Novel Reactivity of the Dioxygen Molecule in the Presence of a Manganese(II) Complex and Reducing Agents

Yuzo Nishida,* Noriko Tanaka, Akira Yamazaki, Tadashi Tokii,† Noriyuki Hashimoto,† Koji Ide,† and Kaku Iwasawa†

Departments of Chemistry, Faculty of Science, Yamagata University, Yamagata 990, Japan, and Faculty of Science and Engineering, Saga University, Saga 840, Japan

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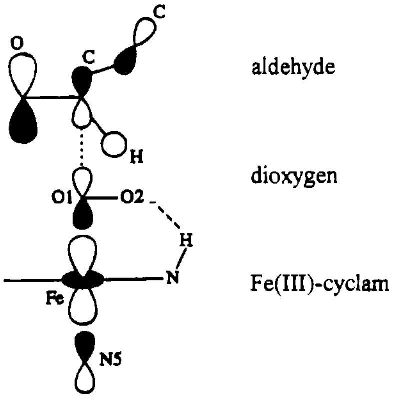
A manganese(II) complex with pentadentate ligand derived from 2,6-diacetylpyridine and triethylenetetramine exhibits high activity for activation of dioxygen in the presence of several aliphatic aldehydes, but the activities of other manganese(II) compounds with tripod-like ligands such as tris(2-benzimidazolylmethyl)amine or bis(2-benzimidazolylmethyl) ether are almost negligible. On the basis of these facts including electrochemical data under dioxygen atmosphere, the importance of an intermediate complex formation among aliphatic aldehyde, Mn(II) complex, and dioxygen is pointed out; in the intermediate, the dioxygen molecule is assumed to coordinate to a manganese(II) ion by hydrogen bonding with the hydrogen atom of the chelate (−NH group), and the novel reactivity of dioxygen, i.e., the dioxygen molecule accepts an electron from the aldehyde through formation of the intermediate to yield an organic peracid without the change of the oxidation state of the metal ion, is postulated.

Introduction

In our previous papers,[1,2] we have shown that *trans*-[FeCl$_2$(cyclam)]$^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) exhibits high activity for the degradation of TCPN (tetraphenylcyclopentadienone, one of the singlet oxygen ($^1\Delta_g$) quencheres) in the presence of reducing reagents such as aliphatic aldehydes or unsaturated fatty acids such as linolenic acid, but the activity of the corresponding *cis*-isomer is completely negligible for the reactions. For the explanation on the above facts, we have postulated the formation of an intermediate complex, as shown in structure **I**; in this intermediate, dioxygen molecule coordinates to an iron(III) ion, associated with the hydrogen bonding between oxygen atom and hydrogen atom of the (cyclam),[3] and the electrons in the HOMO of the aldehyde are transfered to dioxygen, which may be facilitated by the favorable phase relationship of the interacting orbitals. It should be noted here that activation of dioxygen molecule in this case is assumed to proceed without the change of oxidation state of an iron(III) ion. The formation of a peracid, which may occur through the formation of the above intermediate, was also confirmed in terms of the ESR method.[2]



I

A similar interaction between dioxygen molecule and reducing agents was also assumed for the elucidation of olefin epoxidation reaction catalyzed by nickel(II)−acetylacetonato or cobalt(II)−acetylacetonato compounds in the presence of aliphatic alcohols or aldehydes.[4,5] In order to obtain more detailed information on the unique reactivity of dioxygen molecule in the presence of both the reducing agent and a metal compound, we have in this study investigated the reaction mixture of dioxygen molecule, aliphatic aldehyde, and a manganese(II) complex; the Mn(II) ion has a structure isoelectronic to the structure of an iron(III) ion, and it is generally believed that the reduction reaction of Mn(II) to Mn(I) is unfavorable under the usual conditions.

