Peroxo-, Oxo-, and catena-Oxo-Manganese Complexes with *N,N'*-Ethylenebis(salicylideneimine) Analogues[1]

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By the reaction of Mn^{II}(salen) (salen = *N,N'*-ethylenebis(salicylideneiminato) dianion) and its analogues with molecular oxygen in organic solvents, three types of complexes including as structural units the Mn^{III}–O_2–Mn^{III}, –(–Mn^{IV}–O–)–$_n$, and Mn^{IV}=O bonds respectively, have been obtained, and characterized by means of their electronic and infrared spectra, by thermogravimetric analysis, and in terms of their magnetic properties. The lower magnetic moments for $[Mn^{III}(salen)]_2O_2$ and –[–Mn^{IV}(salen)–O–]–$_n$ than those expected have been interpreted in terms of antiferromagnetic interactions. The oxo complex was found to give the catena-oxo complex quantitatively in a DMF, DMSO, or Py solution. The effects of the oxygen partial pressure and the nature of the substituent in the organic part on the complex formation were investigated. A lower partial pressure of oxygen has the advantage of yielding the μ-peroxo complex in a higher yield. A discussion of the reaction mechanism is also included.

The Mn^{II}(salen)[2] was first reported by Tsumaki[3] to react with oxygen to yield Mn^{III}(salen)OH, for which Lewis *et al.*[4] later proposed a polymeric structure including unitary Mn^{III}(salen)–O–Mn^{III}(salen)·H_2O on the basis of the magnetic property. Recently, Johnson *et al.*[5] have reported that Mn^{II}(salpr)[2] takes up molecular oxygen in a benzene solution. In the present study, three types of complexes involving Mn^{III}-O_2-Mn^{III}, –(–Mn^{IV}–O–)–$_n$, and Mn^{IV}=O bonds respectively are shown to be obtainable upon reacting the Mn^{II}(salen) and its analogues with molecular oxygen in organic solvents.

Experimental

Manganese(II) Complexes. The preparation of Mn^{II}(salen) and Mn^{II}(3-MeO-salen)·H_2O[2] was carried out in a nitrogen atmosphere according to a modification of the procedure of the literature.[4] Mn^{II}(5-NO_2-salen)[2] was obtained by allowing the pyridine adduct, Mn^{II}(5-NO_2-salen)·2Py, which had been prepared by the reaction of 5-NO_2-salenH_2 with $MnCl_2 \cdot 4H_2O$ in a *ca.* 50% aqueous pyridine solution, to stand *in vacuo* at 90—100 °C for 12 hours. The compounds were confirmed by elemental analyses.

*Peroxo-, Oxo-, and catena-Oxo-Manganese Complexes. μ-Peroxo-bis-*NN'*-ethylenebis(salicylideneiminato)manganese(III),* $[Mn^{III}(salen)]_2O_2$: Mn^{II}(salen) (2.0 g) was dissolved in DMSO (150 ml) in a nitrogen atmosphere, and then the solution was kept in oxygen (1 atm) at room temperature for about 12 hours. Two grams of precipitates were thus separated. The precipitates were extracted with CH_2Cl_2 (1 l), and then the solvent was evaporated to *ca.* 50 ml to leave reddish-brown crystals. They were separated by filtration and then dried *in vacuo* at 50 °C for 6 hours. Yield: 0.2 g. When the solution of Mn^{II}(salen) was kept in a nitrogen atmosphere which contained about 2.0 vol% of oxygen, the crystals of the μ-peroxo complex could be obtained in a *ca.* 90% yield. The μ-peroxo complex is soluble in CH_2Cl_2 (*ca.* 0.4 g/l) and is slightly souble in DMSO and DMF.

*Oxo-*N,N'*-ethylenebis(3-methoxy-salicylideneiminato) manganese (IV) Methanol Adduct,* $O=Mn^{IV}(3\text{-MeO-salen}) \cdot 2MeOH$: Mn^{II}(3-MeO-salen)·H_2O (2.0 g) was suspended in absolute MeOH (200 ml), and then oxygen gas was bubbled through the mixture while it was being stirred for *ca.* 20 hours. The solution turned greenish-brown, and dark-green, crystalline needles were separated. The crystals were filtered and dried *in vacuo.* Further crystals were obtained by concentrating the filtrate. Yield: 1.4 g. The complex was recrystallized from methanol.

