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Reactions of Manganese(III) Schiff Base Complexes with Superoxide Ion in Dimethyl Sulfoxide

Takayuki MATSUSHITA* and Toshiyuki SHONO

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

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The reactions of the chloromanganese(III) complexes of the Schiff bases derived from salicylaldehydes or β-diketones and diamines or monoamines with superoxide ion, O_2^-, in dimethyl sulfoxide were investigated. The complexes were found to react to give either the oxygenated Mn Schiff base complexes or the reduced Mn(II) Schiff base complexes. The difference in the reactivity toward O_2^- was correlated to the polarographic half-wave potentials corresponding to the reduction of Mn(III) to Mn(II) of the complexes. Some oxygenated complexes were isolated and characterized.

Manganese complexes have been of interest in connection with the biological redox processes including catalytic disproportionation of superoxide ion, O_2^-. Examples are the manganese-containing superoxide dismutases (Mn–SOD) and the oxygen evolving photosystem II in green plants.[1)] In the Mn–SOD process, a manganese ion may exist in the oxidation state of +III.[2,3)] Recently, McAdam *et al.* have reported that the reaction of the Mn–SOD with O_2^- depends on a ratio of O_2^- concentration to the enzyme and that at high ratios (>15) it can not be explained by the simple two-step mechanism proposed for the Cu–SOD. Thus, they have postulated a kinetic model including a form of the enzyme, E_C, as follows:

$$E_A + O_2^- \longrightarrow E_B + O_2$$

$$E_B + O_2^- \xrightarrow{2H^+} E_A + H_2O_2$$

$$E_B + O_2^- \longrightarrow E_C$$

$$E_C \longrightarrow E_A,$$

where E_A represents a native oxidized enzyme, E_B a reduced enzyme, and E_C an enzyme unreactive toward O_2^-.[4)]

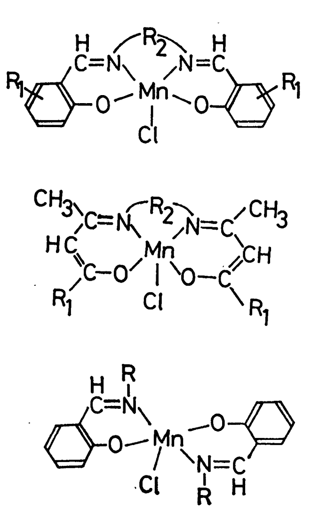
Howie *et al.* have reported that the reaction of the manganese(II) and -(III) 8-quinolinol complexes with O_2^- in dimethyl sulfoxide (DMSO) can be considered as a redox model for the Mn–SOD.[5)] Valentine *et al.* have found that $Mn^{III}(tpp)Cl$ reacts with O_2^- in DMSO to give $Mn^{II}(tpp)$; here tpp denotes tetraphenylporphyrin dianion.[6)] Recently, Stein *et al.* have reported that $Mn^{III}(cydta)^-$ and $Mn^{III}(edta)^-$ react with O_2^- in DMSO to give $Mn^{II}(cydta)^{2-}$ and $Mn^{II}(edta)^{2-}$, respectively, where H_4cydta and H_4edta denote 1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetic acid and ethylenediaminetetraacetic acid, respectively.[7)]

In this paper we report on the reactions of a series of the chloromanganese(III) Schiff base complexes (Fig. 1) with O_2^- in DMSO.

Experimental

Preparation of Chloromanganese(III) Schiff Base Complexes. All the chloromanganese(III) Schiff base complexes were prepared by the following method, adapted from the literature.[8,9)]

Chloro[N,N′-*bis(2-benzoyl-1-methylethylidene)ethylenediaminato*]-*manganese(III), Mn(bzacen)Cl.* To a dichloromethane ($50\ cm^3$)-methanol ($50\ cm^3$) solution of *N,N′*-bis(2-benzoyl-1-methylethylidene)ethylenediamine (3.47 g), manganese(III) acetate dihydrate, $Mn(CH_3COO)_3 \cdot 2H_2O$ (2.68 g), was added. The mixture was allowed to stand at 40 °C for 30 min, and then lithium chloride (0.6 g) was added. After having been