Experimental Section

Mn(II) Compounds. Mn(II) compounds used in this study are Mn(L)(H$_2$O)$_2$ClClO$_4$,[6] Mn(obz)Cl$_2$(CH$_3$OH), Mn(ntb)ClClO$_4$,[7] and Mn(ntb)(NCS)$_2$,[7] where (L) is the pentadentate ligand derived from 2,6-diacetylpyridine and triethylenetetramine, and the chemical structures of the ligands are illustrated in Figure 1. These manganese(II) complexes were obtained according to the literature methods except for the (obz) complex; the latter complex was prepared in this study as follows: to a methanol solution of (obz) was added methanol solution containing of calculated amount of MnCl$_2$·4H$_2$O, and the crystals precipitated after 2 days were filtered. Anal. Calcd for Mn(obz)Cl$_2$(CH$_3$OH): C, 46.81; H, 4.16; N, 12.84. Found: C, 46.87; H, 4.17; N, 12.80.

Crystal Structure Determinations. The crystal structures of two Mn(II) compounds, Mn(L)(H$_2$O)$_2$ClClO$_4$ and Mn-

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* To whom correspondence should be addressed at Yamagata University.

† Saga University.

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(1) Nishida, Y.; Tanaka, N.; Takahashi, S. *Chem. Lett.* **1993**, 411−414.

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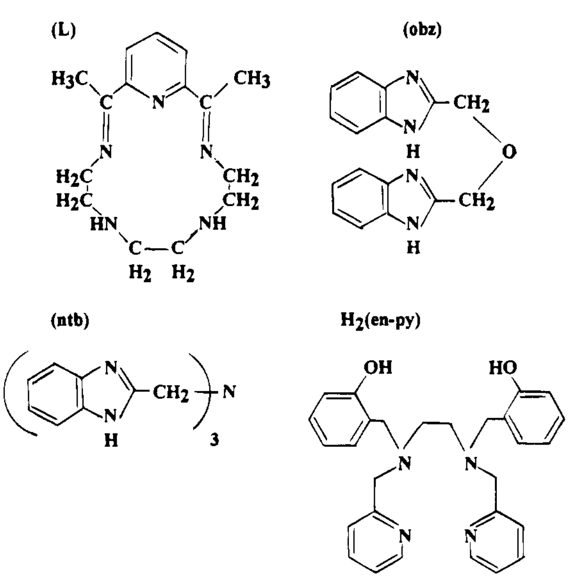

Figure 1. Chemical structures of ligands cited in this study.

Table 1. Crystal Data of the Compounds

	$Mn(L)(H_2O)_2ClClO_4$	$Mn(obz)Cl_2(CH_3OH)$
empirical formula	$C_{15}H_{27}N_5O_6Cl_2Mn$	$C_{17}H_{18}N_4O_2Cl_2Mn$
cryst dimens, mm	0.30 × 0.4 × 0.4	0.15 × 0.10 × 0.40
cryst syst	monoclinic	monoclinic
no. of reflcns used for unit cell determination (2θ range, deg)	25 (20.3–25.9)	25 (20.3–25.3)
lattice params		
a, Å	10.618(3)	7.069(4)
b, Å	27.842(4)	14.620(2)
c, Å	7.928(3)	18.523(2)
β, deg	109.29(2)	93.45(2)°
V, Å^3	2211.1(9)	1911(1) Å^3
space group	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
Z	4	4
D_{calc}, g/cm^3	1.500 g/cm^3	1.516 g/cm^3
$F(000)$	1036	892
μ(Mo Kα), cm^{-1}	8.55	9.64
scan type	$\omega-2\theta$	$\omega-2\theta$
scan rate, deg/min	32.0	8.0
no. of observns	1043	1265
no. of variables	134	235
residuals	$R = 0.074$	$R = 0.069$
	$R_w = 0.092$	$R_w = 0.077$
goodness of fit indicator	2.80	1.83
max peak in final dif F, e/Å^3	0.79	0.51