*Poly, catena-oxo-*N,N'*-ethylenebis(salicylideneiminato)manganese-(IV),* –[–Mn^{IV}(salen)–O–]–$_n$: Mn^{II}(salen) (1.0 g) was dissolved in Py (100 ml) under a nitrogen atmosphere, and then the solution was allowed to stand for about 20 hours in dry oxygen (1 atm). The brown precipitates thus separated were centrifuged, washed with MeOH, and then dried *in vacuo.* Yield: 0.95 g.

*Poly, catena-oxo-*N,N'*-ethylenebis(3-methoxy-salicylideneiminato)-manganese(IV),* –[–Mn^{IV}(3-MeO-salen)–O–]–$_n$: The complex was obtained from Mn^{II}(3-MeO-salen)·H_2O in the way described above. Yield: 93%.

*Poly, catena-oxo-*N,N'*-ethylenebis(5-nitro-salicylideneiminato)-manganese(IV) Dimethylformamide Adduct,* –[–Mn^{IV}(5-NO_2-salen)–O–]–$_n$(DMF)$_n$: The complex was prepared by a similar reaction of Mn^{II}(5-NO_2-salen) in a DMF solution. Yield: 90%.

These catena-oxo complexes are amorphous, and they are insoluble in water and in common organic solvents.

Measurements. The oxygen uptake was measured by using a Warburg manometer. The infrared spectra were obtained in Nujol mulls using a JASCO IR-L spectrophotometer in the 400—4000 cm^{-1} region, and a Hitachi EPI-L spectrophotometer in the 200—700 cm^{-1} region. The electronic spectra were recorded on a Hitachi EPS-3 spectrophotometer. The magnetic susceptibility was measured for a powder sample by the Faraday method, using a torsion balance[6] over the temperature range from 77 to 293 K,

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[1] Preliminary communication; T. Yarino, T. Matsushita, I. Masuda, and K. Shinra, *Chem. Commun.*, **1970**, 1317.

[2] The following abbreviations are used; salenH_2; *N,N'*-ethylenebis(salicylideneimine), 3-MeO-salenH_2; *N,N'*-ethylenebis-(3-methoxy-salicylideneimine), 5-NO_2-salenH_2; *N,N'*-ethylenebis-(5-nitro-salicylideneimine), salprH_2; *N,N'*-1,3-propanebis(salicylideneimine), DMF; *N,N'*-dimethylformamide, DMSO; dimethylsulfoxide, Py; pyridine, MeOH; methanol.

[3] T. Tsumaki, *Nippon Kagaku Zasshi*, **55**, 1245 (1934).

[4] J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc. A*, **1968**, 1699.

[5] G. L. Johnson, and W. D. Beveridge, *Inorg. Nucl. Chem. Lett.*, **3**, 323 (1967).

[6] T. Mori, C. Miyake, and T. Sano, *Trans. JIM*, **4**, 158 (1963).

Table 1. Analytical data

	Complex[2]	Calcd %				Found %			
		C	H	N	Mn	C	H	N	Mn
I	$[\mathrm{Mn^{III}(salen)}]_2\mathrm{O}_2$	57.00	4.19	8.31	16.29	56.00	4.04	8.13	16.60
II	$-[-\mathrm{Mn^{IV}(salen)}-\mathrm{O}-]-_n$	57.00	4.19	8.31	16.29	56.12	4.04	8.26	16.47
III	$-[-\mathrm{Mn^{IV}(3\text{-}MeO\text{-}salen)}-\mathrm{O}-]-_n$	54.41	4.57	7.05	13.76	53.50	4.65	6.84	13.63
IV	$-[-\mathrm{Mn^{IV}(5\text{-}NO_2\text{-}salen)}-\mathrm{O}-]-_n\cdot(\mathrm{DMF})_n$	45.60	3.84	14.00	10.98	45.39	3.77	13.77	10.89
V	$\mathrm{O{=}Mn^{IV}(3\text{-}MeO\text{-}salen)\cdot 2MeOH}$	51.85	5.63	6.04	11.85	51.75	5.93	5.76	12.13

and by the Gouy method at room temperature. The equipment was calibrated using a standard nickel chloride solution. Thermogravimetric and differential thermal analyses were carried out using a Rigaku Denki DG–CIH Thermoflex, at a heating rate of 5 °C/min or 2.5 °C/min, and under a nitrogen stream.