R_1	R_2	L
H	CH_2CH_2	salen
5-CH_3	CH_2CH_2	5-Mesalen
5-Br	CH_2CH_2	5-Brasalen
5-NO_2	CH_2CH_2	5-NO_2salen
5,6-Benzo	CH_2CH_2	5,6-Benzosalen
3-OCH_3	CH_2CH_2	3-MeOsalen
H	C_6H_4	salphen
H	C_6H_{10}	salchxn
H	$CH(CH_3)CH_2$	salpln
CH_3	CH_2CH_2	acacen
C_6H_5	CH_2CH_2	bzacen
CH_3	$CH(CH_3)CH_2$	acacpln
C_6H_5	$CH(CH_3)CH_2$	bzacpln
R	L′	
C_3H_7	*N*-Prsai	
C_4H_9	*N*-Busai	
C_6H_{11}	*N*-c-Hxsai	

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

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(acacen)Cl·$(H_2O)_{0.5}$	44.81	5.95	8.71	16.92	45.02	5.72	8.97	17.08	4.96
Mn(acacpln)Cl·$(H_2O)_{0.3}$	46.98	6.22	8.51	16.40	46.93	6.21	8.42	16.51	4.77
Mn(bzacen)Cl	60.20	4.91	6.23	12.35	60.49	5.08	6.41	12.58	4.91
Mn(bzacpln)Cl	61.75	5.60	6.08	12.02	61.27	5.37	6.21	12.19	4.81
Mn(5,6-Benzosalen)Cl	62.84	3.96	5.93	11.89	63.10	3.97	6.13	12.03	4.97

a) Measured at room temperature.

stirred for 1 h, the solution was concentrated to *ca.* 20 cm^3 under reduced pressure. Ether (200 cm^3) was then added to precipitate brown solids. They were collected on a glass filter, washed with small volumes of water, 2-propanol, and then ether, and then dried *in vacuo*. They were recrystallized from dichloromethane. The yield was *ca.* 60%. The analytical data and the magnetic moments of some manganese(III) complexes are given in Table 1.

Isolation of Oxygenated Complexes. *[Mn(salen)]$_2$O$_2$, Complex* **1** *and [Mn(salen)O]$_n$, Complex* **2**. To a DMSO solution of Mn(salen)Cl·H_2O (0.7 g) and 18-crown-6 ether (0.5 g), potassium superoxide, KO_2 (0.15 g) was added in a nitrogen atmosphere at room temperature. After having been stirred for 2 h, the solution was evaporated to remove DMSO under reduced pressure. The reddish brown solids which separated were collected on a glass filter, washed with water, methanol, and then ether, and then dried *in vacuo*. The solids were extracted with dichloromethane (500 cm^3). The dichloromethane solution was evaporated under reduced pressure to give reddish brown needles, complex **1**, which was identified to be [Mn(salen)]$_2$O$_2$ by the infrared spectrum and the magnetic susceptibilities. On the other hand, the insoluble product in dichloromethane was identified to be [Mn(salen)O]$_n$, complex **2**. The yields of complexes **1** and **2** were 0.21 and 0.43 g, respectively. When the reaction of Mn(salen)Cl·H_2O with KO_2 in DMSO was carried out in the absence of 18-crown-6 ether, the yields of complexes **1** and **2** were 0.03 and 0.50 g, respectively.