(obz)$Cl_2(CH_3OH)$, were determined in this study. Crystals were mounted on a glass fiber. All measurements were made on a Rigaku 5S diffractometer with graphite monochromated Mo Kα radiation at 296 K and a 12 KV rotating anode generator at Saga University. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angle of 25 carefully centered reflections. The cell constants and the crystal data were summarized in Table 1. The data were corrected for Lorentz and polarization effects. The structures were solved by direct method, and the non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Weber.[8] Anomalous dispersion effects were included in F_{cal}, the values for $\Delta f'$ and $\Delta f''$ were those of Cromer. All the calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.[9]

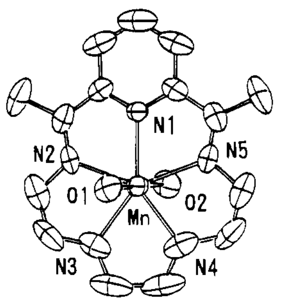

Figure 2. Molecular structure of $Mn(L)(H_2O)_2^{2+}$.

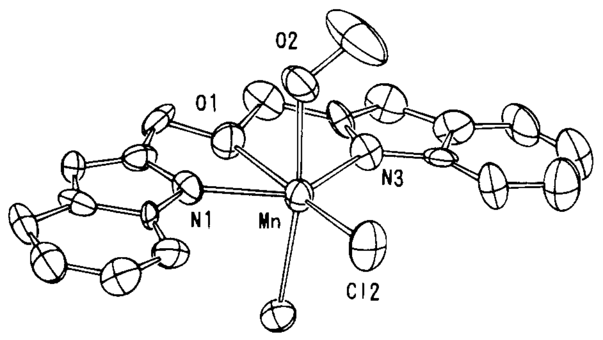

Figure 3. Molecular structure of $Mn(obz)Cl_2(CH_3OH)$.

Electrochemical Measurements. The cyclic voltammograms (CV) of the Mn(II) compounds were measured in the usual manner: in a dimethyl sulfoxide (dmso) solution, containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte, 0.001 M metal complex at 25 °C, and a glassy carbon electrode, with the potential referenced to saturated sodium-chloride electrode(SSCE). For the CV measurements under O_2 pressure, dry dioxygen gas was bubbled through the cell for 15 min before the measurements. The concentration of the dioxygen molecule in the reaction mixture was estimated to be 2.1 mM on the results reported by Sawyer et al.[10]

Evaluation on Activation of Dioxygen Molecule. Time dependence of the decrease of absorbance at 507 nm of the solution mixture of a Mn(II) complex (2 mL, $^1/_{250}$ M dmso solution), TCPN(25 mL, $^1/_{1500}$ M 1,2-dichloroethane solution), and cyclohexanecarboxyaldehyde (4 mL), was recorded at 298 K.[1,4] At the same time, the reaction mixture containing a Mn(II) complex, cyclohexanecarboxyaldehyde, and *trans*-stilbene was examined in terms of HPLC(High performance liquid chromatography), which detects the formation of *trans*-stilbene oxide.

Results

Crystal Structure. In Figures 2 and 3, the crystal structures of $Mn(L)(H_2O)_2^{2+}$ and $Mn(obz)Cl_2(CH_3OH)$ are shown; the former complex is a unique pentagonal bipyramid, which is very similar to that of the corresponding iron(III) compounds.[11] Because of the *Z*-value, the Mn(II) atom in this compound is present at the special position, and only the half-atoms of the molecule are crystallographically independent. The axial sites were occupied by water molecules. Selected bond distances (Å) and angles (deg) are summarized in Table 2.

In the case of $Mn(obz)Cl_2(CH_3OH)$, the geometry around the Mn(II) ion is of a six-coordinated octahedron, and the selected bond distances (Å) and angles (deg) are listed in Table 3.

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(8) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*, The Kynoch Press: Birmingham, England, 1974; Vol. IV.

(9) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(10) Sawyer, D. T.; Roberts, J. L., Jr. *J. Electroanal. Chem.* **1966**, *12*, 90–101. Sawyer, D. T.; Calderwood, T. S.; Yamaguchi, K.; Angelis, C. H. *Inorg. Chem.* **1983**, *22*, 2577–2583.

