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

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A series of monomeric chloroiron(III) complexes with the quadridentate or quinquedentate Schiff bases such as *N,N'*-disalicylideneethylenediamine or bis[3-(salicylideneamino)propyl]amine react with superoxide ions, O_2^-, in dimethyl sulfoxide to give the corresponding μ-oxo dimers. The polymeric chloroiron(III) complexes with the polymeric (oligomeric) Schiff bases derived from 5,5'-methylenedisalicylaldehyde and triamines react with O_2^- in dimethyl sulfoxide to give the oxygenated complexes, probably dioxygen adducts, $Fe^{III}–O_2^-$. This is suggested by the absorption spectra and the polarographic measurements.

The reactions of iron complexes with superoxide ions, O_2^-, are of interest in connection with the biological processes: the disproportionation of O_2^- by the iron-containing superoxide dismutases (Fe–SOD) and the catalytic utilization of molecular oxygen by the hemoproteins.

Hill *et al.* reported that $Fe^{III}(ppde)ClO_4$ reacts with O_2^- in *N,N*-dimethylformamide (DMF) to give $Fe(ppde)–O_2$ at low temperature (−50 °C).[1,2] McClune *et al.* proposed the formation of the peroxo complex, $[Fe^{III}(edta)–O_2]^{2-}$, by the reaction of $[Fe^{III}(edta)]^-$ with O_2^- in water on the basis of a stopped-flow spectrophotometry.[3] Recently, McCandlish *et al.* have reported that four different reaction pathways occurred in the reactions of O_2^- with iron porphyrins, as follows:

$$Fe^{III}(por)^+ + O_2^- \longrightarrow Fe^{II}(por) + O_2$$

$$2\,Fe^{III}(por)^+ + O_2^- \longrightarrow [Fe^{III}(por)]_2O$$

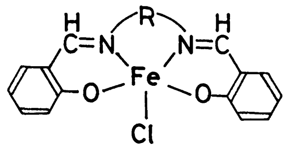
$$Fe^{III}(por)^+ + O_2^- \longrightarrow Fe(por)(O_2)$$

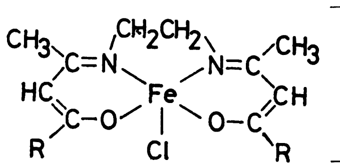
$$Fe^{II}(por) + O_2^- \longrightarrow Fe^{III}(por)(O_2^{2-}).$$

These reactions depend on conditions such as the solvent, the concentration, the presence or absence of traces of water, and the temperature.[4]

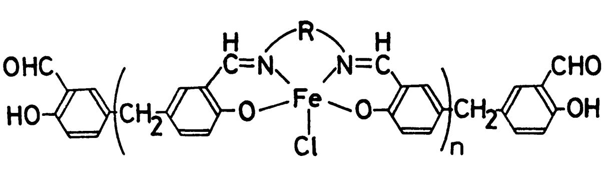
We have previously reported on the reactions of the monomeric and polymeric chloromanganese(III) Schiff base complexes with O_2^- in dimethyl sulfoxide (DMSO). With the monomeric complexes, they can be classified into two types in the reactivity toward O_2^-: one gives the oxygenated complexes and the other is reduced to the corresponding manganese(II) complexes. The reactivities toward O_2^- are found to be correlated to the polarographic half-wave potentials corresponding to the reduction from Mn(III) to Mn(II).[5] In the reactions of the polymeric complexes, the formation of their oxygenated complexes has been found.[6]

This paper describes the reactions between O_2^- and the monomeric and polymeric chloroiron(III) Schiff base complexes in DMSO. Some of the polymeric complexes showed a clearly different behavior in the changes of the absorption spectra and polarograms





R	Abbreviation of ligands
CH_2CH_2	salen
C_6H_4	salphen
$CH(CH_3)CH_2$	salpln
C_6H_{10}	salchxn
$(CH_2)_2NH(CH_2)_2$	saldien
$(CH_2)_3NH(CH_2)_3$	saldpt
$(CH_2)_3N(CH_3)(CH_2)_3$	salMedpt
CH_3	acacen
C_6H_5	bzacen



R	Abbreviation of ligands	R	Abbreviation of ligands
CH_2CH_2	p-salen	$(CH_2)_2NH(CH_2)_2$	p-saldien
C_6H_4	p-salphen	$(CH_2)_3NH(CH_2)_3$	p-saldpt
$CH(CH_3)CH_2$	p-salpln	$(CH_2)_3N(CH_3)(CH_2)_3$	p-salMedpt
C_6H_{10}	p-salchxn		

during the reactions with O_2^-, as compared with those observed for the monomeric complexes which react with O_2^- to give μ-oxo dimers.

