Structures of Four Types of Novel High-Valent Manganese Complexes Obtained by the Reactions of $KMnO_4$ with Tridentate Schiff Base Ligands

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Four types of novel manganese complexes, Mn^{IV}(*N*-EtO-sal)$_2$, Mn^{III}(*N*-PhO-sal)(L), [Mn^{IV}(5,6-Benzo-L)$_2$(μ-O)$_2$]$_2$, and Mn^{III}(L-4-Me)$_3$ have been found to be obtained by the reactions of $KMnO_4$ with tridentate Schiff base ligands (*N*-EtOH-salH, *N*-PhOH-salH and their derivatives) in dry MeCN, where *N*-EtOH-salH, *N*-PhOH-salH, LH, 5,6-Benzo-LH, and L-4-MeH denote *N*-2-hydroxyethyl-salicylideneamine, *N*-2-hydroxyphenyl-salicylideneamine, 2-(2-hydroxyphenyl)-benzoxazole, 2-(2-hydroxynaphthyl)-benzoxazole, and 2-(2-hydroxyphenyl)-5-methylbenzoxazole, respectively.

High-valent manganese complexes have been investigated in relation to the biological functions of manganese ions included in the redox enzymes. One of them is the oxygen evolving center(OEC) existing in photosystem II of green plants in which dioxygen is evolved by water oxidation in photosynthesis.[1,2] Although this OEC is proposed to consist of a tetranuclear manganese cluster, the details have not yet been clarified.[1] We have reported that a series of di-μ-oxo dimanganese(IV) complexes has been prepared by the reaction of $KMnO_4$ with bi- and tetradentate Schiff base ligands in MeCN and characterized in order to mimic OEC.[2]

In this letter, we describe that the reactions of $KMnO_4$ with tridentate Schiff base ligands, *N*-ROH-X^1-salH{R = C_2H_4(Et), 1,2-C_6H_{10}, X^1 = H, 5,6-Benzo} or *N*-X^2-PhOH-X^1-salH(X^1 = H, 5,6-Benzo, 5-Br, 3-MeO, X^2=H, 4-Me) gave the four types of manganese complexes: Mn^{IV}(*N*-RO-sal)$_2$, Mn^{III}(*N*-PhO-sal)(L), [Mn^{IV}(5,6-Benzo-L)$_2$(μ-O)$_2$]$_2$, and Mn^{III}(L-4-Me)$_3$, where *N*-ROH-X^1-salH, *N*-X^2-PhOH-X^1-salH, LH, 5,6-Benzo-LH and L-4-MeH denote *N*-2-hydroxy-alkyl-X^1-salicylideneamine, *N*-2-hydroxy-X^2-phenyl-X^1-salicylideneamine, 2-(2-hydroxyphenyl)-benzoxazole, 2-(2-hydroxynaphthyl)-benzoxazole, and 2-(2-hydroxyphenyl)-5-methyl-benzoxazole, respectively.

The manganese(IV) complex, Mn^{IV}(*N*-EtO-sal)$_2$, **1** was obtained as follows: A solution of $KMnO_4$ (0.790 g, 5 mmol) and *N*-EtOH-salH (1.652 g, 10 mmol) in MeCN (200 ml) changed from purple to brown upon allowing to stand in the dark place. After 12 h, the resulting precipitates were collected on a glass filter and recrystallized from a mixed solvent of CH_2Cl_2 and MeCN. Other manganese complexes were obtained in the same manner. The yields of these complexes were in the range of 10 to 20%, depending on the ligands. Single crystals of Mn^{IV}(*N*-EtO-sal)$_2$, **1**[3], Mn^{III}(*N*-PhO-sal)(L), **2**[4], [Mn^{IV}(5,6-Benzo-L)$_2$(μ-O)$_2$]$_2$, **3**[5], and Mn^{III}(L-4-Me)$_3$, **4**[6] were used for X-ray crystallographic analysis.