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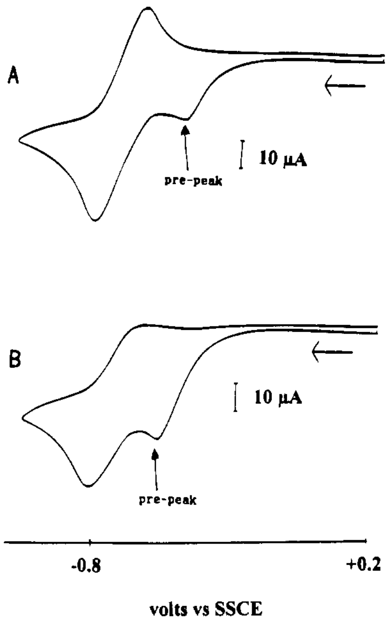

Figure 4. CV of dioxygen molecule in the presence of Mn(obz)Cl_2(CH_3OH): (A) Mn(II), 1 mM; (B) Mn(II), 2 mM.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) with Standard Deviations in Parentheses for Mn(L)$(H_2O)_2^{2+}$

	Bond Length		
Mn−N1	2.259(9)	Mn−N2	2.296(8)
Mn−N3	2.294(8)	Mn−N4	2.294(8)
Mn−N5	2.296(8)	Mn−O1	2.288(6)
Mn−O2	2.288(6)		
	Bond Angle		
N1−Mn−N2	69.2(2)	N1−Mn−N5	69.2(2)
N1−Mn−N3	141.9(2)	N4−Mn−N5	141.9(2)
N2−Mn−N5	138.3(4)	N2−Mn−N3	73.1(3)
N2−Mn−N4	148.2(3)	N5−Mn−N3	148.2(3)
N4−Mn−N5	73.1(3)	N3−Mn−N4	76.3(5)
N1−Mn−O1	90.2(2)	N1−Mn−O2	90.2(2)
O1−Mn−O2	179.6(3)	O1−Mn−N3	92.6(2)
O1−Mn−N4	87.0(2)	O1−Mn−N2	86.1(2)
O1−Mn−N5	94.0(2)	O1−Mn−N3	87.0(2)
O2−Mn−N2	94.0(2)	O2−Mn−N5	86.1(2)
O2−Mn−N3	92.6(2)	O2−Mn−N4	87.0(2)
O2−Mn−N2	86.1(2)	O2−Mn−N5	94.0(2)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) with Standard Deviations in Parentheses for Mn(obz)Cl_2(CH_3OH)

	Bond Length		
Mn−Cl1	2.583(4)	Mn−Cl2	2.391(4)
Mn−N1	1.19(1)	Mn−N3	2.20(1)
Mn−O1	2.430(9)	Mn−O2	2.29(1)
	Bond Angle		
N1−Mn−N3	136.8(4)	N1−Mn−O2	81.0(4)
N1−Mn−C12	110.7(3)	N1−Mn−O1	68.4(4)
N1−Mn−Cl1	91.5(3)	N3−Mn−O2	86.0(4)
N3−Mn−Cl2	111.4(4)	N3−Mn−O1	69.3(3)
N3−Mn−Cl1	119.0(3)	O2−Mn−C12	95.1(3)
O2−Mn−O1	83.3(4)	O2−Mn−Cl1	169.1(3)
Cl2−Mn−O1	178.2(3)	Cl2−Mn−Cl1	95.0(1)
O1−Mn−Cl1	86.5(3)		

Electrochemical Data. Since all the manganese compounds used in this study are of an oxidation state of II, no oxidation and reduction peak was observed in the CV diagram with the range −1.0 ~ +1.0 V(*vs* SSCE) under an argon atmosphere. In Figure 4, the CV of Mn(obz)Cl_2(CH_3OH) measured under the oxygen atmosphere is illustrated. It is noteworthy that one another reduction peak is observed at −0.44 V in addition to the reduction peak of dioxygen at −0.78 V (*vs* SSCE). In our previous paper,[12] we have reported that we can sometimes observe a small prepeak as mentioned above in the CV of dioxygen when a metal compound is present, and have concluded that this prepeak should correspond to the reduction of a dioxygen which is weakly interacting with a metal ion. As shown in Figure 4, the reduction current of this pre-peak increases with increasing the Mn(II) complex added. This is indicating that there is an equilibrium shown below; here Mn(II)$\cdot\cdot\cdot O_2$ denotes the presence of weak interaction between the Mn(II) atom and dioxygen molecule.

