Pergamon

PII: S0277-5387(97)00003-X

Polyhedron Vol. 16, No. 15, pp. 2553–2561, 1997

0277-5387/97 $17.00+0.00

Chemical mechanism of dioxygen activation by manganese(III) Schiff base compound in the presence of aliphatic aldehydes

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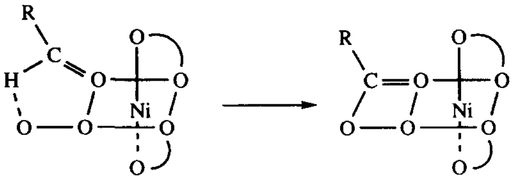
(Received 27 November 1996; accepted 12 December 1996)

Abstract—The manganese(III) complexes with tetradentate Schiff base [$H_2(L)$] derived from salicylaldehyde and 2-amino-1-benzylamine [abbreviated as H_2(salabza)], ethylenedimaine and 2-hydroxybenzophenone [H_2(7-Phe-salen)], ethylenediamine and 2-hydroxyacetophenone [H_2(7-Me-salen)] showed much higher activity for degradation of tetraphenylcyclopentadienone(TCPN) the singlet oxygen ($^1\Delta_g$) scavenger, in the presence of cyclohexanecarboxaldehyde than those of the compounds with H_2(salen) and H_2(salphen), which are derived from salicyaldehyde and ethylenediamine, and *o*-phenylenediamine, respectively. X-ray crystal structural determinations of the former three compounds and electrochemical data of all the compounds have given strong support for the conclusion that the active species for degradation of TCPN is an acylperoxo Mn^{III} species coordinated by an aliphatic peracid chelate, which should be derived from aliphatic aldehyde and dioxygen, where the geometry of the tetradentate Schiff base around the Mn^{III} ion is of *cis*-*β*-configuration. Under the same experimental conditions, the corresponding iron(III) compounds exhibited negligible activity towards the activation of the dioxygen molecule. This was explained in terms of the difference in electronic structures between the two metal ions. © 1997 Elsevier Science Ltd

Keywords: Mn(III) Schiff base compounds; activation of dioxygen; dioxygen and aldehyde; Mn(III) and Fe(III) compounds.

Molecular oxygen is vital to almost all the animals on earth, including man, for metabolism and to provide energy for life. In the chemical industry as well much has been expected of molecular oxygen as the most available oxidant for mass production. The ground state of molecular oxygen is a triplet with two unpaired electrons having parallel spins. Therefore, direct reaction of molecular oxygen with a spin-singlet organic compound is a spin-forbidden process [1]. On the other hand, the radical chain reaction is one practical process which organic compounds may be oxidized with molecular oxygen using transition metal catalysts [2].

In 1992, Mukaiyama and co-workers reported that in the presence of a catalytic amount of a bis(1,3-diketonato)nickel(II) complex, trisubstituted and *exo*-terminal olefins or norbornene analogues were smoothly monooxygenated into the corresponding epoxides in near quantitative yields on treatment with aldehyde under atmospheric pressure of oxygen at room temperature [3]. Nishida *et al.* have reported [4] that the nickel(II) solution described above exhibits high activity for degradation of tetraphenylcyclopentadienone(TCPN), a singlet oxygen ($^1\Delta_g$) scavenger, and that an intrinsically active species for the epoxidation should be a nickel(II)-organic peracid derivative, which should be formed through an intermediate as illustrated below [5]. The same dis-



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cussion has already been applied to the case of cobalt(II) complexes and alcohols [5].

Recently, Mn^{III} complexes with tetradentate Schiff bases have been used for epoxidation of olefins in the presence of aliphatic aldehydes [6], in these systems, many approaches have been tried to develop efficient, enantioselective epoxidations of non-functional olefins [7]. As an active species in these systems, the formation of an acylperoxo-Mn^{III} species has been assumed [8], similar to the cases of Ni^{II} and Co^{II} [4,5], however, there is no chemical evidence to support the above consideration.

In previous papers, we have proposed that the study of the reaction between the oxidant and the singlet oxygen scavenger, such as TCPN, is highly effective in identifying an active species in the oxidant and several examples support this consideration [4,5,9,10]. Thus, in this study, we have studied the reaction between TCPN and several manganese(III) Schiff base complex solutions containing an aliphatic aldehyde and we propose a new scheme for dioxygen activation in these systems.

EXPERIMENTAL

Synthetic methods

Chemical structures of the ligands cited in this study are illustrated in Fig. 1. The Schiff bases H_2(salabza), H_2(7-Phe-salen) and H_2(7-Me-salen) were obtained from the reaction mixture of salicylaldehyde and 2-amino-1-benzylamine, ethylenediamine and 2-hydroxybenzophenone, and ethylenediamine and 2-hydroxyacetophenone, respectively. The manganese(III) complexes with Schiff bases were obtained according to the general methods. A methanol solution containing Mn^{III} acetate and the ligand was refluxed for 1 h, and the desired compounds were obtained by adding an appropriate salt, such as lithium chloride, sodium perchlorate or ammonium hexafluorophosphate. By these procedures, Mn(salabza)Cl (**1**), Mn(7-Phe-salen)$(CH_3OH)ClO_4$ (**2**), Mn_2(7-Me-salen)$_2(CH_3COO)ClO_4$ were obtained. By refluxing an ethanol solution containing $Mn(acac)_3$ and the ligand, Mn(salabza)(acac) and Mn(7-Phe-salen)(acac) were obtained, where H(acac) denotes acetylacetone. By the similar ways, several new iron(III) compounds with Schiff bases were also prepared; these are Fe(salabza)Cl, Fe(salabza)(acac) (**3**) and Fe(7-Phe-salen)Cl.