Results and Discussion

As is shown in Table 1, the analytical data of the aerial oxidation products of $\mathrm{Mn^{II}}$(X-salen) are in fair agreement with the Mn(X-salen)O formula. The data of the manometric measurements shown in Table 2 indicate that the $\mathrm{Mn^{II}}$(X-salen) uptake oxygen in a Mn : O_2 molar ratio of 1 : 0.5 is consistent with the above results. However, as will be discussed below, these products can be classified into three types of complexes, including $\mathrm{Mn^{III}–O_2–Mn^{III}}$, $-(-\mathrm{Mn^{IV}–O}-)-_n$, and $\mathrm{Mn^{IV}{=}O}$ bonds respectively, on the basis of their physicochemical data.

Table 2. Oxygen uptake of $\mathrm{Mn^{II}}$ (X-salen)[a)]

Complex	Solvent	Molar ratio: O_2/complex	Time:[b)] min.
$\mathrm{Mn^{II}(salen)}$	DMSO	0.53	30
	DMF	0.46	5
	MeOH	0.30	1440
$\mathrm{Mn^{II}(3\text{-}MeO\text{-}salen)\cdot H_2O}$	DMSO	0.48	40
	MeOH	0.40	1200
$\mathrm{Mn^{II}(5\text{-}NO_2\text{-}salen)\cdot 2Py}$	DMF	0.40	2160

a) Measurements were carried out at 20 °C.
b) The time needed for attaining equilibrium.

Solubility. Complex I (*cf.* Table 1) is slightly soluble in such organic solvents as CH_2Cl_2, DMF and DMSO, while Complexes II and III are insoluble in these solvents. Complex IV is soluble in DMSO, but sparingly so. It should be noted that Complex V is soluble in MeOH without decomposition, whereas in a Py, DMF, DMSO, or CH_2Cl_2 solution it is converted to an insoluble complex, III, in an almost quantitative yield.

Thermogravimetric Analyses. Complexes II, III, and IV show a similar pattern in the TGA curves (Fig. 1), decreasing in weight in the 200—225 °C range and with subsequent decomposition. These weight losses correspond to that caused by the release of 0.5 mole of oxygen per manganese atom.

Though Complex I shows a similar weight loss at 198 °C which is thought to be caused by the liberation of 0.5 mole of oxygen per manganese atom (observed, 4.6%; calcd, 5.3%), no other remarkable decomposition is, in this case, observed to occur until *ca.* 250 °C. It should be noticed that, upon heating at about 200 °C for 1 hour *in vacuo*, the complex was converted to the $\mathrm{Mn^{II}}$(salen) in an 85% yield.

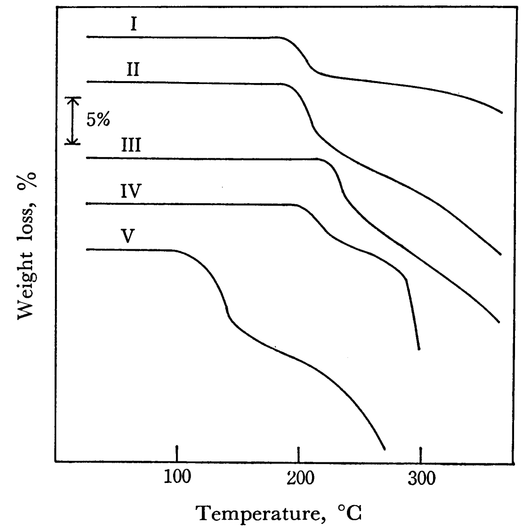

Fig. 1. TGA curves.
I: $[\mathrm{Mn^{III}(salen)}]_2\mathrm{O}_2$, II: $-[-\mathrm{Mn^{IV}(salen)}-\mathrm{O}-]-_n$, III: $-[-\mathrm{Mn^{IV}(3\text{-}MeO\text{-}salen)}-\mathrm{O}-]-_n$, IV: $-[-\mathrm{Mn^{IV}(5\text{-}NO_2\text{-}salen)}-\mathrm{O}-]-_n$, V: $\mathrm{O{=}Mn^{IV}(3\text{-}MeO\text{-}salen)\cdot 2MeOH}$.

Complex V decreases in weight corresponding to the release of two moles of MeOH per manganese atom between 70 and 140 °C, and then it decomposes.