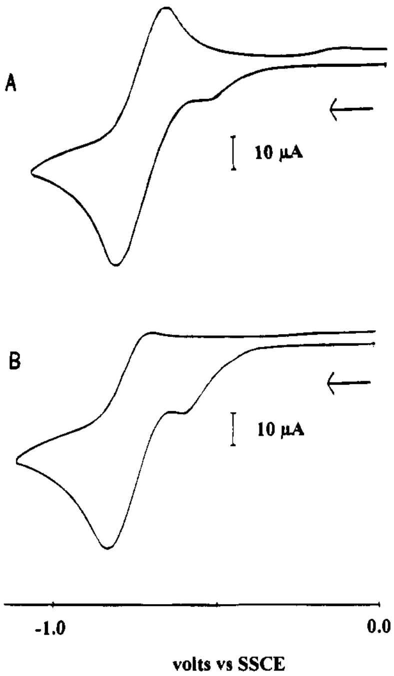

Figure 5. CV of dioxygen molecule in the presence of Mn(L)$(H_2O)_2^{2+}$: (A) Mn(II), 1 mM; (B) Mn(II), 2 mM.

$$\mathrm{Mn(II)} + O_2 \rightleftharpoons \mathrm{Mn(II)}\cdot\cdot\cdot O_2$$

In the case of 2 mM of Mn(II) complex is added, the reoxidation step of superoxide ion formed at −0.78 V becomes irreversible (see trace B in Figure 4); this is consistent with our previous report that Mn(obz)Cl_2(CH_3OH) acts as a good quencher for superoxide anion.[7]

Similarly, a small prepeak was also observed in the CV of solution containing dioxygen and Mn(L)$(H_2O)_2^{2+}$ complex (see Figure 5). In this case, the peak current is lower than that in the case of Mn(obz)Cl_2(CH_3OH); this may be due to weaker interaction between dioxygen molecule and the Mn(II) ion in the complex. In the cases of Mn(ntb)ClClO_4 and Mn(ntb)$(NCS)_2$, the reduction current due to the prepeak was much weaker than that of Mn(obz)Cl_2(CH_3OH) (see Figure 6); this may be due to that dioxygen molecule cannot approach to a Mn(II) atom in these cases because of the coordinating anion or solvent molecule (dmso) on the metal complex, and also steric hindrance of the ligand. Above discussion may be supported by the fact that a prepeak was not detected in the solution containing a six-coordinate Mn(II) complex, derived from Mn(en-py)ClO_4[13] (see Figure 6, trace A).

These are all demonstrating that dioxygen molecule can interact weakly with the Mn(II) ion in the Mn(obz)Cl_2(CH_3OH) and Mn(L)$(H_2O)_2^{2+}$ in the presence of a reducing agent;

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(12) Nishida, Y.; Watanabe, I.; Takahashi, S.; Yamazaki, A.; Sakamoto, M. *Polyhedron* **1994**, *13*, 2205−2209.

(13) Neves, A.; Erthal, S. M. D.; Vencato, I.; Ceccato, A. S.; Mascarenhas, Y. P. M.; Nascimento, O. R.; Horner, M.; Batista, A. A. *Inorg. Chem.* **1992**, *31*, 4749−4755.