Experimental

*Preparation of Monomeric Chloroiron(III) Schiff Base Complexess Chloro(*N,N'*-disalicylideneethylenediaminato)iron(III), Fe(salen)Cl:* This complex was obtained by a modified method described in the literature[7] as follows. Anhydrous iron(III) chloride (0.81 g) was added to an absolute ethanol solution (100 cm^3) containing *N,N'*-disalicylideneethylenediamine (salenH_2, 1.34 g) and triethylamine (1.01 g). The mixture was stirred at 70 °C for 1 h, and then allowed to stand overnight in a refrigerator. The resulting precipitates were collected on a glass filter, washed with ethanol and ether, and then dried *in vacuo*. They were recrystallized from dichloromethane. The yield was 1.1 g.

The other monomeric chloroiron(III) Schiff base complexes were prepared in a similar manner. The analytical data for some of the complexes are given in Table 1.

Preparation of Polymeric (Oligomeric) Schiff Base Ligands. The oligomers of the Schiff bases were prepared by the polycondensation of 5,5'-methylenedisalicylaldehyde with diamine or triamines under the controlled conditions: the molar ratio of 5,5'-methylenedisalicylaldehyde to amines was maintained at 1.25; the temperature was kept below 20 °C; the reaction was stopped within 5 min; a dichloromethane was used as solvent for the polycondensation.

Polymeric Schiff Base, p-saldienH_2: A dichloromethane solution (20 cm^3) of bis(2-aminoethyl)amine (1.4 g, 0.016 mol) was added to a dichloromethane solution (50 cm^3) of 5,5'-methylenedisalicylaldehyde (5.2 g, 0.02 mol) with stirring below 20 °C. After the solution had been stirred for 5 min, it was poured into a large volume of ether (300 cm^3) with vigorous stirring. The resulting yellow precipitates were collected on a glass filter, washed with ether, and then dried *in vacuo*. They were reprecipitated twice from a mixture of dichloromethane and ether. The yield was 3.1 g. Found: C, 69.95; H, 6.40; N, 11.63%. Calcd for a hexamer: C, 70.54; H, 6.33; N, 11.45%. ^{1}H NMR ($CDCl_3$) δ=12.2 (br, OH), 9.70 (s, CHO), 8.27 (s, CH=N), *ca.* 7 (m, ϕ), 3.80 (s, ϕ-CH_2-ϕ), 3.65 (t, CH_2N=), 2.95 (t, CH_2N-). The specific viscosity (η_{sp}) measured in chloroform (0.4 g/100 cm^3) at 25±0.1 °C was 0.037. The degree of condensation (n) was estimated to be six from the analytical data, the ratios of the peak intensities in the ^{1}H NMR spectra, and the specific viscosity.

The polymeric Schiff bases, p-salplnH_2, p-salchxnH_2, p-saldptH_2, and p-salMedptH_2, prepared previously[6] were used. They were found to be oligomers (n=3 to 5) on the basis of the above measurements. The other polymeric Schiff bases, p-salenH_2 and p-salphenH_2, were prepared in a similar manner. However, their NMR spectra and viscosities could not be measured owing to their poor solubility in organic solvents.

Preparation of Polymeric Chloroiron(III) Schiff Base Complexes. Fe(p-saldien)Cl: To a dichloromethane (50 cm^3)–methanol (20 cm^3) solution containing p-saldienH_2 (1.1 g) and triethylamine (0.6 g), anhydrous iron(III) chloride (0.5 g) was added with stirring at room temperature. The precipitated wine-red solids were collected on a glass filter, washed with water, ethanol, and then ether, and then dried *in vacuo*. They were partly soluble in DMSO or *N,N*-dimethylformamide (DMF) and were insoluble in dichloromethane or methanol. They were extracted with DMF (300 cm^3). The DMF solution was concentrated to *ca.* 30 cm^3 under reduced pressure, and poured into methanol (200 cm^3). The precipitates were collected on a glass filter, washed with ether, and dried *in vacuo*. The yield was 0.2 g.

The other polymeric iron(III) complexes were prepared in a similar manner. They are slightly soluble in DMSO or DMF (*ca.* 0.1 g/100 cm^3) and are insoluble in methanol or dichloromethane. Therefore, the viscosity for them could not be measured. The infrared spectra of the polymeric complexes indicate that the Schiff base ligands coordinate to iron ions in the same features as the corresponding monomeric complexes. The magnetic moments of the polymeric complexes were determined on the basis of their iron contents.

Isolation of the Reaction Products of Monomeric Complexes with KO_2. [Fe(acacen)]$_2$O: To a dichloromethane solution (50 cm^3) containing Fe(acacen)Cl (0.63 g, 0.002 mol) and 18-crown-6 (0.56 g, 0.002 mol), potassium superoxide, KO_2, (0.22 g, 0.003 mol) was added. The mixture was stirred for 1 h at room temperature. The wine-colored solution turned gradually orange. The mixture was filtered, and the filtrate was evaporated under reduced pressure to yield orange solids. They were collected on a glass filter, washed with a little volume of water and methanol, and then ether, and dried *in vacuo*. They were recrystallized from dichloromethane to give orange crystals. The yield was 0.3 g. Found: C, 50.20; H, 6.37; N, 9.84; Fe, 19.23%. Calcd for $Fe_2C_{24}H_{36}N_4O_5$: C, 50.37; H, 6.34; N, 9.79; Fe, 19.52%.