Reaction with TCPN

The time course of the absorbance of the mixed solution of TCPN (10 cm^3 of 1/1500 mol dm^{-3} in 1,2-dichloroethane) and metal complex (40 cm^3, 1/500 mol dm^{-3} dmso solution) and cyclohexanecarboxaldehyde (1 cm^3) was measured at 298 K. Decrease of the absorbance indicates the degradation of TCPN by the system [4,5].

Crystallography

Single crystal of [Mn(salazba)Cl], [Mn(7-Phe-salen)$(CH_3OH)]ClO_4$, [Mn_2(7-Me-salen)$_2(CH_3COO)]ClO_4$ and [Fe(salabza)(acac)]$\cdot C_2H_5OH$ were mounted on a Rigaku AFC-5 four-circle diffractometer at Keio University for data collection. The structures were solved by the direct and heavy-atom methods and refined by full-matrix least-squares. Table 1 summarizes the crystallographic data of the compounds. A full report of the refinement procedures and the

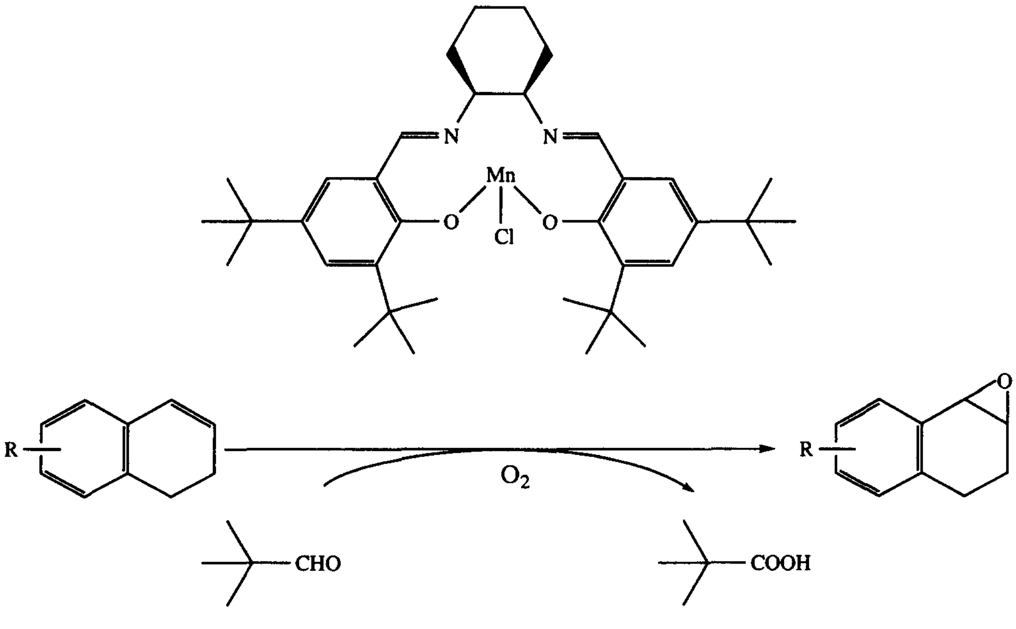


Table 1. Crystallographic data of the compounds

	1	**2**	**3**·C_2H_5OH
Formula	$C_{21}H_{16}ClMnN_2O_2$	$C_{29}H_{26}MnN_2O_7Cl$	$C_{28}H_{29}FeN_2O_5$
M	418.8	604.93	529.40
Crystal system	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/c$	$Pnaa$	$P2_1/n$
a (Å)	9.955(2)	16.189(3)	13.731(5)
b (Å)	12.701(2)	31.858(3)	19.050(7)
c (Å)	14.903(3)	10.518(3)	11.158(6)
β (°)	108.60(2)		113.71(3)
V (Å^3)	1785.9(6)	5424.6(15)	2672.3(20)
Z	4	8	4
D_0 (g cm^{-3})	1.558	1.481	1.316
μ(Mo-K_α) (cm^{-1})	9.08	6.36	6.03
(Observed reflections [$F_0 > 3\sigma(F_0)$]	2973	3171	2506
No. variables	308	453	348
R	0.053	0.056	0.081
Rw	0.047	0.048	0.063

Details in common; scan type, w-type; R, function minimized on F; $w = 1/[\sigma^2(F) + 0.000225F^2]$.

atomic coordinates are available as supplementary data.

