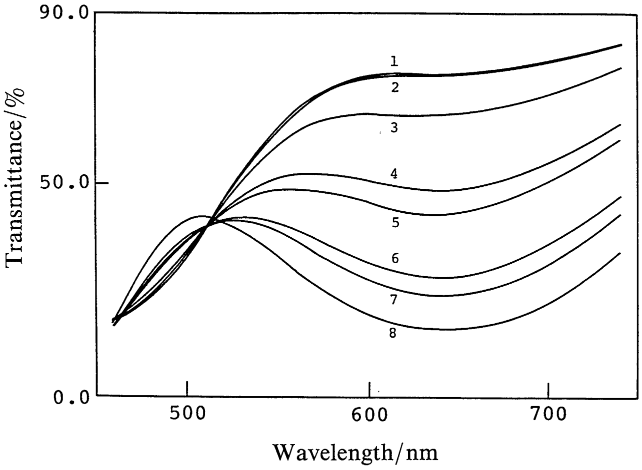

Fig. 2. Spectral changes on addition of perchloric acid to an acetonitrile solution of 5.0×10^{-4} mol dm^{-3} Mn(saltn)Cl in different molar ratios. 1: $[HClO_4]/[complex]=0.00$, 2: 0.02, 3: 0.10, 4: 0.30, 5: 0.40, 6: 0.80, 7: 1.00, 8: 2.00.

It is noted that those oxidation potentials (0.26—0.30 V) appear at a more negative region than does the reduction potential of Mn(IV/III) (0.36 V) for the dichloromanganese(IV) complex with 1,2-bis(salicylideneamino)-1-phenylethane.⁶⁾ This significant cathodic shift of the potentials is interpreted as meaning that the manganese(IV) state formed electrochemically is stabilized by a further participation of chloride ions to the manganese(IV) coordination sphere. However, only an addition of excess chloride ions to the manganese(III) complex solution is not sufficient to obtain the manganese(IV) complex.

When perchloric acid was added to the acetonitrile solution of the chloro complexes, Mn(salen)Cl and Mn(saltn)Cl, a new absorption band appeared around 640 nm. Figure 2 shows the spectral changes of Mn(saltn)Cl as an example. This band can be assigned to the CT band of the Cl^- to Mn(IV).⁴⁾ Accordingly, this spectral change suggests the formation of dichloromanganese(IV) complexes. The intensity of the CT band is increased with an increase in the concentrations of chloride and hydrogen ions. However, rapid decolorization occurs upon adding these excess ions, indicating a decomposition of the complexes. The most intense absorption band was obtained with an acetonitrile solution containing TBACl and perchloric acid at a molar ratio of $[complex]:[TBACl]:[HClO_4]=1:3:2$, in which $[complex]=5.0\times10^{-4}$ mol dm^{-3}. The yield of $Mn(salen)Cl_2$ under the above-mentioned conditions is about 42%, which is determined spectrophotometrically based on literature data for its CT band.⁴⁾

The CT band was observed by using sulfuric acid instead of perchloric acid as a hydrogen ion source, but was not detected by using acetic acid, whose dissociation constant in acetonitrile is $10^{-22.3}$.¹²⁾ Furthermore, the presence of oxygen is necessary for the above reaction, since the CT band can not be obtained under anaerobic conditions. In a methanol solution, only the decomposition of the complexes is observed for any concentration ratios of TBACl and $HClO_4$ under aerobic conditions. These results imply that the dichloromanganese(IV) complex is formed by the addition of chloride and hydrogen ions to a solution containing the corresponding pentacoordinated chloromanganese(III) complexes under aerobic conditions.

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