The reaction product of Fe(bzacen)Cl with KO_2 was obtained in a similar manner. The reaction products of the other monomeric complexes with KO_2 were obtained similarly, using DMSO in place of dichloromethane as reaction solvent.

Preparation of KO_2 DMSO Solution. DMSO solutions of KO_2 (*ca.* 10^{-2} M, 1 M=1 mol dm^{-3}) were prepared by dissolving KO_2 (0.018 g) into dry DMSO (25 cm^3) in the presence of 18-crown-6 (0.10 g). The O_2^- concentration of the KO_2 DMSO solution was determined by spectrophotometry.[8] The reactions of the iron(III) complexes with KO_2 in DMSO were carried out in a nitrogen atmosphere.

TABLE 1. ELEMENTAL ANALYSES OF IRON(III) SCHIFF BASE COMPLEXES

Complex	Found (%)				Calcd (%)			
	C	H	N	Fe	C	H	N	Fe
Fe(salchxn)Cl	57.84	5.07	6.94	13.35	58.35	4.90	6.80	13.57
Fe(bzacen)Cl	59.77	5.13	6.49	12.62	60.37	5.07	6.40	12.76
Fe(acacen)Cl	45.65	5.89	8.81	18.34	45.96	5.79	8.93	17.81
Fe(saldien)Cl·H_2O	51.68	4.80	10.23	14.43	51.64	5.06	10.05	14.44
Fe(saldpt)Cl·$(H_2O)_{0.5}$	54.88	5.30	9.73	13.03	54.88	5.53	9.60	13.06
Fe(salMedpt)Cl·$(CH_2Cl_2)_{0.9}$	50.73	5.26	8.11	10.97	50.67	5.20	8.09	10.76

Table 2. Physical properties of iron(III) Schiff base complexes

Ligand	μ_{eff} [a)] BM		λ_{max} [b)] nm		$-E_{1/2}$ [c)] vs. Hg pool V	
	Monomer	Polymer	Monomer	Polymer	Monomer	Polymer
salen	5.29	5.25	482	506	0.20	0.22
salphen	5.64	5.72	560	572	0.11	−0.01
salpln	5.49	5.73	486	510	0.24	−0.03
salchxn	5.41	5.38	482	510	0.21	−0.04
saldien	5.99	5.82	502	524	0.25	−0.03
saldpt	6.05	5.17	496	512	0.06	−0.02
salMedpt	5.57	5.56	516	528	0.03	−0.01
acacen	5.92		510		0.28	
bzacen	5.99		512		0.21	

a) Measured at room temperature. b) Measured in DMSO. c) Measured in DMSO containing 0.1 M Bu_4NClO_4 at 25 °C.

Material. Iron(III) chloride was 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. Other solvents were purified by a usual method.

Measurements. All the physical measurements were made by the methods described elsewhere.[5)]

Results and Discussion

The monomeric and polymeric chloroiron(III) Schiff base complexes were synthesized and their reactions with O_2^- in DMSO were investigated. The degree of the condensation (*n*) of the polymeric iron(III) complexes could not be determined by the molecular weight and the viscosity measurements owing to their poor solubility. However, they are considered to be oligomers ($n=3$ to 6) from the degree of the condensation of the Schiff base ligands.

Table 2 includes the magnetic moments, the absorption maxima in the visible region, and the polarographic half-wave potentials corresponding to the reduction from Fe(III) to Fe(II). The magnetic moments of the monomeric complexes fall within the range of 5.29 to 6.05 BM, indicating that these complexes have a d^5 high-spin electron configuration.[7,9)] The magnetic moments of the polymeric complexes also fall within the range of 5.17 to 5.85 BM. The low value (5.17 BM) observed for the Fe(p-saldpt)Cl complex may be caused by antiferromagnetic interactions between iron atoms in the complex. No further investigation on the magnetic properties was made in the present work.