Electrochemical measurements

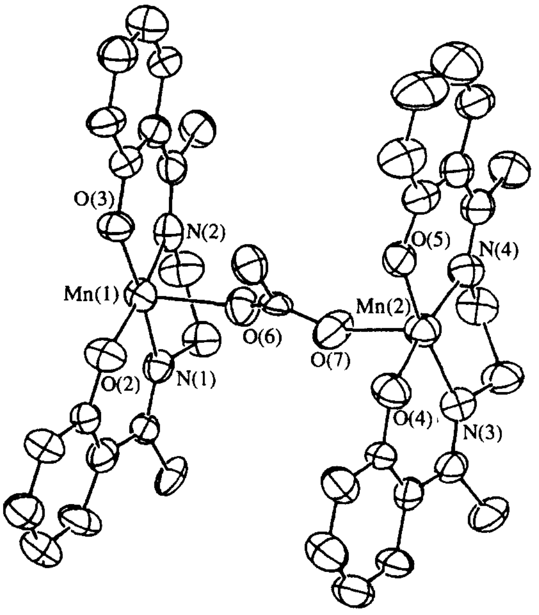
The electrochemical measurements were performed in the usual manner [11], in dimethylsulfoxide (dmso), under Ar atmosphere, 25°C, with a glassy carbon electrode and tetra(n-butyl)ammonium tetrafluoroborate as an electrolyte and the potential was referenced to a saturated sodium chloride calomel electrode(SSCE).

Physical measurements

Absorption spectra of the compounds were obtained with a Shimadzu spectrophotometer mode UV-2200 at 298 K.

RESULTS

Crystallography



In Figs 2 and 3, the ORTEP drawings of the [Mn(salabza)Cl] and [Mn(7-Phe-salen)(CH_3OH)]$^+$ are shown and the selected bond distances and angles are listed in Table 2. The overall features of the structure of [Mn(salabza)Cl] are similar to those observed for Mn(salen)Cl [12], the coordination polyhedron can be described as a square pyramid with the Mn^{III} ion being displaced from the O(3), N(5), N(6) and O(4) plane by 0.26 Å, which is larger than that observed for the Mn(salen)Cl (0.19 Å). This may be due to steric requirements of the ligand. In the case of [Mn(7-Phe-salen)(CH_3OH)]$^+$, the displacement of the Mn^{III} ion from the O(3), N(10), N(11) and O(4) plane is 0.08 Å. Other bond distances are similar to those observed for Mn(salen)Cl. In the case of [Mn(7-Me-salen)]$_2$(CH_3COO)ClO_4, this complex consists of a dimeric structure with a μ-acetate bridge (Mn—Mn distance is 6.434 Å), as shown above, however, due to poor crystalinity, R did not decrease below 10%.*

Activity for dioxygen activation

In Figs 4 and 5 the time course of the absorbance at 505 nm of the reaction mixture is illustrated. These

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*Crystal data: monoclinic, $P2_1/c$, $Z = 4$, $a = 15.652(9)$, $b = 16.251(8)$, $c = 15.834(10)$ Å, $\beta = 92.97(5)°$, $V = 4022(4)$ Å^3, $R = 0.140$ for 3630 observed reflections.

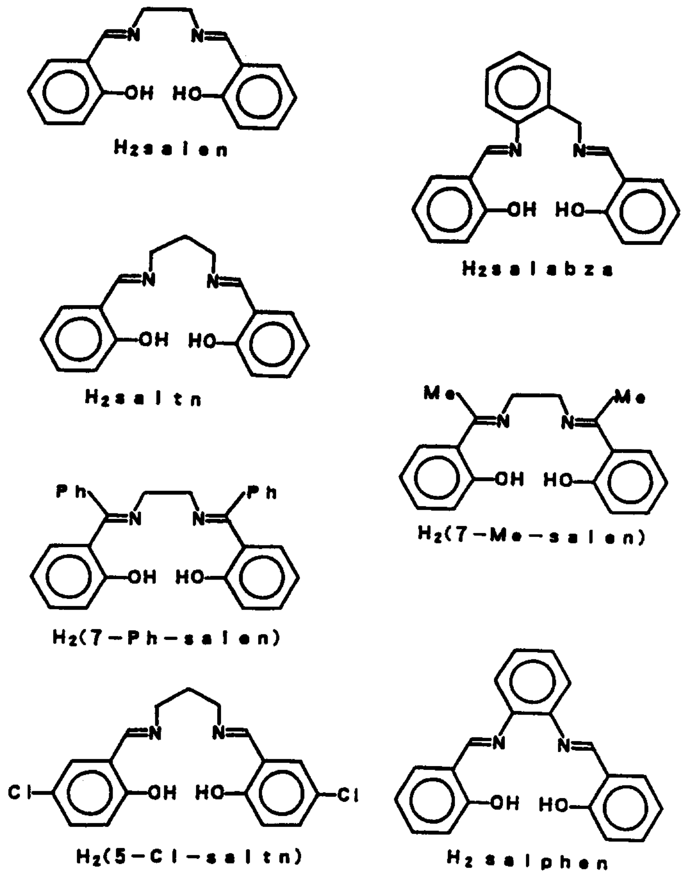


Fig. 1. Chemical structures of the ligands cited in this study.

