Preparation and Characterization of Di-μ-oxo Dimanganese(IV) Complexes with Bidentate Schiff Bases, *N*-Alkyl-salicylideneamine

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Novel di-μ-oxo dimanganese(IV) complexes, $[Mn^{IV}(N\text{-R-sal})_2(\mu\text{-O})]_2$, with bidentate Schiff base ligands, *N*-alkyl-salicylideneamine, *N*-R-salH (R = n-C_3H_7 (Pr), n-C_4H_9 (Bu), n-C_6H_{13} (Hx), n-C_8H_{17} (Oct), n-$C_{12}H_{25}$ (Dod), or n-$C_{18}H_{37}$ (Octd)), have been prepared and characterized by spectroscopies, magnetic susceptibilities, thermal analysis and X-ray crystallography.

Manganese plays an important role in biological redox systems, which is exemplified by the oxygen-evolving complex of photosystem II (PSII OEC) in green plants. The possibility is that a binuclear or tetranuclear cluster forms the active site in OEC of PSII,[1] although their precise arrangement and oxidation levels have not been determined unambiguously. X-Ray absorption experiments have established the existence of at least two 2.7 Å Mn-Mn contacts within the OEC.[1] Therefore, polynuclear high-valent manganese complexes have been investigated as functional and/or structural models for Mn-cofactor in OEC. In a previous paper, we have reported that di-μ-oxo dimanganese(IV) complexes are obtained by the reaction of $KMnO_4$ with tetradentate Schiff base ligands such as *N,N'*-disalicylidene-1,2-diaminobenzene (salophenH_2) and *N,N'*-disalicylidene-1,4-diaminobutane (salbnH_2) in acetonitrile (MeCN) and their structures are different in the coordination fashion of the ligands.[2]

In this letter, we describe the preparation and characterization of novel di-μ-oxo dimanganese(IV) complexes with bidentate Schiff base ligands, $[Mn^{IV}(N\text{-R-sal})_2(\mu\text{-O})]_2$. The bidentate Schiff base ligands, *N*-alkyl-salicylideneamine, *N*-R-salH, where R can be n-C_3H_7 (Pr), n-C_4H_9 (Bu), n-C_6H_{13} (Hx), n-C_8H_{17} (Oct), n-$C_{12}H_{25}$ (Dod), and n-$C_{18}H_{37}$ (Octd), were prepared according to the method described in the literature.[3] The manganese(IV) complex, $[Mn^{IV}(N\text{-Hx-sal})_2(\mu\text{-O})]_2$ was prepared by the reaction of *N*-Hx-salH (2.05 g, 10.0 mmol) and $KMnO_4$ (0.79 g, 5.0 mmol) in MeCN (200 ml) with stirring at room temparature. The solution color changed from purple to brown and 24 h after the resulting brown solids were collected on a glass filter and dried *in vacuo* (2.20 g). They were extracted with dichloromethane (CH_2Cl_2) (100 ml), and the solution was reprecipitated by the addition of MeCN. The resulting brownish red micro crystals were collected on a glass filter and dried *in vacuo*. They were recrystallized from CH_2Cl_2 and MeCN (yield 1.60 g, 67%).[4] The other di-μ-oxo dimanganese(IV) complexes $[Mn^{IV}(N\text{-R-sal})_2(\mu\text{-O})]_2$ (R = Pr, Bu, Oct, Dod, and Octd) were prepared in the same manner. This synthetic method has the advantage that high-valent manganese complexes can be obtained in 60-70% yields, in which MnO_4^- may be reduced with a part of the ligands. Single crystals of $[Mn^{IV}(N\text{-Hx-sal})_2(\mu\text{-O})]_2$ have been used for X-ray crystallographic characterization.[5]

Elemental analyses were made on Yanaco Model CHN-CORDER MT-5. UV-visible and IR spectra were recorded on a Shimadzu Model UV-3100 spectrophotometer and Shimadzu Model IR-470 infrared spectrophotometer, respectively. Electrochemical studies were performed under argon, using a BAS Model CV-27 voltammograph equipped with a Graphtec Model WX 2400 XY recorder and a standard three-electrode assembly (glassy carbon working, Pt wire auxiliary, SCE reference) with 0.1 M n-Bu_4NClO_4 as the supporting electrolyte. X-Ray structure analyses were taken on a Rigaku AFC7R automatic 4-circle X-ray diffractometer. Magnetic susceptibillity measurements were carried out by the Gouy method at room temperature. A differential scanning calorimetry (DSC) and a thermogravimetric and differential thermal analysis (TG-DTA) were carried out by using a Rigaku TAS-200 thermal analysis system.

