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

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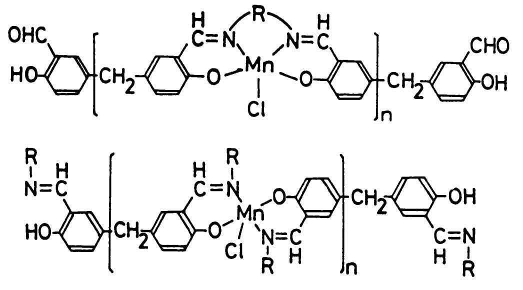
Synopsis. The polymeric Mn(III) Schiff base complexes react with superoxide ions (O_2^-) in dimethyl sulfoxide (DMSO) to give the oxygenated complexes, while the corresponding monomeric Mn(III) complexes are reduced with O_2^- to the Mn(II) complexes.

Manganese ions play an important role in biological redox processes, the disproportionation of O_2^- by manganese-containing superoxide dismutases, and the photosynthetic water oxidation in green plants.[1–3] In the previous paper,[4] the monomeric Mn(III) Schiff base complexes are classified into two types according to their reactivity toward O_2^-: one gives the oxygenated complexes and the other is reduced to the Mn(II) complexes. This behavior can be correlated to the polarographic half-wave potentials for the reduction of Mn(III) to Mn(II). In this Note, the reactions of the polymeric Mn(III) complexes (shown below) with O_2^- in DMSO will be reported.



R	Abbreviation
$CH(CH_3)CH_2$	Mn(p-salpln)Cl
C_6H_{10}	Mn(p-salchxn)Cl
$(CH_2)_3NH(CH_2)_3$	Mn(p-saldpt)Cl
$(CH_2)_3N(CH_3)(CH_2)_3$	Mn(p-salMedpt)Cl
n-C_3H_7	Mn(*N*-Prdisai)Cl
n-C_4H_9	Mn(*N*-Budisai)Cl
c-C_6H_{11}	Mn(*N*-*c*-Hxdisai)Cl

Polymeric Mn(III) Schiff base complexes studied.

Experimental

The monomeric Mn(III) complexes, Mn(salpln)Cl, Mn(salchxn)Cl, Mn(saldpt)Cl, Mn(salMedpt)Cl, and chlorobis(*N*-alkylsalicylideneaminato)manganese(III), $Mn(N\text{-}Rsai)_2Cl$ ($R=n\text{-}C_3H_7$ (Pr), $n\text{-}C_4H_9$ (Bu), and $c\text{-}C_6H_{11}$ (c-Hx)), were prepared by a modification of the method described elsewhere;[4] $salplnH_2$: *N,N'*-disalicylidenepropylenediamine, $salchxnH_2$: *N,N'*-disalicylidene-1,2-cyclohexanediamine, $saldptH_2$: bis[3-(salicylideneamino)propyl]amine, $salMedptH_2$: bis[3-(salicylideneamino)propyl]methylamine.

Polymeric Schiff Bases. The polymeric Schiff base, p-$salplnH_2$ was obtained by polycondensation of 5,5'-methylenedisalicylaldehyde ($disalH_2$) with propylenediamine in dichloromethane (CH_2Cl_2). This was reprecipitated from a mixture of CH_2Cl_2–ether. The other polymeric Schiff bases, p-$salchxnH_2$, p-$saldptH_2$, and p-$salMedptH_2$, were obtained in a similar manner. The analytical data, specific viscosities (Table 1), and ^1H NMR data indicate that these polymeric Schiff bases are oligomers whose degrees of condensation (n) are within a range of three to five.

N,N'-Dibutyl-5,5'-methylenedisalicylideneamine, *N*-Bu-$disaiH_2$, was obtained by the condensation of $disalH_2$ with *n*-butylamine in tetrahydrofuran. This was recrystallized from a mixture of ether–petroleum ether. The other Schiff bases, *N*-$PrdisaiH_2$ and *N*-*c*-$HxdisaiH_2$ were obtained in a similar manner.