The oxygenated manganese complexes, Mn(salchxn)O·H_2O and Mn(5,6-benzosalen)O·H_2O were obtained by the reactions of the corresponding chloromaganese(III) complexes with KO_2 in DMSO and benzene, respectively. These complexes were reddish brown powders and were insoluble in common organic solvents. Therefore, further purification could not be performed. Mn(salchxn)O·H_2O: Found: C, 58.70; H, 4.98; N, 6.98; Mn, 13.23%. Calcd for Mn($C_{20}H_{22}N_2O_4$): C, 58.69; H, 5.42; N, 6.84; Mn, 13.42%. IR: 650 and 618 cm^{-1} (νMn–O). Magnetic moment at room temperature: 1.89 BM. Mn(5,6-Benzosalen)O·H_2O: Found: C, 63.93; H, 3.99; N, 6.23; Mn, 12.25%. Calcd for Mn($C_{24}H_{20}N_2O_4$): C, 63.31; H, 4.43; N, 6.15; Mn, 12.06%. IR: 653 and 603 cm^{-1} (νMn–O). Magnetic moment at room temperature: 2.90 BM.

[Mn(bzacen)O]·$(CH_2Cl_2)_{0.3}$: To a benzene solution (200 cm^3) containing Mn(bzacen)Cl (0.7 g) and 18-crown-6 ether (0.5 g), KO_2 (0.15 g) was added in a nitrogen atmosphere. The solution turned the color from brown to reddish brown gradually on stirring for 2 h. The mixture was filtered and the filtrate was evaporated under reduced pressure. The precipitated solids were collected on a filter, washed with small volumes of water and methanol and then thoroughly with ether, and then dried *in vacuo*. On recrystallization from dichloromethane, reddish brown needles were obtained. The yield was *ca.* 0.2 g. The complex is soluble in dichloromethane and slightly soluble in DMSO. Found: C, 60.07; H, 5.16; N, 6.10; Mn, 12.39%. Calcd for Mn($C_{22}H_{22}N_2O_3$)(CH_2Cl_2)$_{0.3}$: C, 60.48; H, 5.14; N, 6.33; Mn, 12.40%. IR: 650 cm^{-1} (νMn–O). Magnetic moment at room temperature: 2.55 BM.

The oxygenated complex, Mn(bzacpln)O·$(CH_2Cl_2)_{0.4}$ was obtained in a similar manner. Found: C, 60.45; H, 5.25; N, 6.02; Mn, 11.84%. Calcd for Mn($C_{23}H_{24}N_2O_3$)(CH_2Cl_2)$_{0.4}$: C, 60.40; H, 5.37; N, 6.02; Mn, 11.81%. IR: 644 cm^{-1} (νMn–O). Magnetic moment at room temperature: 1.87 BM.

Reagents. All reagents were of reagent grade. Potassium superoxide, KO_2, was purchased from Alfa products Inc. (Above 96.5%). Dimethyl sulfoxide was distilled twice under reduced pressure prior to use. Benzene was distilled over sodium. Acetonitrile was refluxed over diphosphorus pentaoxide and distilled twice prior to use. Dichloromethane was distilled over calcium chloride.

Preparation of DMSO Solution of KO_2. A DMSO solution of KO_2 (*ca.* 10^{-2} M, 1 M=1 mol dm^{-3}) was prepared by dissolving KO_2 (18.7 mg) into DMSO (25 cm^3) in the presence of 18-crown-6 ether (0.1 g). The O_2^- concentration of the solution was determined by spectrophotometry.[10)]

Measurements. The UV, V, and NIR spectra were recorded on Hitachi EPS-3 and Hitachi 340 recording spectrophotometers. The IR spectra in the 4000—650 and 700—250 cm^{-1} regions were recorded on a Hitachi 215 and on a Hitachi EPI-L grating spectrophotometer, respectively. Polarograms were obtained by using a Yanagimoto p-8 polarograph. A dropping mercury electrode and a mercury pool were used as the working and the reference electrode, respectively; this avoided any effect of water on the reaction systems that would occur if a saturated calomel electrode was used. Tetrabutylammonium perchlorate, $(Bu)_4NClO_4$, was used as the supporting electrolyte and Triton-X 100 as the maximum suppressor. Magnetic susceptibilities were measured by a Gouy method at room temperature. The reactions of the manganese(III) complexes with O_2^- were carried out under nitrogen atmosphere.