Magnetic Properties. Lewis *et al.*[4)] have reported that polymeric $[\mathrm{Mn(salen)–O–Mn(salen)}]\cdot\mathrm{H_2O}$ shows a room-temperature magnetic moment of 2.03—1.92 B.M., and that there exists a large antiferromagnetic interaction with $J=-90\ \mathrm{cm^{-1}}$ for a binuclear cluster ($S=2$, $g=2.00$, and $N\alpha=0$ or $S=1$, $g=2.05$, and $N\alpha=0$). Complex I in the present work shows 1.96 B.M. (Table 3) at room temperature, a value which is considerably lower than those (4.96—4.98 B.M.) found for the $\mathrm{Mn^{III}}$(salen)X-type complexes where X is $\mathrm{Br^-}$ or $\mathrm{I^-}$.[7)] Moreover, a significant deviation from the Curie-Weiss law is observed over the temperature range from 77 to 296 K (Fig. 2). Below *ca.* 130 K, the data fit fairly well a curve calculated by assuming a binuclear cluster, $\mathrm{Mn–O_2–Mn}$, with $J=-85\ \mathrm{cm^{-1}}$, $S=1$, $g=2.00$, and $N\alpha=0$. However, at higher temperatures they deviate from the curve and fit, rather, one calculated for $J=-90\ \mathrm{cm^{-1}}$, $S=2$, $g=2.00$, and $N\alpha=0$. These magnetic data can

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7) C. P. Probhakaran, and C. C. Patel, *J. Inorg. Nucl. Chem.*, **31**, 3319 (1969).

Table 3. Magnetic moments, and characteristic IR bands

	Complex	μ_{eff}, B.M.[a]	IR bands, cm^{-1}
	Mn^{II}(salen)	5.28(5.27)[b]	
	Mn^{II}(3-MeO-salen)·H_2O	5.92	
I	$[Mn^{III}(salen)]_2O_2$	1.96	645, 631
II	$-[-Mn^{IV}(salen)-O-]-_n$	1.99	662, 602
III	$-[-Mn^{IV}(3-MeO-salen)-O-]-_n$	1.58	655, 609
V	$O=Mn^{IV}$(3-MeO-salen)·2MeOH	3.81	840

a) At 296 K

b) Taken from Ref. 4.

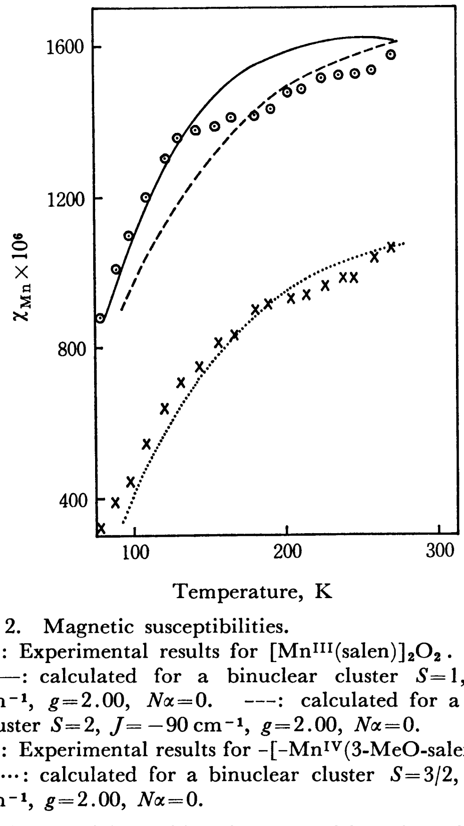

Fig. 2. Magnetic susceptibilities.

⊙: Experimental results for $[Mn^{III}(salen)]_2O_2$.

——: calculated for a binuclear cluster $S=1$, $J=-85$ cm^{-1}, $g=2.00$, $N\alpha=0$. - - -: calculated for a binuclear cluster $S=2$, $J=-90\ cm^{-1}$, $g=2.00$, $N\alpha=0$.

×: Experimental results for $-[-Mn^{IV}(3-MeO-salen)-O-]-_n$.

······: calculated for a binuclear cluster $S=3/2$, $J=-125$ cm^{-1}, $g=2.00$, $N\alpha=0$.

be understood by taking into consideration the thermal equilibrium between spin-free and spin-paired configurations in the complex. As for Complexes II and III, their room-temperature magnetic moments are lower than that (3.75 B.M.) of the spin-only value expected for the octahedral Mn(IV) complexes. Moreover, the magnetic susceptibilities deviate from the Curie-Weiss law (Fig. 2); this deviation is probably caused by antiferromagnetic interaction between manganese atoms bridged by the oxygen atom. Kubo *et al.*[8] have reported that the magnetic susceptibilities of ammonium pentafluoromanganate(III), which has a linear chain structure, fit the curve calculated for a one-dimensional array of Ising spins $S=2$ above 80 K, assuming a "reduced" spin magnetic moment. The data for Complexes II and III do not fit the curve calculated assuming Ising spins $S=3/2$. As is shown in Fig. 2, the data fit, rather, the curve calculated by assuming a binuclear cluster including Mn–O–Mn bonding with $S=3/2$. Moreover, $J=-95\ cm^{-1}$ and $-125\ cm^{-1}$ are proposed Complexes II and III respectively. As for Complex V, the room-temperature magnetic moment, 3.81 B.M., is consistent with that expected for a high-spin Mn(IV). In this case, the magnetic susceptibilities fit the Curie-Weiss law well.