Figure 1 shows the molecular structure of complex **1** which has an octahedral meridonal configuration in which the manganese(IV) ion is located at the position of center of symmetry. Analogous mononuclear manganese(IV) complexes were obtained and characterized crystallographically.[7] On the other hand, the reaction of $KMnO_4$ with *N*-PhOH-salH, which was obtained by the condensation of salicylaldehyde and *o*-aminophenol, afforded the five-coordinate, square-pyramidal

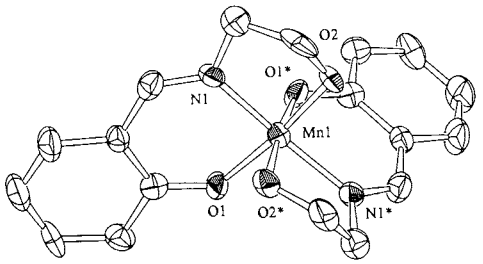

Figure 1. Crystal structure of Mn^{IV}(*N*-EtO-sal)$_2$, **1**, with hydrogen atoms omitted for clarity. Selected bond length (Å) and angles(°) : Mn1-O1 1.904(9), Mn1-O2 1.836(8), Mn1-N1 1.964(9) ; O1-Mn1-N1 96.9(4), O1-Mn1-O2 172.4(4), O2-Mn1-N1 83.5(4), N1-Mn1-N1* 170.7.

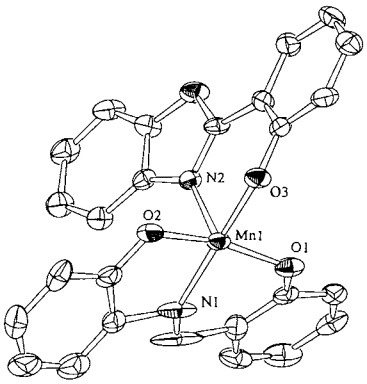

Figure 2. Crystal structure of Mn^{III}(*N*-PhO-sal)L, **2**, with hydrogen atoms omitted for clarity. Selected bond length (Å) and angles(°) : Mn1-O1 1.913(9), Mn1-O2 1.886(9), Mn1-O3 1.868(7), Mn1-N1 1.98(1), Mn1-N2 2.251(9) ; O1-Mn1-O2 166.4(3), O3-Mn1-N1 178.2(5).

manganese(III) complex with mixed ligands, Mn^{III}(*N*-PhO-sal)(L)$_2$. This five-membered ring benzoxazole group of L may be formed by the intramolecular C-O coupling reaction between a carbon atom of -CH=N- and a phenolic oxygen atom of aminophenol moiety. In the structure of complex **2**, one nitrogen and two oxygen atoms of *N*-PhO-sal and a phenolic oxygen atom of L occupied an equatorial plane and a nitrogen atom of benzoxazole group placed at the axial position, as shown in Fig. 2. On the contrary, with *N*-PhOH-5,6-Benzo-salH the di-μ-oxo dimanganese(IV) complex, [Mn^{IV}(5,6-Benzo-L)$_2$(μ-O)$_2$]$_2$, **3** was obtained. The structure of complex **3** consists of two manganese(IV) centers which are bridged by two oxygen atoms to yield a planar Mn_2O_2 core with Mn-Mn separation of 2.749 Å and two benzoxazole derivatives are coordinated to each manganese ion (Fig. 3). Two manganese ions have a roughly octahedral coordination and adoption of this binding model places two phenolic oxygen atoms *trans* and two benzoxazole nitrogen atoms *cis* to a bridging oxo group. Moreover, with *N*-4-Me-PhOH-salH, having a methyl group at the 4-position of *o*-aminophenol, the roughly octahedral manganese(III) complex,