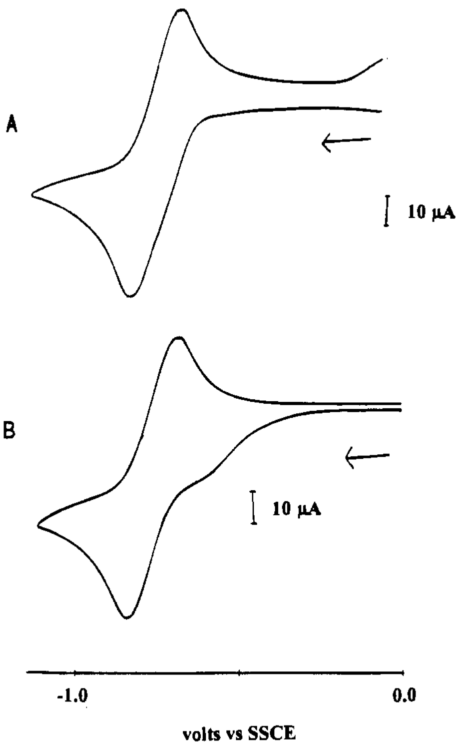
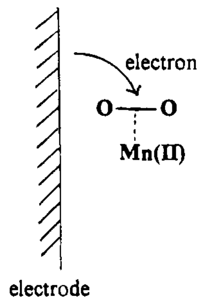


Figure 6. CV of dioxygen molecule in the presence of Mn(II) complexes: (A) Mn(en-py)ClO$_4$ (1 mM); (B) Mn(ntb)ClClO$_4$ (1 mM).

Scheme 1



in these systems the reducing agent is an electrode. This situation may be schematically illustrated in Scheme 1. It seems likely that at this potential formation of a Mn(III)-peroxide adduct may proceed (see Scheme 2).

Scheme 2

$$\mathrm{Mn(II)}\cdot\cdot\mathrm{O_2} \xrightarrow{\text{electron}} \mathrm{Mn(III)-O_2^{2-}}$$

Degradation of TCPN in the Presence of the Mn(II) Compound. It is well-known that TCPN is one of the most effective singlet-oxygen ($^1\Delta_g$) scavengers; it shows a strong absorption band at 507 nm, and reacts with singlet-oxygen to yield the corresponding end-peroxide with decoloration.[1,4] No decrease of the absorbance at 507 nm was detected within a day in the solution containing TCPN, cyclohexanecarboxyaldehyde, and a manganese(II) complex such as Mn(obz)Cl$_2$(CH$_3$OH), Mn(ntb)ClClO$_4$, and Mn(ntb)(NCS)$_2$ (not shown). Contrary to this, a remarkable decrease of absorbance was observed in the solution of Mn(L)(H$_2$O)$_2^{2+}$, as shown in Figure 7. This suggests that activation of dioxygen molecule occurs only in the latter solution, which is consistent with the fact that the formation of *trans*-stilbene oxide was detected only for the solution containing Mn(L)(H$_2$O)$_2^{2+}$, cyclohexanecarboxyaldehyde, and *trans*-stilbene. Similar facts were also observed in the solutions containing pivalaldehyde instead of cyclohexanecarboxyaldehyde.

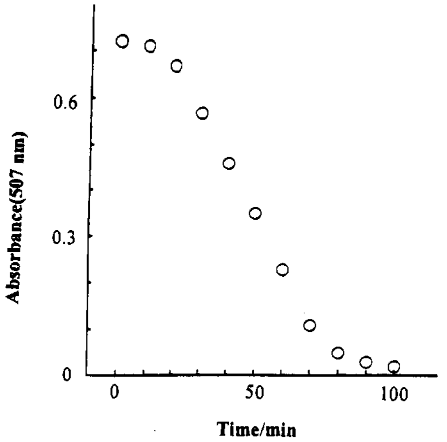
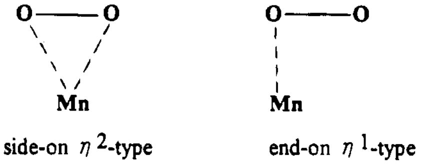


Figure 7. Time dependence of absorbance at 507 nm of reaction mixture containing Mn(L)(H$_2$O)$_2^{2+}$, TCPN, and cyclohexanecarboxyaldehyde (see Experimental Section).