Results and Discussion

It is supposed that in the native Mn–SOD the nitrogen and/or oxygen atoms of the amino acid residues of the proteins are coordinated with manganese ions, although the details of coordination structure have not yet been clarified. Recently, the manganese ion in the native Mn–SOD has been found to be in the oxidation state +III.[2,3)] The reactions of the manganese(III) Schiff base complexes with O_2^- investigated here afford information in connection with the catalytic disproportionation of O_2^- by the Mn–SOD.

Visible Absorption Spectra. Figure 2 shows the

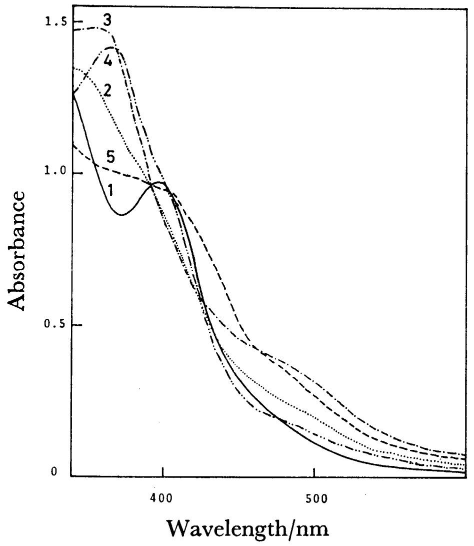


Fig. 2. Spectral changes of a DMSO solution of Mn(salen)Cl·H_2O, 2×10^{-4} M, caused by the addition of KO_2.
1): No addition, 2): $[KO_2]/[\text{complex}]=2$, 3): 4, 4): 6, 5): after passing O_2 through the solution shown by curve 4. Cell length: 1 cm.

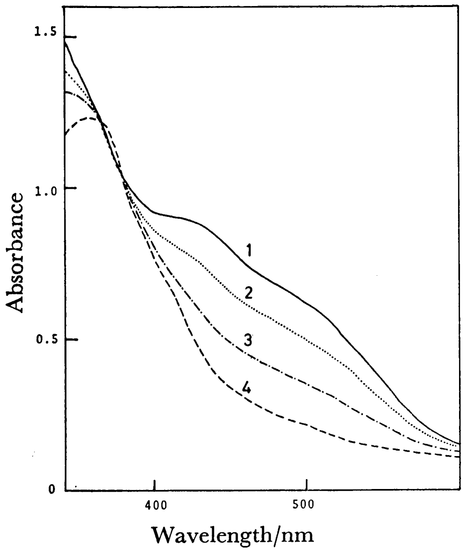


Fig. 3. Spectral changes of a DMSO solution of $[Mn(salen)]_2O_2$, 8×10^{-5} M, caused by the addition of KO_2.
1): No addition, 2): $[KO_2]/[\text{complex}]=3$, 3): 6, 4): 10. Cell length: 1 cm.

spectral changes of Mn(salen)Cl·H_2O in the DMSO solution caused by the addition of KO_2 in different molar ratios. The spectra changed remarkably, showing an isosbestic point at 390 nm. And a broad absorption band which appeared for the first time around 480 nm increased in intensity on the addition of KO_2 up to $[KO_2]/[\text{complex}]=4$; further amounts of KO_2 caused an decrease in the intensity and the appearance of an absorption band at 364 nm. These spectral changes can be interpreted as follows. The absorption band around 480 nm may be due to the formation of the oxygenated complex. This is supported by the fact that the oxygenated complex, $[Mn(salen)]_2O_2$, obtained by the reaction of Mn^{II}(salen) with molecular oxygen in DMSO is characterized by an intense absorption band in the same region.[11] The spectral changes observed on the further addition of KO_2 are considered to be due to a reaction of the oxygenated complex formed in solution with an excess amount of O_2^- to yield the manganese(II) complex, Mn^{II}(salen). This is confirmed by the facts that the absorption spectrum shown by curve 4 is in agreement with that of Mn^{II}(salen) in DMSO, and that by introducing molecular oxygen (O_2) into this solution it comes to show an absorption curve similar to that of the oxygenated complex, $[Mn(salen)]_2O_2$; this complex again reacts with O_2^-, showing similar spectral changes, as seen in Fig. 3.