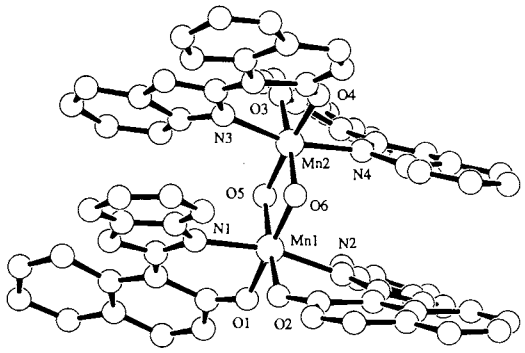

Figure 3. Crystal structure of $[Mn^{IV}(N\text{-}5,6\text{-Benzo-L})_2(\mu\text{-O})]_2$, **3**, with hydrogen atoms omitted for clarity. Selected bond length(Å) and angles(°) : Mn1-Mn2 2.749(7), Mn1-O1 1.85(2), Mn1-O2 1.93(2), Mn2-O3 1.91(2), Mn2-O4 1.85(3), Mn1-O5 1.83(2), Mn1-O6 1.83(2), Mn2-O5 1.80(2), Mn2-O6 1.85(1), Mn1-N1 2.06(2), Mn1-N2 1.95(2), Mn2-N3 2.00(2), Mn2-N4 1.96(2) ; O5-Mn1-O6 82.3.(7), O5-Mn2-O6 82.4(8), Mn1-O5-Mn2 98.5(9), Mn1-O6-Mn2 96.8(7), O1-Mn1-O6 174.3(8), O2-Mn1-O5 172.6(9), O3-Mn2-O6 174.3(9), O4-Mn2-O5 174.4(9), N1-Mn1-N2 164.7(9), N3-Mn2-N4 167.6(9).

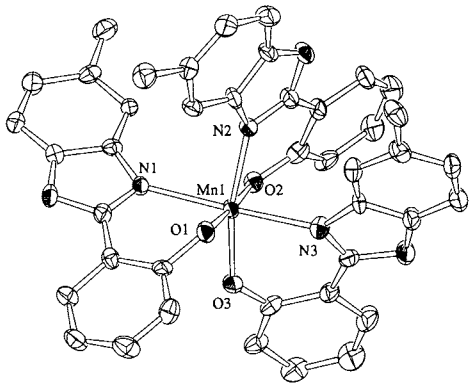

Figure 4. Crystal structure of $Mn^{III}(4\text{-Me-L})_3$, **4**, with hydrogen atoms omitted for clarity. Selected bond length (Å) and angles(°) : Mn1-O1 1.889(7), Mn1-O2 1.873(7), Mn1-O3 1.908(7), Mn1-N1 2.253(8), Mn1-N2 2.109(8), Mn1-N3 2.261(9) ; O1-Mn1-O2 176.6, N1-Mn1-N3 172.1(3), O3-Mn1-N2 167.3(3).

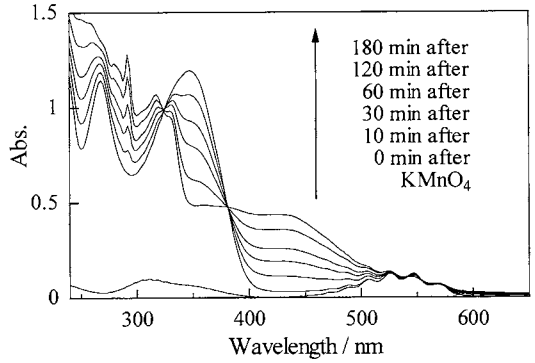

Figure 5. Spectral changes of a MeCN solution of $KMnO_4$ (5×10^{-4} M) caused by the addition of a MeCN solution of *N*-PhOH-salH. ($KMnO_4$: *N*-PhOH-salH = 1 : 2, Cell length ; 1 cm).

$Mn^{III}(L\text{-}4\text{-Me})_3$, **4** was obtained. As shown in Fig. 4, the metal center is surrounded octahedrally by a N_3O_3 donor set and the Jahn-Teller effect on the manganese ion may occur along the axis containing *trans* nitrogen atoms of the ligands. In these cases, all of the tridentate Schiff base ligands were converted to benzoxazole derivatives, which act as a bidentate ligand.