The absorption spectra of the monomeric and polymeric complexes in DMSO show an intense absorption band ($\varepsilon \fallingdotseq 4000$) around 500 nm, which can be assigned to a charge-transfer transition.[10)] The absorption maxima of the polymeric complexes were observed at lower energies than those of the corresponding monomeric complexes. Similar behavior was observed for the monomeric and the polymeric chloromanganese(III) Schiff base complexes.[6)] The monomeric chloroiron(III) complexes with the quadridentate ligands (N_2O_2) in DMSO may have a weak six-coordinate structure by coordination of a DMSO molecule to the central iron atom. It was reported that the Fe(salen)Cl complex is nonelectrolyte in pyridine (py) and has a six-coordinate structure of Fe(salen)Cl–py.[9)] The monomeric chloroiron(III) complexes with the quinquedentate ligands (N_3O_2) may have a six-coordinate structure of a donor set of N_3O_2Cl in DMSO. Wilson *et al.* have reported that the Fe(saltrien)$^+$ cation has a six-coordinate structure (N_4O_2) and that the solvent effect on its spin-equilibrium in solution can be attributed to the hydrogen-bonding interactions between the NH groups of saltrien and solvents, where saltrien denotes the dianion of *N*,*N'*-disalicylidenetriethylenetetramine.[10,11)] On the other hand, the coordination features of the polymeric chloroiron(III) complexes are considered to be similar to those of the monomeric complexes. However, the coordination or interaction of DMSO with the polymeric complexes may be weaker than that of the monomeric complexes, because the iron atoms in the former complexes are not so isolated from the surroundings as are the latter complexes. This may be one reason why the lower energy shifts were observed in the polymeric complexes.

The polarograms of the chloroiron(III) Schiff base complexes in DMSO show the cathodic wave at the half-wave potential around −0.1 V (*vs.* Hg pool) in Table 2, which can be assigned to the one-electron reduction of Fe(III) to Fe(II).[12)] The reduction of the polymeric complexes occurred at more positive potentials than those for the corresponding monomeric complexes. These results are consistent with the absorption spectral data mentioned above on the basis of the electron density in the central iron atoms of the complexes.

Visible Absorption Spectra. Figure 1 shows the absorption spectral changes of a DMSO solution of Fe(salen)Cl caused by the addition of a KO_2 DMSO solution in different molar ratios. The intensity of the absorption band at 490 nm decreased with increasing the molar ratio of KO_2 to the complex, showing an isosbestic point at 458 nm. The absorption spectrum at the $[KO_2]/[\text{complex}]=3$ is almost the same as that of the μ-oxo dimer, $[Fe(salen)]_2O$. This indicates that Fe(salen)Cl reacts with O_2^- in DMSO at room temper-

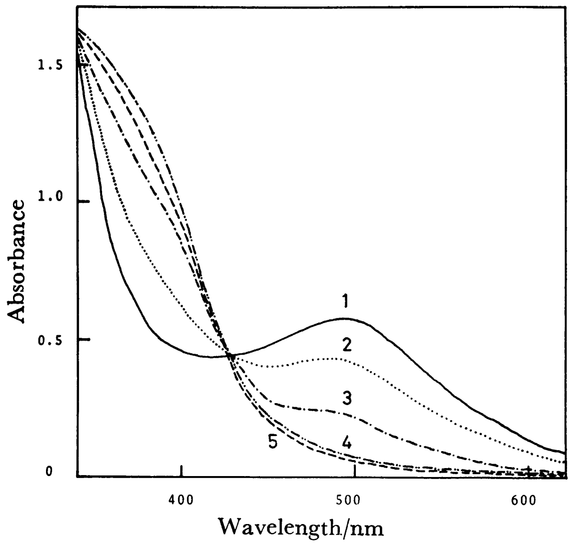


Fig. 1. Spectral changes on the addition of KO_2 to a DMSO solution of 6×10^{-5} M Fe(salen)Cl in different molar ratios.
1): No addition, 2): $[KO_2]/[complex]=1$, 3): 2, 4): 3, 5): spectrum of 3×10^{-5} M $[Fe(salen)]_2O$ in DMSO. Cell length: 1.0 cm.

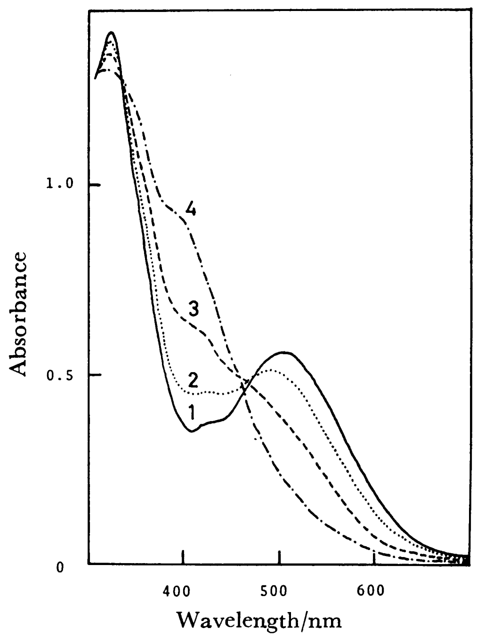


Fig. 2. Spectral changes on the addition of KO_2 to a DMSO solution of 1×10^{-4} M Fe(saldien)Cl in different molar ratios.
1): No addition, 2): $[KO_2]/[complex]=1$, 3): 2, 4): 4. Cell length: 1.0 cm.