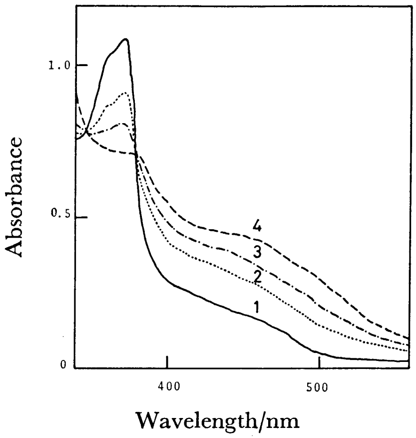


Fig. 4. Spectral changes of a DMSO solution of Mn(acacpln)Cl·$(H_2O)_{0.3}$, 2×10^{-4} M, caused by the addition of KO_2.
1): No addition, 2): $[KO_2]/[\text{complex}]=1.5$, 3): 2, 4): 2.5. Cell length: 1 cm.

Figure 4 shows the spectral changes for the complex Mn(acacpln)Cl by the addition of KO_2. These are similar to those observed for the complex Mn(salen)Cl·H_2O. This indicates that the oxygenation of Mn(acacpln)Cl occurs because of the reaction with O_2^-.

Figure 5 shows the spectral changes for the complex Mn(5-NO_2salen)Cl. Unlike the above two complexes, the intensity of the weak absorption band around 500 nm decreases with increasing intensity of a new absorption band at 402 nm. The final absorption curve shown by curve 4 in Fig. 5 is coincident with that of Mn^{II}(5-NO_2salen) in DMSO. This indicates that Mn(5-NO_2salen)Cl is reduced with O_2^- to form the manganese(II) complex. The spectral changes for the complex Mn^{III}(3-MeOsalen)Cl·H_2O are shown in Fig. 6. We previously reported that Mn^{II}(3-MeOsalen)·H_2O was readily oxidized by O_2 in common organic solvents to give the oxidized complex.[11] It is clearly evidenced in Fig. 6 that Mn^{III}(3-MeOsalen)Cl·H_2O is reduced with O_2^- to the manganese(II) complex. Bubbling O_2 into the solution including $[KO_2]/[\text{complex}]=3$ and showing absorption curve 4 results in the change of the absorption

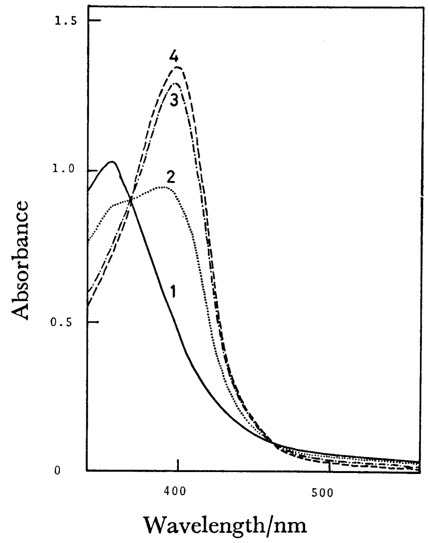


Fig. 5. Spectral changes of a DMSO solution of Mn(5-NO_2salen)Cl, 4×10^{-5} M, caused by the addition of KO_2.
1): No addition, 2): $[KO_2]/[complex]=1$, 3): 2, 4): 3. Cell length: 1 cm.

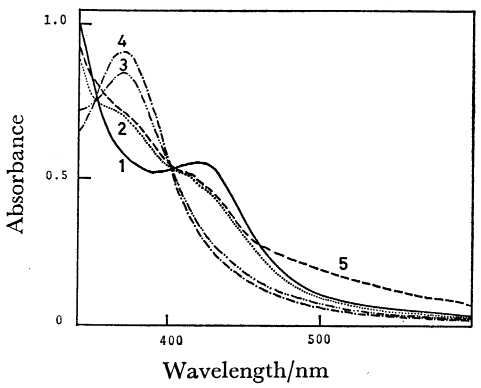


Fig. 6. Spectral changes of a DMSO solution of Mn(3-MeOsalen)Cl·H_2O, 1.0×10^{-4} M, caused by the addition of KO_2.
1): No addition, 2): $[KO_2]/[complex]=1$, 3): 2, 4): 3, 5): after passing O_2 through the solution shown by curve 4. Cell length: 1 cm.

to curve 5, which is quite like that observed in the reaction of Mn^{II}(3-MeOsalen)·H_2O with O_2 in DMSO.