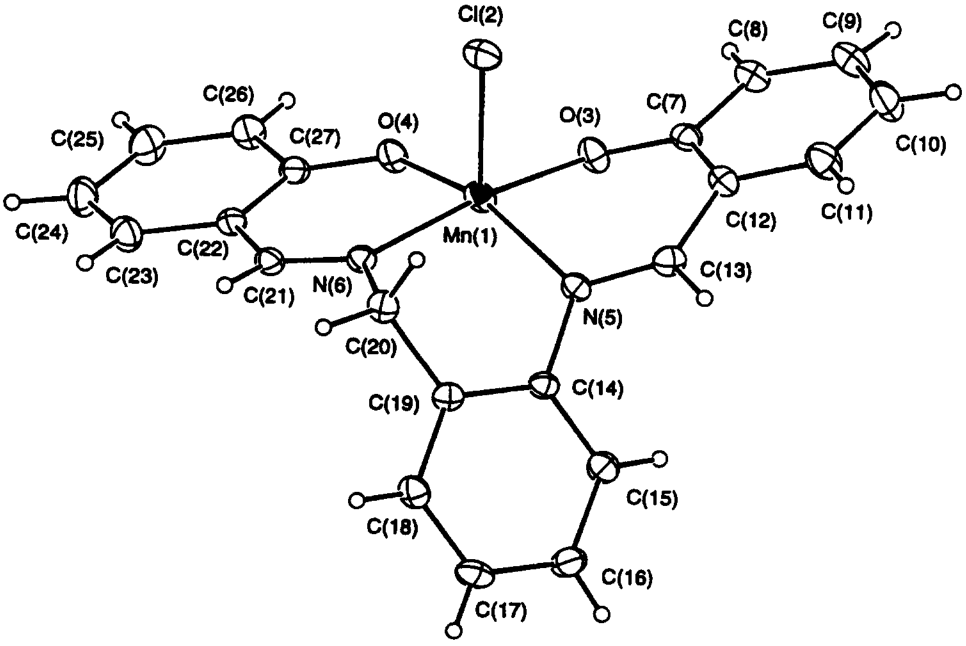


Fig. 2. ORTEP drawing of Mn(salabza)Cl.

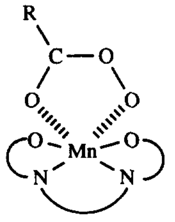
clearly show that the activity of the Mn(saltn)Br, Mn(salabza)Cl and Mn(7-Phe-salen)(CH_3OH)ClO_4 for degradation of TCPN in the presence of cyclohexanecarboxaldehyde [4,5] is much higher than that of the Mn(salen)Cl or Mn(salphen)Cl, where H_2(salphen) denotes the Schiff base derived from salicylaldehyde and *o*-phenylenediamine. This indicates that the former three Mn^{III} compounds exhibit high activity to activate dioxygen molecule in the presence of an aliphatic aldehyde. In Fig 6 the results observed for the corresponding iron(III) compounds are also illustrated; this demonstrates that the iron(III) compounds with Schiff bases are generally inactive for dioxygen activation in the presence of cyclohexanecarboxaldehyde.

Electrochemical data

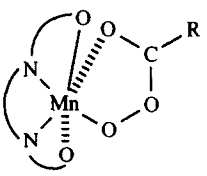
In Fig. 7 the cyclic voltammograms of some Mn^{III} compounds are shown. The complexes studied in this study undergo reversible Mn^{III} ↔ Mn^{II} reaction in the region −0.15–0.39 (*vs* SCE), as listed in Table 3.

DISCUSSION

It is generally accepted that aldehydes act as reducing agents in the reaction with metal compounds. Since the reduction potential (Mn^{III} → Mn^{II}) of the Mn^{III}) compounds is not related with the activity for degradation of TCPN (see Table 3 and Figs 4 and 5), the reduction of the Mn^{III} ion is not essential for the activation of dioxygen; thus, in these cases it seems quite likely that the activation of dioxygen proceeds without change of the oxidation state of the Mn^{III} ion, as described for several cases such as Ni^{II}, Co^{II} and Mn^{II} compounds [4,5,13]. For the latter cases, we have pointed out the importance of the formation of an intermediate consisting of a metal complex, dioxygen and an aldehyde, leading to formation of an acylperoxo-metal complex, which should be an intrinsic active species for degrading TCPN, and also for epoxidation of olefins.



(a)



(b)

In the formation of an acylperoxo-Mn^{III} complex, there are two conformations for the species; the (a)-type, where the Schiff base occupies four corners of the square plane, and the (b)-type where the tetradentate Schif base ligand is of *cis-β*-configuration; three corners of the square plane are occupied by the Schiff base, as illustrated above.