Preparation of Polymeric Mn(III) Complexes. The polymeric Mn(III) complex, Mn(p-salpln)Cl, was obtained by reacting p-$salplnH_2$ with $Mn(CH_3COO)_3\cdot 2H_2O$ and LiCl in a mixture of CH_2Cl_2–MeOH, and was reprecipitated from a mixture of MeOH–ether. Mn(p-salchxn)Cl, Mn(p-saldpt)Cl, and Mn(p-salMedpt)Cl were obtained in a similar manner. The other polymeric complexes, Mn(*N*-Rdisai)Cl (R=Pr, Bu, and *c*-Hx), were obtained in a manner similar to that used for Mn(p-salpln)Cl, and were reprecipitated from a mixture of CH_2Cl_2–ether. These polymeric complexes are soluble in MeOH and DMSO. The analytical data and specific viscosities (Table 1) indicate that they are oligomers whose degrees of condensation are within a range of three to five.

Measurements. ^1H NMR spectra were taken on a JEOL JNM-PS 100 spectrometer using TMS as the internal standard. The specific viscosities were determined using an Ostwald's viscometer at 25 ± 0.1 °C (0.40 g/solvent 100 cm^3). The other physical measurements were carried out by the method described elsewhere.[4]

Reactions of the Mn(III) complexes with KO_2 in DMSO were made by the procedure described elsewhere.[4]

Results and Discussion

We have previously found that the absorption spectral and polarographic changes can be used to distinguish clearly between the formation of the oxygenated complexes and the reduction of Mn(III) to Mn(II)

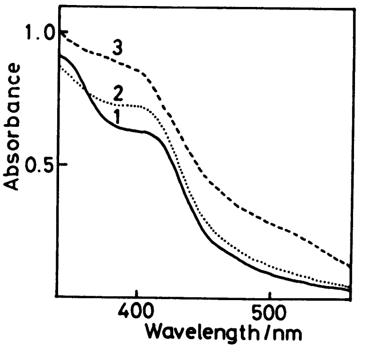


Fig. 1. Spectral changes of a DMSO solution of Mn(p-salpln)Cl (1×10^{-4} unit mol dm^{-3}) caused by the addition of KO_2.

1): No addition, 2): $[KO_2]/[Mn]=1$, 3): 3. Cell length: 1 cm.

TABLE 1. PROPERTIES OF POLYMERIC Mn(III) COMPLEXES, Mn(p-L)Cl AND Mn(*N*-Rdisai)Cl, AND OF CORRESPONDING MONOMERIC Mn(III) COMPLEXES, Mn(L)Cl AND Mn(*N*-Rsai)$_2$Cl

Ligand		$\eta_{sp}^{b)}$	$\frac{\mu_{eff}^{e)}}{BM}$	$\frac{\lambda_{max}^{f)}}{nm}$		$\frac{-E_{1/2}\ vs.\ \text{Hg pool}^{g)}}{V}$
p-L	$\eta_{sp}^{a)}$			DMSO	Solid	
p-salpln	0.049	0.051	4.92 (5.03)	620sh (605)	630sh (618sh)	0.07 (0.18)
p-salchxn	0.057	0.058	4.97 (4.96)	605 (588)	628sh (612sh)	0.00$^{h)}$ (0.21)
p-saldpt	0.028	0.033	4.96 (5.14)	595 (584)	618 (610)	0.01 (0.05)
p-salMedpt	0.035	0.044$^{c)}$	5.10 (4.77)	592 (570)	616 (608)	−0.01 (0.16)
N-Prdisai	—	0.028$^{c)}$	5.04 (4.86)	596 (580)	670 (666)	0.02$^{h)}$ (0.05)
N-Budisai	—	0.028$^{d)}$	4.94 (5.03)	584 (579)	670 (658)	0.02 (0.02)
N-*c*-Hxdisai	—	0.020$^{d)}$	5.06 (4.89)	566 (572)	636sh (679)	0.02 (0.00)

Values in parentheses correspond to the monomeric complexes. a) Specific viscosities of polymeric Schiff bases measured in $CHCl_3$. b) Specific viscosities measured in DMSO. c) In MeOH. d) In $CHCl_3$. e) Magnetic susceptibilities measured at room temperature and calculated from manganese content for the polymeric complexes. f) Absorption maxima. g) Reduction potentials measured in CH_3CN containing 0.1 mol dm^{-3} Bu_4NClO_4. h) In DMSO.