Polarograms. The polarograms of the manganese(III) complexes show one cathodic wave around −0.2 V and one- or two-step cathodic waves in the −1.5—−2.0 V range. The polarogram of Mn(5-NO_2salen)Cl in DMSO is shown by curve 1 in Fig. 7. The first cathodic wave can be assigned to the reduction of Mn(III) to Mn(II) and the second and third waves may involve the reductions of the coordinated Schiff base ligand.[12,13] An addition of KO_2 to the solution of the complex ($[KO_2]/[complex]=2$) caused a decrease in the height of the first cathodic wave and the appearance of a new cathodic wave at a half-wave potential of −0.6 V. With increasing amounts of KO_2, the wave height of the former decreased and that of the latter increased. The above new cathodic wave can be easily assigned to the reduction of free O_2 in the solution, because the half-wave potential is nearly equal to that observed for dissolved O_2 and the wave would disappear readily if nitrogen gas was passed through the solution. The solution obtained after passing nitrogen gas has a polarogram which resembles that of Mn^{II}(5-NO_2salen). These results indicate that Mn(5-NO_2salen)Cl is reduced with O_2^- to yield the manganese(II) complex and O_2, $Mn^{III}L^+ + O_2^- \rightarrow Mn^{II}L + O_2$, where L denotes 5-$NO_2$-salen. This is consistent with the results observed in the absorption spectral changes.

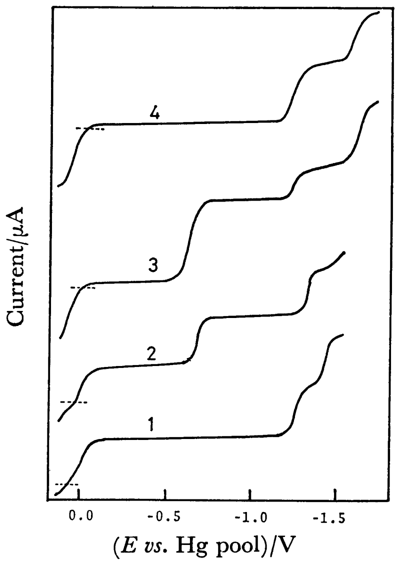


Fig. 7. Changes in polarograms during the reaction of Mn(5-NO_2salen)Cl, 2×10^{-4} M, with KO_2 in DMSO.
1): No addition of KO_2, 2): $[KO_2]/[complex]=2$, 3): 4, 4): after passing N_2 through the solution shown by curve 3.

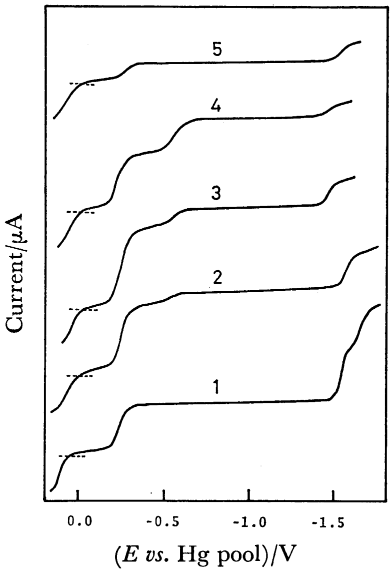


Fig. 8. Changes in polarograms during the reaction of Mn(bzacen)Cl, 2×10^{-4} M, with KO_2 in DMSO.
1): No addition of KO_2, 2): $[KO_2]/[complex]=1$, 3): 2, 4): 4, 5): after passing N_2 through the solution shown by curve 4.