Based on the results that the Mn^{III} complexes with a (6–6–6) fused ring system, such as H_2(saltn) and H_2(5-Cl-saltn) [14], show higher activity than those of the (6–5–6) fused ring systems, such as H_2(salen) and

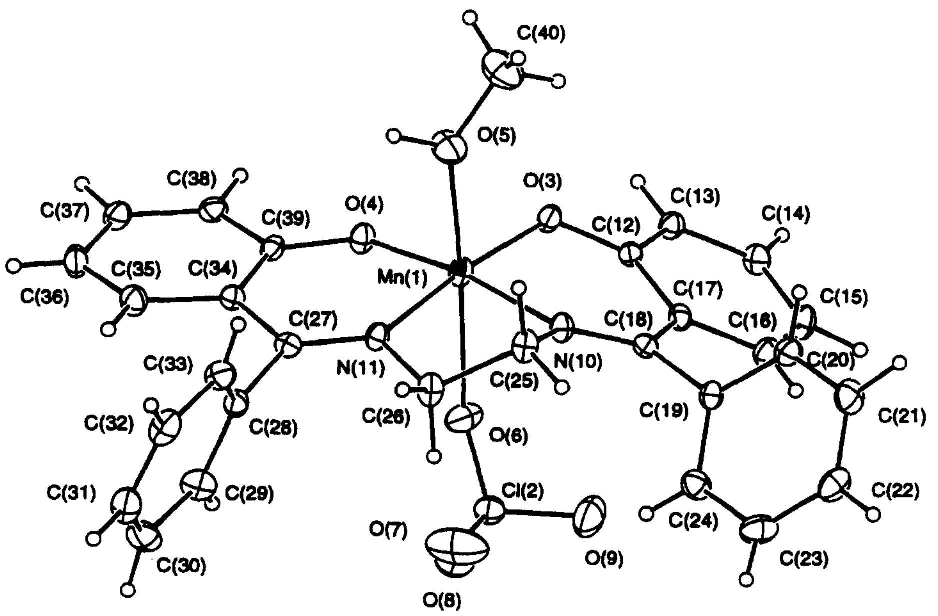


Fig. 3. ORTEP drawing of Mn(7-Phen-salen)(CH_3OH)$^+$.

Table 2. Selected bond lengths (Å) and angles (°) of the compounds

Mn(salabza)Cl (**1**)			
Mn(1)—Cl(2)	2.404(2)	Mn(1)—O(3)	1.884(3)
Mn(1)—O(4)	1.887(3)	Mn(1)—N(5)	2.028(3)
Mn(1)—N(6)	2.001(3)		
Cl(2)—Mn(1)—O(3)	95.5(1)	Cl(2)—Mn(1)—O(4)	104.2(1)
Cl(2)—Mn(1)—N(5)	97.9(1)	Cl(2)—Mn(1)—N(6)	92.5(1)
O(3)—Mn(1)—O(4)	89.2(1)	O(3)—Mn(1)—N(5)	88.6(1)
O(3)—Mn(1)—N(6)	171.9(2)	O(4)—Mn(1)—N(5)	157.9(1)
O(4)—Mn(1)—N(6)	90.1(1)	N(5)—Mn(1)—N(6)	89.1(2)
Mn(7-Phen-salen)(CH_3OH)ClO_4 (**2**)			
Mn(1)—O(3)	1.848(4)	Mn(1)—O(4)	1.857(4)
Mn(1)—O(5)	2.219(5)	Mn(1)—O(6)	2.516(5)
Mn(1)—N(10)	1.978(5)	Mn(1)—N(11)	1.995(5)
O(3)—Mn(1)—O(4)	94.0(2)	O(3)—Mn(1)—O(5)	92.8(2)
O(3)—Mn(1)—O(6)	91.4(2)	O(3)—Mn(1)—N(10)	89.6(2)
O(3)—Mn(1)—N(11)	174.0(2)	O(4)—Mn(1)—O(5)	93.7(2)
O(4)—Mn(1)—O(6)	85.3(2)	O(4)—Mn(1)—N(10)	171.0(2)
O(4)—Mn(1)—N(11)	91.7(2)	O(5)—Mn(1)—O(6)	175.8(2)
O(5)—Mn(1)—N(10)	94.3(2)	O(5)—Mn(1)—N(11)	88.6(2)
O(6)—Mn(1)—N(10)	86.4(2)	O(6)—Mn(1)—N(11)	87.3(2)
N(10)—Mn(1)—N(11)	84.5(2)		
Fe(salabza)(acac) (**3**)			
Fe(1)—O(2)	2.032(7)	Fe(1)—O(3)	2.018(7)
Fe(1)—O(4)	1.937(7)	Fe(1)—O(5)	1.922(7)
Fe(1)—N(7)	2.139(8)	Fe(1)—N(8)	2.119(8)
O(2)—Fe(1)—O(3)	84.5(3)	O(2)—Fe(1)—O(4)	169.4(3)
O(2)—Fe(1)—O(5)	94.4(3)	O(2)—Fe(1)—N(7)	87.9(3)
O(2)—Fe(1)—N(8)	83.2(3)	O(3)—Fe(1)—O(4)	87.9(3)
O(3)—Fe(1)—O(5)	98.9(3)	O(3)—Fe(1)—N(7)	89.6(3)
O(3)—Fe(1)—N(8)	166.5(3)	O(4)—Fe(1)—O(5)	94.2(3)
O(4)—Fe(1)—N(7)	84.6(3)	O(4)—Fe(1)—N(8)	103.5(3)
O(5)—Fe(1)—N(7)	171.3(3)	O(5)—Fe(1)—N(8)	87.5(3)
N(7)—Fe(1)—N(8)	84.4(3)		