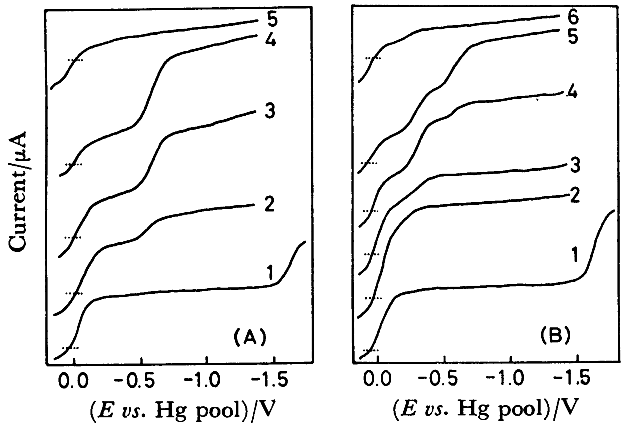


Fig. 2. Polarograms in the reactions of Mn(*N*-Prsai)$_2$Cl (A) and of Mn(*N*-Prdisai)Cl (B) with KO_2 in DMSO containing 0.1 mol dm^{-3} Bu_4NClO_4 at 25 °C.
(A); [Complex]$=2\times10^{-4}$ mol dm^{-3}, 1): no addition, 2): $[KO_2]/[Mn]=1$, 3): 3, 4): 6, 5): after passing N_2 through the solution shown by the curve 4. (B); [Complex]$=2\times10^{-4}$ unit mol dm^{-3}, 1): no addition, 2): $[KO_2]/[Mn]=1$, 3): 2, 4): 3, 5): 4, 6): after passing N_2 through the solution shown by the curve 5.

in the reactions of the Mn(III) Schiff base complexes with O_2^- in DMSO.[4] Figure 1 shows the spectral changes of a DMSO solution of Mn(p-salpln)Cl caused by the addition of a KO_2 DMSO solution. A broad absorption band appeared around 500 nm at the $KO_2/Mn=3$, indicating the formation of the oxygenated complex. The other polymeric Mn(III) complexes show spectral changes similar to the above.

Figures 2-A and 2-B show the changes in polarograms in the reactions of O_2^- with the monomeric Mn(*N*-Prsai)$_2$Cl and polymeric Mn(*N*-Prdisai)Cl in DMSO, respectively. In the case of Mn(*N*-Prsai)$_2$Cl, as the ratio of KO_2/Mn increased, the wave height at −0.03 V due to the reduction of Mn(III) to Mn(II) decreased and a new cathodic wave appeared at −0.55 V; this can be assigned to the reduction of free molecular oxygen. This indicates that Mn(*N*-Prsai)$_2$Cl is reduced to the Mn(II) complex and O_2^- is oxidized to O_2. In the case of Mn(*N*-Prdisai)Cl, a new cathodic wave was observed at *ca.* −0.25 V by the addition of KO_2 (KO_2/Mn= 1—3), indicating the formation of the oxygenated complex. The other polymeric Mn(III) complexes show polarograms similar to the above. These results indicate that all the polymeric Mn(III) complexes investigated here react with O_2^- to give the oxygenated complexes, although the corresponding monomeric Mn(III) complexes are reduced with O_2^- to the Mn(II) complexes, with the exception of Mn(salchxn)Cl which gives the oxygenated complex.[4]

The polymeric complexes showed slightly positive reduction potentials compared with those for the monomeric complexes (Table 1). Nevertheless, the oxygenated complexes are found to be stabilized in the polymeric complexes. This may be caused by a polymeric sturcture in which the central manganese atoms are not isolated from the surroundings, unlike the monomeric complexes. In such an environment, interaction between DMSO molecules and the central manganese atom may be weakened by steric repulsion and thus the oxygenated complex may be protected from dissociation into the Mn(II) complex and O_2, because the dissociation should proceed *via* displacement of coordinated dioxygen with DMSO molecules. This consideration is not inconsistent with the spectral data (Table 1): the ligand field bands assignable to the $d_{xy}\rightarrow d_{x^2-y^2}$ transition[5] are observed at lower energies in the polymeric complexes than those for the monomeric complexes.

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