The polarogram of Mn(bzacen)Cl shown in Fig. 8 exhibits three cathodic waves at the half-wave potentials of −0.3, −1.6, and −1.8 V. The first cathodic wave is due to the reduction of Mn(III) to Mn(II). By the addition of KO_2, the cathodic wave due to free O_2 barely appeared in the solution composed with $[KO_2]/[\text{complex}]=2$, though the wave height around −0.3 V was observed to increase. Further addition of KO_2 ($[KO_2]/[\text{complex}]=4$) caused a decrease in this wave height and an increase in the wave height due to free O_2. The polarogram obtained after passing nitrogen gas through the solution (shown by curve 4 in Fig. 8) exhibits only a small wave height at −0.3 V; this may be due to the residue of the manganese(III) complex. From these polarographic observation, the reaction of Mn(bzacen)Cl with O_2^- can be explained as follows. The increase in the wave height at −0.3 V observed at the molar ratio change from 1 to 2 may be caused by the formation of the oxygenated complex, hence the cathodic wave due to O_2 is slightly observed. At the molar ratio of 4 the oxygenated complex reacts with O_2^- to give the manganese(II) complex and O_2.

Reactivity toward O_2^-. In view of the reactivity toward O_2^- observed in the spectral and polarographic behavior, the chloromanganese(III) Schiff base complexes investigated here can be classified into two types: one involving the complexes which form the oxygenated complex in the solution containing KO_2 in the molar ratio of $[KO_2]/[\text{complex}]<2$—3, and the other involving the complexes which are only reduced to the corresponding manganese(II) complexes with the evolution of molecular oxygen. These results are summarized in Table 2, along with the half-wave potentials for the reduction of Mn(III) to Mn(II). The reactivity toward O_2^- is clearly correlated with the reduction potentials of the complexes. That is, the complexes having more negative potentials than that of Mn(salen)Cl·H_2O form the oxygenated complexes, whereas the complexes having more positive potentials than that of Mn(salpln)Cl are reduced to the manganese(II) complexes.

Table 2. Reduction potentials of manganese(III) complexes and reactivity toward O_2^-

Complex	$-E_{1/2}$[a] *vs.* Hg pool V Mn(III)→Mn(II)	Reactivity toward O_2^-
Mn(acacen)Cl·$(H_2O)_{0.5}$	0.39	Oxygenation
Mn(acacpln)Cl·$(H_2O)_{0.3}$	0.33	Oxygenation
Mn(bzacen)Cl	0.32	Oxygenation
Mn(bzacpln)Cl	0.30	Oxygenation
Mn(salchxn)Cl	0.21	Oxygenation
Mn(5-Mesalen)Cl	0.20	Oxygenation
Mn(5,6-Benzosalen)Cl	0.19	Oxygenation
Mn(salen)Cl·H_2O	0.19	Oxygenation
Mn(salpln)Cl	0.18	Reduction
Mn(3-MeOsalen)Cl·H_2O	0.15	Reduction
Mn(5-Brsalen)Cl	0.15	Reduction
Mn(salphen)Cl	0.08	Reduction
Mn(5-NO_2salen)Cl	0.03	Reduction
Mn(*N*-Busai)$_2$Cl	0.02	Reduction
Mn(*N*-Prsai)$_2$Cl	0.02	Reduction
Mn(*N*-c-Hxsai)$_2$Cl	0.00	Reduction

a) Measured in acetonitrile containing 0.1 mol dm^{-3} $(Bu)_4NClO_4$ at 25 °C.