H_2(salphen), irrespective of their reduction potential (see Fig. 5), it seems reasonable to assume that the structure of an acylperoxo-Mn^{III} species in these systems should be the (b)-type, because it is generally accepted that the (6–6–6) fused ring systems prefer the *cis*-β-configuration over those in the (6–5–6) fused ring systems. In the case of [Mn(7-Phe-salen)(CH_3OH)]$^+$ compound, the steric repulsion between the phenyl ring and acylperoxide species may exclude the possible formation of the (a)-type intermediate. As shown in Fig. 2, the ligand H_2(salabza) does not prefer the planar coordination configuration because of its teric requirements; this may explain the high activity of this complex. The *cis*-β-configuration of the H_2(salabza) ligand was confirmed by the X-ray crystal structural determination of the iron(III) complex, Fe(salabza)(acac) as illustrated in Fig. 8. Although we cannot obtain the crystals suitable for X-ray analysis, the isolation of the Mn(salabza)(acac) and Mn(7-Phe-salen)(acac) may support the above consideration. In the case of the H_2(7-Me-salen) complex, the dimeric structure may prevent the formation of the *cis*-β-configuration and this may explain the rather complicated manner observed in the decrease of absorbance at 505 nm shown in Fig. 4, trace E.

In contrast to the high activity of the Mn^{III} compounds, the corresponding iron(III) are all inactive for dioxygen activation in the presence of cyclohexanecarboxaldehyde (see Fig. 6). Since the formation of the *cis*-β-configuration of the iron(III) complex is possible (see Fig. 8), the origin for the inactivity of the iron(III) analogues should be due to its electronic structure, d^5, compared with that of Mn^{III}, d^4. If we assume that the epoxidation of olefin proceeds through the interaction with an acylperoxo-Mn^{III} species in a concerted manner as described in Fig. 9(a) [5,15], the electronic properties, such as the energy level or occupancy of electrons in the *d*-orbital con-

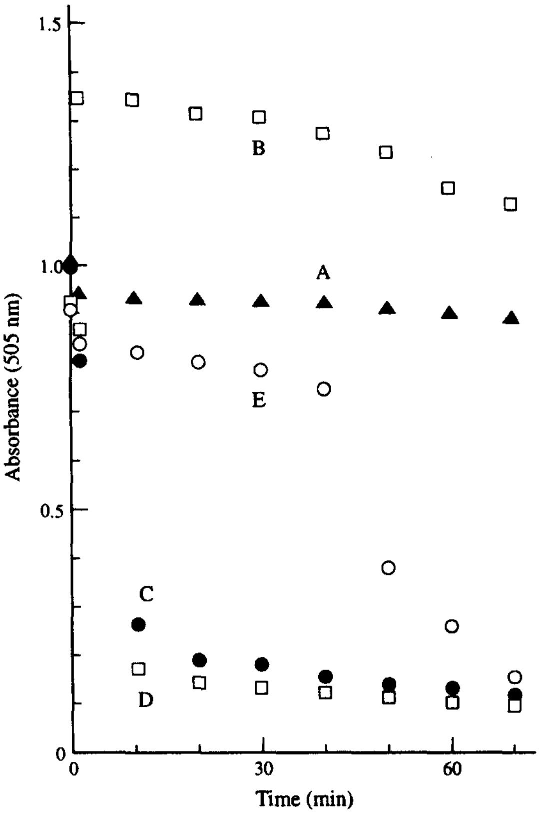


Fig. 4. Time course of absorbance at 505 nm of the mixed solution containing TCPN and Mn^{III} complexes with a (6-5-6) fused ring: (a) Mn(salen)Cl; (b) Mn(salphen)Cl; (c) Mn(salabza)Cl; (d) Mn(7-Phe-salen)(CH_3OH)ClO_4; (e) Mn_2(7-Me-salen)$_2$(CH_3COO)ClO_4.