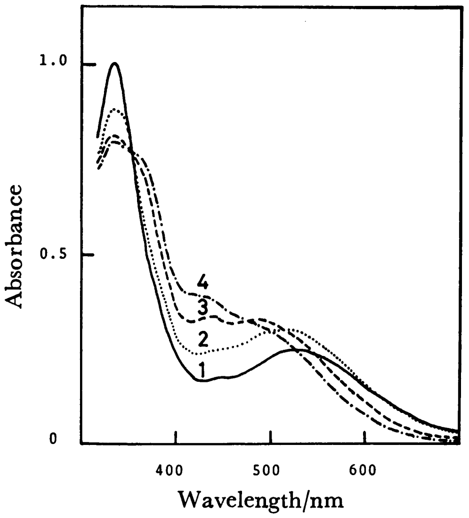


Fig. 3. Spectral changes on the addition of KO_2 to a DMSO solution of 1×10^{-4} unit M Fe(p-saldien)Cl in different molar ratios.
1): No addition, 2): $[KO_2]/[Fe]=2$, 3): 3, 4): 5. Cell length: 1.0 cm.

ature to give a μ-oxo dimer.

All the monomeric chloroiron(III) complexes investigated here showed similar spectral changes to those observed for the above Fe(salen)Cl complex.

Figures 2 and 3 show the comparison of the spectral changes caused by the addition of the KO_2–DMSO solution to the DMSO solutions of Fe(saldien)Cl and Fe(p-saldien)Cl, respectively. The spectral changes for Fe(saldien)Cl are similar to those for Fe(salen)Cl, indicating the formation of the μ-oxo dimer. On the other hand, the spectral changes for the polymeric complex, Fe(p-saldien)Cl, are clearly different from those for the monomeric complex, Fe(saldien)Cl. At the $[KO_2]/[Fe]=2$, the absorption maximum was shifted to higher energy from 524 to 516 nm and the intensity increased slightly. At the $[KO_2]/[Fe]=3$, the absorption maximum was shifted to 492 nm and its intensity increased even more. By the further addition of KO_2 ($[KO_2]/[Fe]=5$), the intensity of the absorption band at 492 nm decreased and a new absorption band appeared around 420 nm. This new absorption band at 420 nm can be assigned to the anion of the Schiff base ligand. This is confirmed by the absorption spectrum of p-saldienH_2 in a KOH–DMSO solution. These spectral changes can be explained as follows. The Fe(p-saldien)Cl reacts with O_2^- in the DMSO solutions ($[KO_2]/[Fe]<3$) to give the oxygenated complex, probably a dioxygen adduct, and it reacts with O_2^- added in excess over the complex ($[KO_2]/[Fe]>3$) to decompose with some dissociation of the Schiff base ligand.

The polymeric iron(III) complexes of Fe(p-saldpt)Cl and Fe(p-salMedpt)Cl showed similar spectral changes to the above Fe(p-saldien)Cl complex. However, the other polymeric complexes, Fe(p-salen)Cl, Fe(p-salphen)Cl, Fe(p-salpln)Cl, and Fe(p-salchxn)Cl, showed the spectral changes similar to those observed for the corresponding monomeric complexes. These results may be attributed to the configurations of the reaction sites in the complexes. As discussed above, the former complexes may have a six-coordinate configuration, while the latter complexes may be taken to have essentially a five-coordinate configuration by neglecting the weak interaction between DMSO molecules and central iron atoms in these polymeric

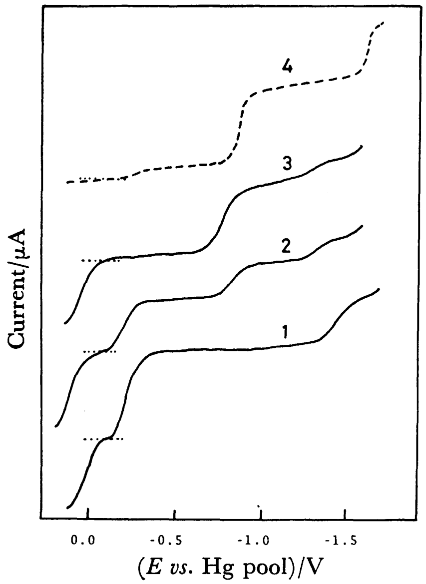


Fig. 4. Polarograms during the reactions of Fe(salen)Cl (5×10^{-4} M) with KO_2 in DMSO at 25 °C.
1): No addition, 2): $[KO_2]/[complex]=1$, 3): 2, 4): polarogram of $[Fe(salen)]_2O$ (2.5×10^{-4} M) in DMSO.