Isolation and Characterization of the Oxygenated Complexes. Several oxygenated manganese complexes were isolated by the reactions of chloromanganese(III) Schiff base complexes with KO_2 in DMSO or benzene. In the case of Mn(salen)Cl·H_2O, two types of the oxygenated complexes, $[\text{Mn(salen)}]_2O_2$ and $[\text{Mn(salen)O}]_n$, were isolated. The former complex shows an intense broad absorption band around 480 nm. In the IR spectrum the former complex shows a strong band assignable to the Mn–O stretching vibration at 645 cm^{-1}, while the latter, which is insoluble in common organic solvents, shows two strong bands due to the Mn–O stretching vibrations at 665 and 605 cm^{-1}. The effective magnetic moments of $[\text{Mn(salen)}]_2O_2$ and $[\text{Mn(salen)O}]_n$ were 2.16 and 2.04 BM, respectively. These values are lower than the spin-only one which is expected for a complex with the d^4 or d^3 high-spin configuration; they may be caused by the antiferromagnetic interactions observed for the complexes where the manganese atoms are probably linked by the oxygen atoms: $\text{Mn}^{III}\text{–}O_2\text{–Mn}^{III}$ and $\text{-}[\text{Mn}^{IV}\text{–O}]\text{-}_n$.[11]

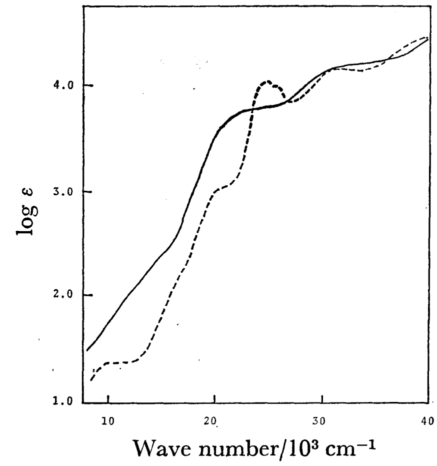


Fig. 9. Electronic spectra.
——: Mn(bzacen)O·$(CH_2Cl_2)_{0.3}$ in dichloromethane,
------: Mn(bzacen)Cl in DMSO.

The other oxygenated manganese complexes obtained in this work also show lower magnetic moments. The IR spectra of the oxygenated complexes, Mn(salchxn)O and Mn(5,6-Benzosalen)O, which are insoluble in common organic solvents, show two strong bands in the 700—600 cm^{-1} region. Therefore, these complexes may have a structure similar to that of $[\text{Mn(salen)O}]_n$. On the other hand, the IR spectra of the oxygenated complexes, Mn(bzacen)O and Mn(bzacpln)O, which are soluble in dichloromethane show one strong band in the 700—600 cm^{-1} region. Moreover, the electronic spectrum of Mn(bzacen)O in dichloromethane shows an intense absorption band around 500 nm, as shown in Fig. 9. These results suggest that the oxygenated complexes may have a structure similar to that of

$[\mathrm{Mn(salen)}]_2\mathrm{O}_2$. Since the manganese(II) complexes with the Schiff bases derived from β-diketones and diamines have not been isolated due to the instabilities, there has been no attempt to prepare their oxygenated complexes by reacting them with O_2.

Among the oxygenated manganese-Schiff base complexes, the compounds with such unitary groups as oxo (Mn=O), μ-oxo (Mn–O–Mn), catena-μ-oxo ($\leftarrow\!\mathrm{Mn{-}O}\!\rightarrow_n$), μ-peroxo (Mn–O–O–Mn), and di-μ-oxo $\left(\mathrm{Mn}\begin{smallmatrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\mathrm{Mn}\right)$ have so far been reported.[1b)] However, these structures have been determined only by the elemental analyses and the conventional physicochemical measurements, with the exception of the oxygenated product of $\mathrm{Mn^{II}}$-(salpn)·$\mathrm{H_2O}$. This has been revealed by X-ray structural analysis to be a di-μ-hydroxo structure $\left(\mathrm{Mn}\begin{smallmatrix}\diagup\mathrm{OH}\diagdown\\ \diagdown\mathrm{OH}\diagup\end{smallmatrix}\mathrm{Mn}\right)$, where salpn$\mathrm{H_2}$ denotes *N*,*N*′-disalicylidene-1,3-propanediamine.[14)]

The reactivity of $\mathrm{KO_2}$ with the present manganese(III) complexes will open a new route for synthesis and will provide a method of characterization for the oxygenated complexes.

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