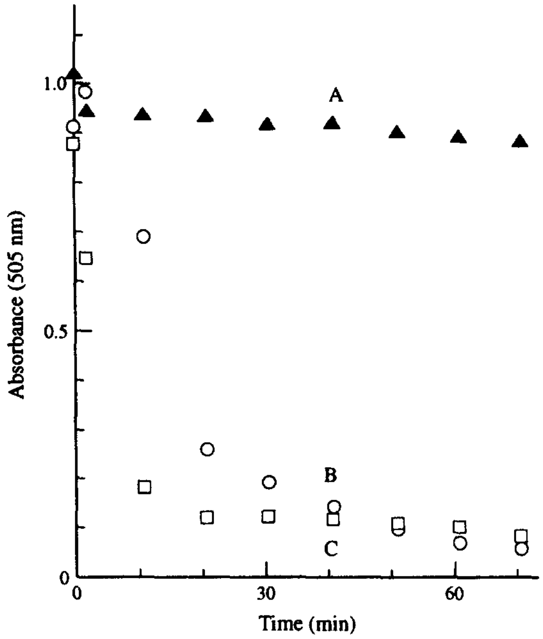


Fig. 5. Time course of absorbance at 505 nm of the mixed solution containing TCPN and MN^{III} compounds with a (6-6-6) fused ring: (a) Mn(salen)Cl; (b) Mn(saltn)Br; (c) Mn(5-Cl-saltn)(CH_3OH)ClO_4.

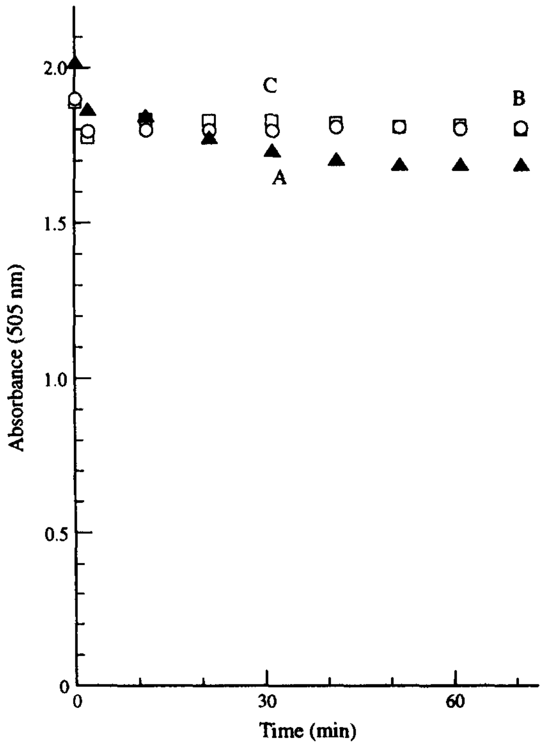


Fig. 6. Time course of absorbance at 505 nm of the mixture containing iron(III) complex and TCPN: (a) Fe(salen)Cl; (b) Fe(salabza)Cl; (c) Fe(salabza)(acac).

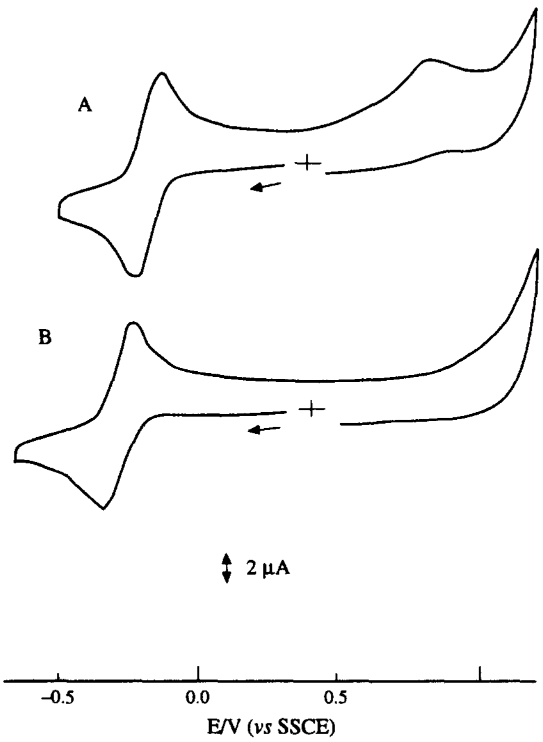


Fig. 7. Cyclicvoltammograms of some Mn^{III} compounds: (a) Mn(saltn)ClO_4; (b) Mn(7-Phe-salen)(CH_3OH)ClO_4.