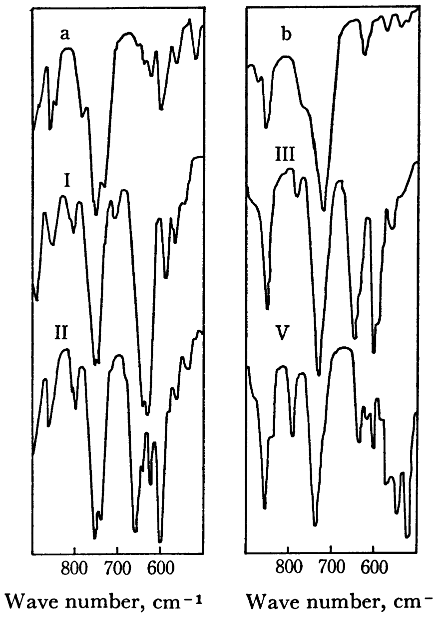

Fig. 3. IR spectra (in Nujol mulls).

a: Mn^{II}(salen), I: $[Mn^{III}(salen)]_2O_2$, II: $-[-Mn^{IV}(salen)-O-]-_n$, b: Mn^{II}(3-MeO-salen)·H_2O, III: $-[-Mn^{IV}(3-MeO-salen)-O-]-_n$, V: $O=Mn^{IV}$(3-MeO-salen)·2MeOH.

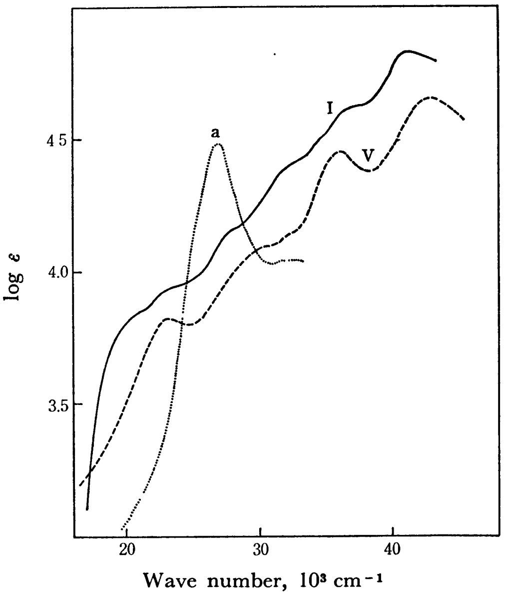

Fig. 4. Electronic spectra.

a: Mn^{II}(salen) in pyridine, I: $[Mn^{III}(salen)]_2O_2$ in dichloromethane, V: $O=Mn^{IV}$(3-MeO-salen)·2MeOH in methanol.

Infrared Spectra. Complexes I–IV show IR spectral frequencies which are comparable with those of the corresponding Mn^{II}(X-salen) in the 700—4000 cm^{-1} region. On the other hand, as is shown in Fig. 3 and Table 3, the spectra of the complexes in the 600—700 cm^{-1} region are characterized by two intense

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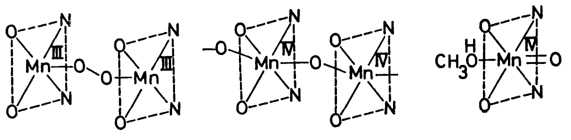
[8] S. Emori, M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **8**, 1385 (1969).

absorption bands. The μ-oxo, $[Fe(salen)]_2O$,[4] and μ-peroxo, $[\{Co(NH_3)_5\}O_2](NO_3)_4$, including a metal-oxygen bond, show similar bands at 820 and 560 cm^{-1} respectively. In the case of Complex V, a new band is observed at 840 cm^{-1}. In view of the fact that the $[O{=}Mn(salen)]_2O_2$ complex, which is considered to involve both Mn=O and $Mn{-}O_2{-}Mn$ bonds, shows the characteristic band at 884 cm^{-1} referred to the Mn=O, and those at 640 and 623 cm^{-1} referred to Mn–O bonds,[9] it is likely to ascribe the above bands in the 600—700 cm^{-1} to the Mn–O bond, and the band at 840 cm^{-1}, to the Mn=O bond.