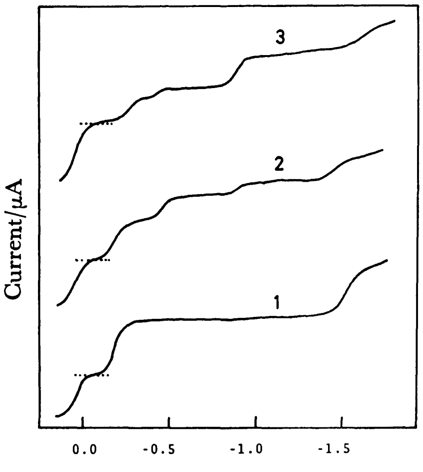


Fig. 5. Polarograms during the reactions of Fe(salen)Cl (5×10^{-4} M) with KO_2 in DMF at −25 °C.
1): No addition, 2): $[KO_2]/[complex]=0.5$, 3): 1.

complexes.

Polarographic Measurements. Figure 4 shows the changes in the polarograms during the reaction of Fe(salen)Cl with KO_2 in DMSO at 25 °C. At the molar ratio of $[KO_2]/[complex]=1$, the wave height at −0.20 V due to the reduction of Fe(III) to Fe(II) decreased and a new cathodic wave appeared around −0.8 V. By the further addition of KO_2 ($[KO_2]/[complex]=2$), the first cathodic wave disappeared and the wave height at −0.8 V increased. The half-wave potential of this cathodic wave is nearly equal to that (−0.89 V) of the μ-oxo dimer, $[Fe(salen)]_2O$. These results indicate that the reaction of Fe(salen)Cl with KO_2 in DMSO at 25 °C produces the μ-oxo dimer. The polarographic observations are consistent with those obtained in the absorption spectra mentioned above. Similar polarographic behavior was observed for all the monomeric iron(III) complexes investigated in this work.

It was reported that the dioxygen adduct of iron(II) porphyrin complexes can be stabilized at low temperature.[13] Thus, we carried out the reaction of Fe(salen)Cl with KO_2 in DMF at −25 °C. Figure 5 shows the changes in the polarograms of Fe(salen)Cl in DMF at −25 °C caused by the addition of a KO_2 DMSO solution. The half-wave potential (−0.19 V) of the first cathodic wave due to the reduction of Fe(III) to Fe(II) is nearly equal to that (−0.20 V) observed in DMSO at 25 °C. At the molar ratio of $[KO_2]/[complex]=0.5$, two new cathodic waves appeared at the half-wave potentials of −0.48 and −0.88 V and the height of the first cathodic wave decreased. By the further addition of KO_2 ($[KO_2]/[complex]=1$), the wave heights of both the first and the second cathodic waves decreased and the third cathodic wave height increased. The second cathodic wave observed at −0.48 V may be attributed to the reduction of the oxygenated complex, Fe(salen)–O_2 or Fe(salen)–$O_2^{\cdot}$–Fe(salen), formed in the solution. This may further react with O_2^- to give the μ-oxo dimer. Similar polarographic behavior was observed in the reaction of Fe(salphen)Cl with KO_2 in DMF at −25 °C. From the available data we propose this scheme for the reactions of Fe(salen)Cl with O_2^-:

$$\mathrm{FeLCl} + \mathrm{O_2^-} \longrightarrow \mathrm{FeL\text{–}O_2} + \mathrm{Cl^-}$$
$$\mathrm{FeL\text{–}O_2} + \mathrm{FeLCl} \longrightarrow \mathrm{FeL\text{–}O_2^{\cdot}\text{–}FeL} + \mathrm{Cl^-}$$
$$\mathrm{FeL\text{–}O_2^{\cdot}\text{–}FeL} + \mathrm{O_2^-} \longrightarrow \mathrm{FeL\text{–}O_2\text{–}FeL} + \mathrm{O_2}$$
$$\mathrm{FeL\text{–}O_2\text{–}FeL} \longrightarrow \mathrm{FeL\text{–}O\text{–}FeL},$$

where L denotes the dianion of *N,N′*-disalicylideneethylenediamine. Recently, Chin *et al.* have reported on the mechanism of autoxidation of Fe^{II}(por) and proposed that the intermediate (por)Fe–O_2–Fe(por) can be stabilized at low temperature (−50 °C). This oxygenated complex reacts with Fe^{II}(por) to give (por)Fe–O–Fe(por) or decomposes thermally to (por)-Fe–O–Fe(por) *via* iron(IV) complex, (por)$Fe^{IV}=O$, in the absence of Fe^{II}(por).[14]

Figures 6 and 7 show the changes in the polarograms during the reactions of Fe(p-saldien)Cl with KO_2 in DMSO. In Fig. 6, the KO_2– DMSO solution was added successively to the DMSO solution of the complex, whereas in Fig. 7, it was added step by step after passing nitrogen gas through the mixed solutions. The changes in the polarograms (in Fig. 6) are clearly different from those observed for Fe(salen)Cl (in Fig. 4). The cathodic wave at the half-wave potential of +0.01 V is due to the reduction of Fe(III) to Fe(II). The addition of KO_2 ($[KO_2]/[Fe]=1$) caused the appearance of a new cathodic wave around −0.3 V. At the $[KO_2]/[Fe]=2$, this wave height decreased slightly and a new cathodic wave appeared at the half-wave potential of −0.6 V; this new wave can be assigned to the reduction of free molecular oxygen liberated during the reactions on the basis of its potential. At the $[KO_2]/[Fe]=3$, the wave height around −0.3 V decreased and the wave