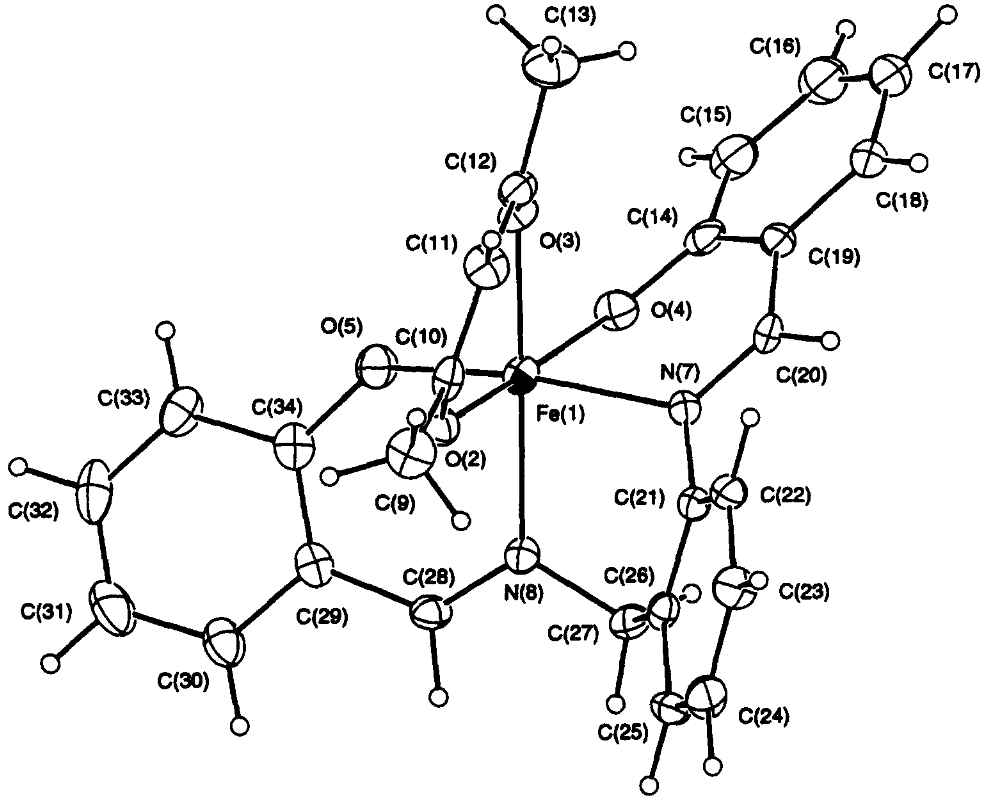


Fig. 8. ORTEP drawing of Fe(salabza)(acac).

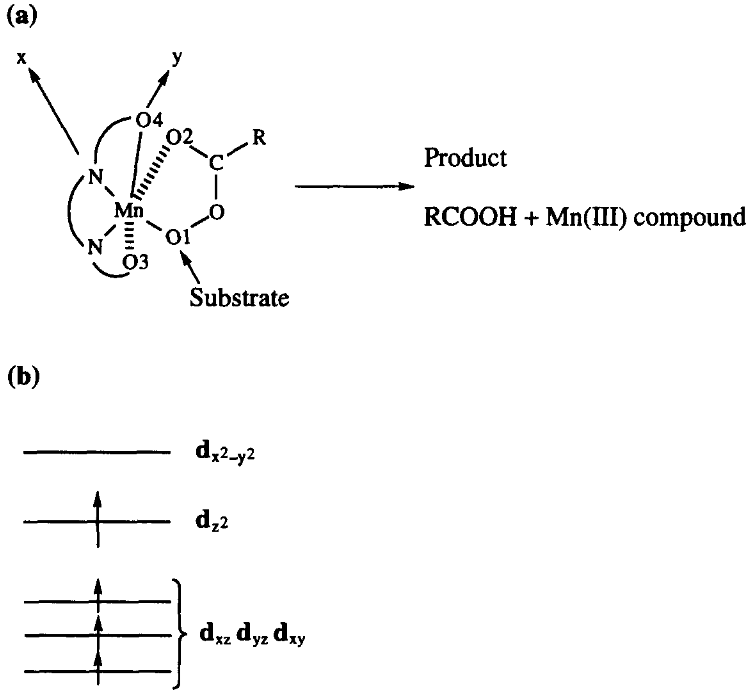


Fig. 9. (a) Assumed intermediate between substrate and acylperoxo Mn^{III} complex; (b) *d*-orbital splitting scheme assumed for intermediate described in (a).

taining the acylperoxide ion, may control the reactivity. In the case of the *cis*-β-configuration, it is likely that oxygen atom O(1) [see Fig. 9(a)] of the acylperoxide which may react with the occupied orbital of the olefin exists in the plane consisting of three atoms [two nitrogen atoms and O(4) of the Schiff base; all four atoms are in the *xy*-plane in Fig. 9 (a)]. Under this circumstance, the *d*-orbital energy level of the acylperoxo Mn^{III} compound may be written schematically as shown in Fig. 9, where the $d_{x^2-y^2}$ orbital, which contains the orbital of the O(1) atom of the acyl-peroxide, is the highest and thus vacant [see Fig. 9(b)]. This situation may lead to facile interaction between the occupied orbital of the substrate and the $d_{x^2-y^2}$ as observed for the mixture of *trans*-[FeCl$_2$(cyclam)]$^+$ and cyclohexanecarboxaldehyde [16,17], and also the d^0-metal alkylhydroperoxide adducts [18]. This may clearly explain the higher activity of the Mn^{III} compound than the corresponding iron(III) compounds studied here; in the latter cases the corresponding $d_{x^2-y^2}$ is occupied by one *d*-electron.

Table 3. Electrochemical data of the Mn^{III} compounds

	$E_{1/2}$ (V *vs* SSCE)
Mn(salen)Cl	-0.20
Mn(saltn)ClO$_4$	-0.18
Mn(salabza)Cl	-0.15
Mn(7-Phe-salen)(CH$_3$OH)ClO$_4$	-0.30
Mn$_2$(7-Me-salen)$_2$(CH$_3$COO)ClO$_4$	-0.39

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