Electronic Spectra. The electronic absorption spectra of the Mn^{II}(salen) and Complexes I and V in solution are represented in Fig. 4. The absorption bands appearing in the wave-number region higher than 25 kK are thought to be associated mainly with the ligand transitions. As may be seen in Fig. 4, the Mn^{II}(salen) shows no intense absorption band in the visible region. Information concerning the structure of the oxygenated complexes may be obtained by inspecting the visible spectral features. It has been reported that the spin-free manganese(III) complexes with an octahedral configuration give rise to a d–d transition band ($^5E_g \rightarrow {}^5T_{2g}$) with log $\varepsilon=2.5$ around 20 kK.[10] On the other hand, the spin-free penta-coordinate Mn^{III}(salen)X, where X is Br^- or I^-, shows two absorption bands, around 20 kK with log $\varepsilon=3.0$ and around 25 kK with log $\varepsilon=3.5$; these have been described by Prabhakaran *et al.*[7] as a d–d transition and a charge-transfer band respectively. As can be seen in Fig. 4, the spectral pattern of Complex I with two absorption bands at *ca.* 20.0 and *ca.* 23.2 kK resembles that of the penta-coordinate manganese(III)-complexes. Thus, as for Complex I, the visible and the IR spectral properties, as well as the thermal property, which indicates a reversible release of oxygen, led us to conclude that Complex I includes a μ-peroxo bond and that the structure can be depicted as is shown in Fig. 5–(a). As has been mentioned, the magnetic moment, 1.96 B.M., of Complex I (*cf.* Table 3), lower than that expected for the penta-coordinate manganese(III)-complexes with a square-pyramidal structure, can be explained in terms of an antiferromagnetic exchange which may be caused by the formation of a binuclear structure through the μ-peroxo bond. The magnetic moment, 3.81 B.M., of Complex V (*cf.* Table 3) agrees with the assumption that the complex includes a spin-free Mn(IV). The visible electronic spectrum of Complex V, unlike that of Complex I, shows only one peak, at 23.2 kK. This spectral feature is not inconsistent with those of such spin-free, octahedral manganese(IV) complexes as $[MnF_6]^{2-}$ and $[MnCl_6]^{2-}$, which show absorption maxima at 21.8 and 17.9 kK respectively.[11] On the basis of these facts, a proposed structure for Complex V is shown in Fig. 5–(c). The insolubility of Complexes II, III, and IV did not allow measurements of the electronic spectra in solution. However, the magnetic properties and the IR spectral data, as well as the fact that they are obtained from the oxo complexes, led us to propose the structure for the complexes shown in Fig. 5-(b).



(a) (b) (c)

Fig. 5. Schematic structures proposed for the complexes.

Effects of Oxygen Partial Pressure, Solvent, and Substituent on the Oxidation Reaction. As has been discussed above, three types of complexes containing a μ-peroxo-, catena-oxo-, or oxo-bond were isolated in the reactions of the Mn^{II}(X-salen) with oxygen in organic solvents. In this section we will consider the effects of the oxygen partial pressure and of the nature of the solvents and substituents, X, on the complex formation.

As has been descrived in the Experimental part, the Mn^{II}(salen) yielded, upon reaction with oxygen in a DMSO solution, the μ-peroxo complex as a precipitate plus precipitates of the catena-oxo complex. As can be seen in Table 4, the amount of the μ-peroxo complex of the above precipitates increases with a decrease in the partial pressure of oxygen applied in the reaction system; it increases up to 86% when oxygen diluted to 1.7 vol% by mixing with nitrogen is used. It can be noticed that, in Py and DMF solutions, the reaction using dilute oxygen gave the μ-peroxo complex, although the reaction using pure oxygen only afforded the catena-oxo complex.

TABLE 4. THE EFFECTS OF OXYGEN PARTIAL PRESSURE AND SOLVENTS ON THE FORMATION OF $[Mn^{III}(salen)]_2O_2$ AND $-[-Mn^{IV}(salen){-}O{-}]-_n$[a)]

P_{O_2} (vol%)[b)]	Yield[c)]		
	DMSO	DMF	Py
1.7	86	82	21
10	—	50	—
20	—	16	0
100	10	0	0

a) The reactions were carried out using Mn^{II}(salen) (1 g) and solvent (50 ml), at room temperature for 15 hr.. $[Mn^{III}(salen)]_2O_2$ was separated as soluble part by extraction with CH_2Cl_2.

b) Represented in volume % of O_2 in mixed O_2+N_2 at atmospheric pressure and room temperature.

c) Corresponds to

$$\frac{[Mn^{III}(salen)]_2O_2}{[Mn^{III}(salen)]_2O_2+-[-Mn^{IV}(salen){-}O{-}]-_n}\times 100 \text{ in gram.}$$

The above results (*cf.* Table 4) suggest that the formation of the μ-peroxo complex is favored in the solvents in the following order; Py<DMF<DMSO, and that it is also favored when oxygen with a lower partial pressure is reacted.