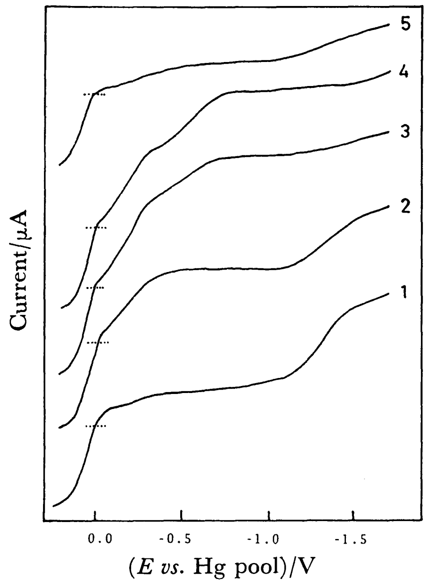


Fig. 6. Polarograms during the reactions of Fe(p-saldien)Cl (5×10^{-4} unit M) with KO_2 in DMSO at 25 °C.
1): No addition, 2): $[KO_2]/[Fe]=1$, 3): 2, 4): 3, 5): after passing nitrogen gas through the solution shown by the curve 4.

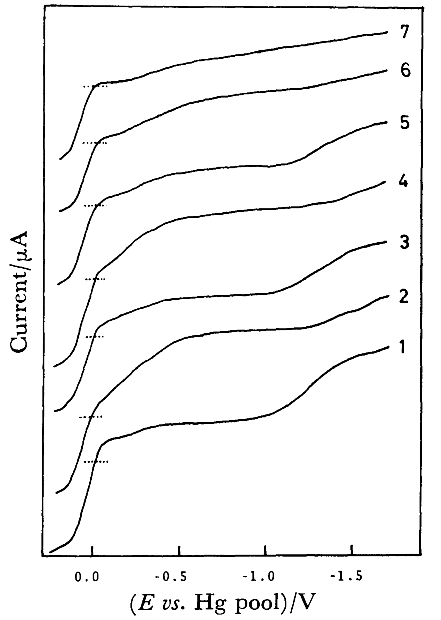


Fig. 7. Polarograms during the reactions of Fe(p-saldien)Cl (5×10^{-4} unit M) with KO_2 in DMSO at 25 °C.
1): No addition, 2): $[KO_2]/[Fe]=1$, 4): 2, 6): 4, 3), 5), and 7): after passing nitrogen gas through the solutions shown by the curves 2, 4, and 6, respectively.

height around −0.6 V increased. By passing nitrogen gas through the mixed solution, both cathodic waves disappeared. The cathodic wave which appeared around −0.3 V may be due to the oxygenated complex, Fe(p-saldien)–O_2. This is confirmed by the observations shown in Fig. 7. The polarograms observed at the $[KO_2]/[Fe]=1$ was identical to that shown by curve 2 in Fig. 6. By passing nitrogen gas through the solution, the wave height around −0.3 V decreased. Such a cycle (adding KO_2 and passing N_2) was made three times. The polarograms shown by curves 2, 4, and 6 in Fig. 7 did not show any cathodic wave at the half-wave potential around −0.6 V. Moreover, the degree of increase in the wave height around −0.3 V lowered gradually by repeating the cycle. These results indicate that the oxygenated complex, Fe(p-saldien)–O_2, may decompose to Fe^{II}(p-saldien) and molecular oxygen by passing nitrogen gas through the mixed solutions. Similar polarographic behavior was observed for the polymeric complexes, Fe(p-saldpt)Cl and Fe(p-salMedpt)Cl.

From the observations in the absorption spectra and the polarographic measurements, the reactions of the polymeric iron(III) complexes with O_2^- may occur as follows:

$$\text{(p-L)FeCl} + O_2^- \longrightarrow$$
$$\text{(p-L)Fe–}O_2 + Cl^- \quad ([KO_2]/[Fe] < 2)$$
$$\text{(p-L)Fe–}O_2 + O_2^- \longrightarrow$$
$$\text{(p-L)Fe–}O_2^- + O_2 \quad ([KO_2]/[Fe] > 2)$$
$$\text{(p-L)Fe–}O_2^- \longrightarrow \text{(p-L)Fe}^- + O_2$$
$$\text{(p-L)Fe}^- \longrightarrow \text{Decomposition,}$$

where (p-L) denotes the dianion of the polymeric Schiff base ligands.