Chart 1



Discussion

In this study, we have found that Mn(L)(H$_2$O)$_2^{2+}$ can, but Mn(obz)Cl$_2$(CH$_3$OH) cannot degrade, TCPN in the presence of cyclohexanecarboxyaldehyde, whereas both the Mn(II) compounds can interact with dioxygen molecule under the condition of electrochemical reduction; under this condition, the formation of a Mn(III)−peroxide adduct is estimated (see Scheme 2). It is generally accepted that the structure of a Mn(III)−peroxide adduct is of a side-on η^2-type (see Chart 1), which is supported by X-ray crystal structure determination done for some examples.[14]

Very recently, we have investigated the reactivity of a peroxide adduct of the Mn(salen) complex in terms of the electrochemical methods and found that organic acid anhydrides exhibit much higher affinity for the peroxide adduct.[15] On the basis of these facts we have concluded that the peroxide adduct might act as an electrophile toward the organic acid anhydrides, and a high affinity between two compounds can be elucidated in terms of the electron distribution in the frontier orbitals of the acid anhydrides. In the same report, we also observed that affinity of cyclohexanecarboxyaldehyde toward the peroxide adduct of Mn(III) with Schiff bases is very low. On the basis of these facts and the present results, it seems very unlikely that activation of dioxygen molecule in the solution containing Mn(L)(H$_2$O)$_2^{2+}$ and the aldehyde proceeds *via* formation of a Mn(III)−peroxide adduct with η^2-type structure.

Thus, we would like to propose that activation of dioxygen molecule in the solution containing Mn(L)(H$_2$O)$_2^{2+}$ and the aldehyde may occur in a manner similar to that assumed for the *trans*-[FeCl$_2$(cyclam)]$^+$ system.[2] In the latter case, an intermediate complex formation among the aldehyde, dioxygen, and the metal complex is assumed (see structure **I**), and in this

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(14) Van Atta, R. B.; Strouse, C. E.; Hanson, L. K.; Valentine, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 1425−1434.

(15) Nishida, Y.; Takahashi, S.; Watanabe, I.; Yamazaki, A.; Itoh, H.; Sakamoto, M. *Polyhedron* **1994**, *13*, 1539−1545.

intermediate the dioxygen molecule coordinates to a metal ion, associated with hydrogen bonding with the ligand system; this corresponds to the η^1-type structure in Chart 1. In the case of $Mn(L)(H_2O)_2^{2+}$, hydrogen-bonding between dioxygen and the ligand system is possible, because the ligand (L) contains −NH groups, whereas this situation is impossible for all the Mn(II) complexes with tripod-like ligands used in this study. This may explain the observed fact that only the $Mn(L)(H_2O)_2^{2+}$ ion can activate the dioxygen molecule in the presence of the aldehyde, leading to the degradation of TCPN and epoxidation of *trans*-stilbene. Through the formation of the intermediate, it is anticipated that the electrons in the HOMO of the aldehyde are transfered to dioxygen, leading to formation of C−OO bonding, in this case formation of a peracid, and the resulted metal−peracid complex should be an intrinsically active species for degradation of TCPN and epoxidation of stilbene. Anyway, it is clear that in the $Mn(L)(H_2O)_2^{2+}$, dioxygen, and aldehyde system the change of oxidation state of manganese ion is not necessary for activating the dioxygen molecule, indicating that in some metal oxygenases the activation of dioxygen molecule may proceed without redox reaction of a metal ion, as pointed out for lipoxygenase[2] and pyrocatechase.[16]

Supporting Information Available: Listings of positional and thermal parameters, bond lengths and angles, and ESR spectra of the Mn(II) compounds (6 pages). Ordering information is given on any current masthead page.

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(16) Nishida, Y.; Yoshizawa, K.; Takahashi, S.; Watanabe, I. *Z. Naturforsch.* **1992**, *42C*, 209−214.