The results obtained in this study indicate that only the tridentate Schiff base ligands containing *o*-aminophenol groups can be converted to the benzoxazole moieties by forming a five-membered ring in their reaction with $KMnO_4$. To clarify the reaction mechanism for the formation of benzoxazole derivatives the reactions of the tridentate Schiff bases with $KMnO_4$ were monitored by UV-vis and EPR spectroscopies. Figure 5 shows the absorption spectra during the reaction of *N*-PhOH-salH and $KMnO_4$ in MeCN: Characteristic absorption bands due to benzoxazole group appeared around 300 nm immediately after mixing *N*-PhOH-salH and $KMnO_4$, and their intensities increased with reaction time. Taking into accounts the EPR results[8], the five-membered ring formation may proceed via a radical reaction initiated by the oxidation of the ligands with MnO_4^- ions at early period in the reaction of $KMnO_4$ and *N*-X^2-PhOH-X^1-salH.

References and Notes

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3 Crystal data for **1**·2MeCN : $C_{22}H_{24}MnN_4O_4$, M_W = 463.39, orthorhombic, space group *Pbcn*, a = 9.385(3) Å, b = 9.818(3) Å, c = 23.953(4) Å, V = 2206(1) Å^3, Z = 4, D_c = 1.395 g/cm^3, R (R_W) = 0.061 (0.079) for 558 reflections ($I > 3.00\sigma(I)$).

4 Crystal data for **2** : $C_{28}H_{20}MnN_3O_4$, M_W = 517.42, triclinic, space group $P\bar{1}$, a = 10.629(3) Å, b = 12.047(5) Å, c = 10.456(3) Å, α = 112.72(2)°, β = 110.24(2)°, γ = 82.01(3)°, V = 1158.8(7) Å^3, Z = 2, D_c = 1.483 g/cm^3, R (R_W) = 0.076 (0.104) for 1646 reflections ($I > 3.00\sigma(I)$).

5 Crystal data for **3**·$2CH_2Cl_2$: $C_{70}H_{44}Cl_4Mn_2N_4O_{10}$, M_W = 1352.83, triclinic, space group $P\bar{1}$, a = 13.746(5) Å, b = 18.247(5) Å, c = 13.49(1) Å, α = 109.70(4)°, β = 111.06(4)°, γ = 89.93(4)°, V = 2943(3) Å^3, Z = 2, D_c = 1.526 g/cm^3, R (R_W) = 0.079 (0.099) for 2138 reflections ($I > 2.50\sigma(I)$).

6 Crystal data for **4** : $C_{42}H_{30}MnN_3O_6$, M_W = 727.65, triclinic, space group $P\bar{1}$, a = 11.995(2) Å, b = 14.531(5) Å, c = 10.184(3) Å, α = 97.99(2)°, β = 107.71(2)°, γ = 81.04(2)°, V = 1662.4(8) Å^3, Z = 2, D_c = 1.454 g/cm^3, R (R_W) = 0.055 (0.071) for 1870 reflections ($I > 3.00\sigma(I)$).

7 Single crystals of $Mn^{IV}(N\text{-EtO-5,6-Benzo-sal})_2$ and $Mn^{IV}(N\text{-chxO-sal})_2$ were obtained and characterized by the X-ray structure analysis where *N*-EtOH-5,6-Benzo-salH and *N*-chxOH-salH denote *N*-2-hydroxyethyl-5,6-benzo-salicylideneamine and *N*-2-hydroxycyclohexyl-salicylideneamine, respectively.

8 EPR spectra of a frozen MeCN solution of $KMnO_4$ and *N*-PhOH-salH measured at 213 K in the presence of spin trapping reagent 5,5-dimethylpyrrolin-*N*-oxide (DMPO) suggest the formation of spin adduct.