The reversible oxygenation of the iron(II) porphyrin complexes can be established by preventing the formation of *μ*-peroxo diiron complex in one or more of the following ways: (1) steric effects, (2) immobilization in rigid surfaces, and (3) low-temperature measurements. In addition, it has been proposed that (4) a five-coordinate structure and (5) a nonpolar, hydrophobic environment around iron(II) complex play an important role for the synthesis of iron(II) porphyrin dioxygen adduct.[13] Recently, Niswander *et al.* have reported that Fe^{II}(salen)·py[15] and Fe^{II}(5-NO_2saldpt)[16] react with molecular oxygen to give only the corresponding *μ*-oxo dimers.

In the present work, the monomeric chloroiron(III) Schiff base complexes react with O_2^- to give only the *μ*-oxo dimers. On the other hand, the polymeric complexes of Fe(p-saldien)Cl, Fe(p-saldpt)Cl, and Fe(p-

TABLE 3. PHYSICAL PROPERTIES OF THE REACTION PRODUCTS OF THE MONOMERIC IRON(III) COMPLEXES WITH KO_2 IN DMSO

Formula	μ_{eff}[a)] / BM	ν(Fe–O–Fe) / cm^{-1}	$-E_{1/2}^{b)}$ *vs.*Hg pool / V
$[Fe(salen)]_2O$	1.91	825	0.89
$[Fe(salphen)]_2O$	2.05	820	0.86
$[Fe(salpln)]_2O$	2.02	815	0.97
$[Fe(salchxn)]_2O$	1.87	820	0.98
$[Fe(acacen)]_2O$[c)]	1.88	838	1.18
$[Fe(bzacen)]_2O$[c)]	2.50	820	1.22

a) Measured at room temperature. b) Measured in DMSO containing 0.1 M Bu_4NClO_4 at 25 °C. c) In dichloromethane.

salMedpt)Cl form the dioxygen adduct in DMSO solution at room temperature by the reaction with O_2^-. Such behavior suggests that these polymeric complexes may satisfy the above requirements (1), (2), and (4).

Reaction Products of the Iron(III) Complexes with KO_2. The reaction products of the monomeric iron(III) complexes, Fe(acacen)Cl, Fe(bzacen)Cl, Fe(salen)Cl, Fe(salphen)Cl, Fe(salpln)Cl, and Fe(salchxn)Cl, were confirmed to be their μ-oxo dimers from the analytical data and physicochemical properties (in Table 3). However, for the other monomeric complexes, Fe(saldien)Cl, Fe(saldpt)Cl, and Fe(salMedpt)Cl, their μ-oxo dimers could not be characterized. On the other hand, the reaction products of the polymeric iron(III) complexes have not been identified with their oxygenated complexes by the analytical data and the physicochemical measurements. This may be caused by the instability of the oxygenated complexes. Further investigation is now in progress.

References

1) Abbreviations used in this work: ppde, protoporphyrin IX dimethyl ester dianion; H_4edta, ethylenediaminetetraacetic acid; por, tetraphenyl porphyrin dianion.

2) H. A. O. Hill, D. R. Turner, and G. Pellizer, *Biochem. Biophys. Res. Commun.*, **56**, 739 (1974).

3) G. J. McClune, J. A. Fee, G. A. McCluskey, and J. T. Groves, *J. Am. Chem. Soc.*, **99**, 5220 (1977).

4) E. McCandlish, A. R. Miksztal, M. Nappa, A. Q. Sprenger, J. S. Valentine, J. D. Stong, and T. G. Spiro, *J. Am. Chem. Soc.*, **102**, 4268 (1980).

5) T. Matsushita and T. Shono, *Bull. Chem. Soc. Jpn.*, **54**, 3743 (1981).

6) T. Matsushita, M. Nishino, and T. Shono, *Bull. Chem. Soc. Jpn.*, **55**, 2663 (1982).

7) M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc., A*, **1968**, 112.

8) S. Kim, R. DiCosimo, and J. San Filippo, Jr., *Anal. Chem.*, **51**, 679 (1979).

9) M. Gullotti, L. Casella, A. Pasini, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, **1977**, 339.

10) M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, **98**, 4824 (1976).

11) E. Sinn, G. Sim, E. V. Dose, M. F. Tweedle, and L. J. Wilson, *J. Am. Chem. Soc.*, **100**, 3375 (1978).

12) K. M. Kadish, K. Das, D. Schaeper, C. L. Merrill, B. R. Welch, and L. J. Wilson, *Inorg. Chem.*, **19**, 2816 (1980).

13) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **79**, 139 (1979).

14) D-H. Chin, G. N. La Mar, and A. L. Balch, *J. Am. Chem. Soc.*, **102**, 4344 (1980).

15) R. H. Niswander and A. E. Martell, *Inorg. Chem.*, **17**, 2341 (1978).

16) R. H. Niswander and A. E. Martell, *Inorg. Chem.*, **17** 1511 (1978).