As for the Mn^{II}(3-MeO-salen)$\cdot H_2O$ and Mn^{II}(5-NO_2-salen)$\cdot$2Py complexes, the corresponding μ-peroxo complex could not be obtained even if the reac-

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9) M. Tamaki, I. Masuda, and K. Shinra, *Chem. Lett.*, **1972** 165.

10) R. Dingle, *Acta Chem. Scand.*, **20**, 33 (1966).

11) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Co., (1963), p. 283.

tion was carried out in a DMSO solution using dilute oxygen of 1.7 vol%. The oxo complex, $O{=}Mn^{IV}$(3-MeO-salen)·2MeOH, was successfully isolated only for the 3-MeO-substituted complex in a MeOH solution. Further, it is of importance that, in a DMF, DMSO, or Py solution, the oxo complex is transformed to the insoluble catena-oxo complex,$-[-Mn^{IV}$(3-MeO-salen)$-O-]-_n$, almost quantitatively, indicating that the reaction forming the catena-oxo complex proceeds *via* the oxo complex. The low solubility of the catena-oxo and μ-peroxo complexes did not allow kinetical measurements. However, in view of the results obtained in the present study, it can be interpreted by assuming that the reactions proceed as follows:

$$\text{S-(Mn}^{\text{II}}\text{)-S} + \text{O}_2 \xrightarrow{k_1} \text{S-(Mn}^{\text{III}}\text{)-O}_2 + \text{S} \qquad (1)$$

$$\text{S-(Mn}^{\text{III}}\text{)-O}_2 + \text{O}_2\text{-(Mn}^{\text{III}}\text{)-S} \xrightarrow{k_2} 2\text{S-(Mn}^{\text{III}}\text{)-O}\cdot + \text{O}_2 \qquad (2)$$

$$\text{S-(Mn}^{\text{III}}\text{)-O}\cdot \longrightarrow \text{S-(Mn}^{\text{IV}}\text{)=O} \qquad (2\text{-}1)$$

$$n[\text{S-(Mn}^{\text{IV}}\text{)=O}] \longrightarrow -[-(\text{Mn}^{\text{IV}})\text{-O-}]-_n + n\cdot\text{S} \qquad (2\text{-}2)$$

$$\text{S-(Mn}^{\text{III}}\text{)-O}_2 + \text{S-(Mn}^{\text{II}}\text{)-S} \xrightarrow{k_3} \text{S-(Mn}^{\text{III}}\text{)-O}_2\text{-(Mn}^{\text{III}}\text{)-S} \qquad (3)$$

((Mn) represents a parent complex, Mn^{II}(X-salen).)

As is illustrated in Fig. 4, the Mn^{II}(salen) shows an electronic absorption maximum at 27.0 kK (log $\varepsilon=4.5$); this maximum is shifted to a lower frequency with the solvents in the order of MeOH (28.7 kK)< DMF (27.7 kK)<DMSO (27.6 kK)<Py (27.0 kK). Similar spectral behavior is observed for the substituted Mn^{II}(X-salen). These results seem to indicate that the complexes are coordinated with the solvent in solutions. In fact, an adduct with a solvent, *e.g.*, Mn^{II}(5-NO_2-salen)·2Py, is isolated. Hence, the reaction of the manganese (II) complexes with oxygen could be initiated by replacing a coordinated solvent molecule with oxygen, thus forming an intermediate superoxo complex, as is shown in Equation (1). When assuming that the unstable superoxo complex thus formed undergoes reactions to yield both oxo- and μ-peroxo complexes, following Equations (2), and (3) respectively, the reaction rate in respect to the superoxo complex can be given as:

$$\begin{aligned}\text{d[S-(Mn}^{\text{III}}\text{)-O}_2]/\text{d}t &= k_1[\text{O}_2][\text{S-(Mn}^{\text{II}}\text{)-S}]\\ &\quad -k_2[\text{S-(Mn}^{\text{III}}\text{)-O}_2]^2 - k_3[\text{S-(Mn}^{\text{II}}\text{)-S}][\text{S-(Mn}^{\text{III}}\text{)-O}_2]\end{aligned} \qquad (4)$$

where k_1, k_2, and k_3 are the rate constants in Reactions (1), (2), and (3) respectively.[12] Reactions (2—1) and (2—2) are thought to follow Reaction (2) very rapidly in DMF, DMSO, and Py solutions. In view of the fact that the catena-oxo, and μ-peroxo complexes were separated out of the reaction system as precipitates, the concentration of the superoxo complex involved in solution must remain approximately constant during the reaction; that is,

$$\text{d[S-(Mn}^{\text{III}}\text{)-O}_2]/\text{d}t \fallingdotseq 0 \qquad (5)$$

Thus, the ratio of the yield of the catena-oxo complex to the μ-peroxo complex can qualitatively be described as:[12]

$$\frac{\text{catena-oxo complex}}{\mu\text{-peroxo complex}} \propto \frac{k_1k_2}{k_3^2}\cdot\frac{[\text{O}_2]}{[\text{S-(Mn}^{\text{II}}\text{)-S}]} \qquad (6)$$

proportional to the ratio of $[O_2]$ to [S-(Mn^{II})-S]. This relation can explain the experimental finding (*cf.* Table 4) that the yield of the catena-oxo complex decreases with a decrease in the oxygen concentration.

In a solvent such as Py, which tends to coordinate with a stronger affinity toward the central manganese ion, it is not unreasonable to expect a smaller k_1 than in another solvent. Hence, the higher yield of the catena-oxo complex by the reaction in the Py solution implies smaller k_3 and k_1 values. The failure to obtain the μ-peroxo compound of the Mn^{II}(3-MeO-salen)·H_2O may be attributed mainly to a larger k_1 caused by the electron-donating MeO group, which weakens the bonding of the central manganese ion with the solvent. The fact that the Mn^{II}(5-NO_2-salen)·2Py yielded the catena-oxo complex, even in the DMSO solution, can be explained in terms of a stronger bonding with the solvent due to the electron-withdrawing NO_2 group.

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[12] From Eqs. (4) and (5), concentration of superoxo complex is given as follows,

$$[\text{S-(Mn}^{\text{III}}\text{)-O}_2] = \frac{[\text{S-(Mn}^{\text{II}}\text{)-S}]}{2k_2} \times \left(-k_3+\sqrt{k_3^2+4k_1k_2[\text{O}_2]/[\text{S-(Mn}^{\text{II}}\text{)-S}]}\right). \qquad (\text{i})$$

And, the rate equation respect to catena-oxo-, and μ-peroxo-complexes are given by Eqs. (ii) and (iii), respectively:

$$\begin{aligned}\text{d}[-(-(\text{Mn}^{\text{IV}})\text{-O-})-_n]/\text{d}t &= (1/n)\cdot\text{d[S-(Mn}^{\text{III}}\text{)-O}\cdot]/\text{d}t\\ &= (k_2/n)\cdot[\text{S-(Mn}^{\text{III}}\text{)-O}_2]^2\end{aligned} \qquad (\text{ii})$$

$$\text{d[S-(Mn}^{\text{III}}\text{)-O}_2\text{-(Mn}^{\text{III}}\text{)-S]}/\text{d}t = k_3[\text{S-(Mn}^{\text{III}}\text{)-O}_2][\text{S-(Mn}^{\text{II}}\text{)-S}] \qquad (\text{iii})$$

Then, from the Eqs. (i), (ii) and (iii) the ratio of reaction rate for catena-oxo complex to that for μ-peroxo complex is derived as,

$$\begin{aligned}\frac{\text{d}[-(-(\text{Mn}^{\text{IV}})\text{-O-})-_n]/\text{d}t}{\text{d[S-(Mn}^{\text{III}}\text{)-O}_2\text{-(Mn}^{\text{III}}\text{)-S]}/\text{d}t} &= \frac{k_2[\text{S-(Mn}^{\text{III}}\text{)-O}_2]}{nk_3[\text{S-(Mn}^{\text{II}}\text{)-S}]}\\ &= (1/2n)\left(-1+\sqrt{1+(4k_1k_2/k_3^2)\frac{[\text{O}_2]}{[\text{S-(Mn}^{\text{II}}\text{)-S}]}}\right)\end{aligned} \qquad (\text{iv})$$

Eq. (iv) can be qualitatively transformed as shown by Eq. (6).