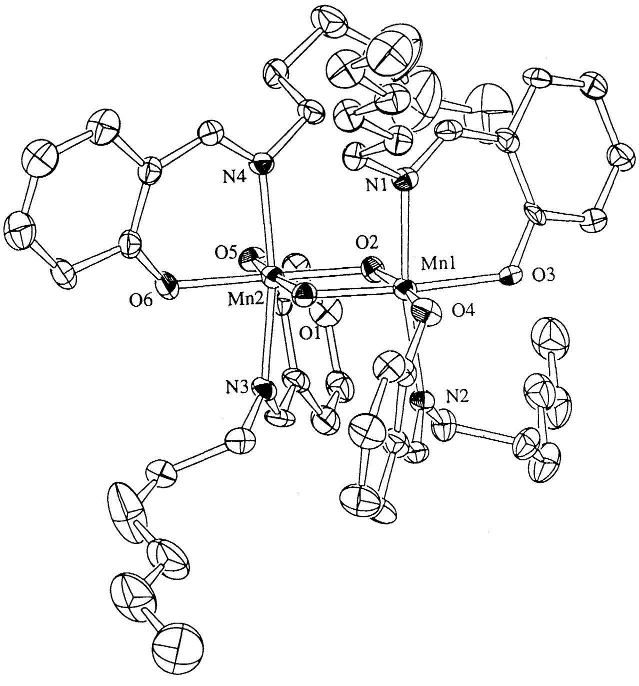

Figure 1. The molecular structure of $[Mn^{IV}(N\text{-Hx-sal})_2(\mu\text{-O})]_2$, **1**, with hydrogen atoms omitted for clarity, drawing in 30% probability. Selected interatomic distances (Å) and angles (deg) : Mn1-Mn2 2.780(2), Mn1-O1 1.817(7), Mn1-O2 1.818(7), Mn1-O3 1.950(7), Mn1-O4 1.920(7), Mn1-N1 2.025(9), Mn1-N2 2.044(9), Mn2-O1 1.826(7), Mn2-O2 1.815(7), Mn2-O5 1.942(7), Mn2-O6 1.933(7), Mn2-N3 2.022(9), Mn2-N4 2.020(9); Mn1-O1-Mn2 99.5(3), Mn1-O2-Mn2 99.9(3), O1-Mn1-O2 80.4(3), O1-Mn1-O3 172.0(3), O1-Mn1-O4 92.8(3), O1-Mn1-N1 90.8(3), O1-Mn1-N2 90.7(3), O2-Mn1-O3 92.0(3), O2-Mn1-O4 173.1(3), O2-Mn1-N1 96.3(3), O2-Mn1-N2 92.0(3), O3-Mn1-O4 94.8(3), O3-Mn1-N1 87.6(3), O3-Mn1-N2 85.7(3), O4-Mn1-N1 84.4(3), O4-Mn1-N2 88.2(3), N1-Mn1-N2 169.5(3), O1-Mn2-O2 80.2(3), O1-Mn2-O5 172.4(3), O1-Mn2-O6 93.7(3), O1-Mn2-N3 91.6(3), O1-Mn2-N4 95.3(3), O2-Mn2-O5 92.4(3), O2-Mn2-O6 173.9(3), O2-Mn2-N3 97.0(3), O2-Mn2-N4 92.1(3), O5-Mn2-O6 93.7(3), O5-Mn2-N3 87.8(3), O5-Mn2-N4 86.4(3), O6-Mn2-N3 83.6(3), O6-Mn2-N4 87.9(3), N3-Mn2-N4 169.4(4).

Figure 1 shows the ORTEP plot and selected interatomic distances and angles of $[\mathrm{Mn^{IV}}(N\text{-Hx-sal})_2(\mu\text{-O})]_2$, **1**. The structure consists of two Mn(IV) centers bridged by two oxygen atoms to yield a planar $\mathrm{Mn_2O_2}$ core with Mn-Mn separation of 2.780(2) Å for **1**. This distance is longer than those of $[\mathrm{Mn^{IV}}(\text{salophen})(\mu\text{-O})]_2$ and $[\mathrm{Mn^{IV}}(\text{salbn})(\mu\text{-O})]_2$ (2.718(2) and 2.729(1) Å),[2] and the longest one among all of the Mn-Mn distances observed for the structurally characterized $\mathrm{Mn^{IV}{}_2O_2}$ complexes (2.580(1)-2.757(3) Å) prior to this work.[6] It is considered that the long Mn-Mn distance of **1** is caused by the existence of the alkyl groups of the ligands. In the structure of **1**, two *N*-Hx-sal ligands around each manganese atom bond via two phenolic oxygen atoms and two imine nitrogen atoms to complete the roughly octahedral coordination environment. Adoption of this binding model places two phenolic oxygen atoms trans and two imine nitrogen atoms of two *N*-Hx-sal ligands cis to a bridging oxo group.

From magnetic susceptibility measurements on powdered samples of $[\mathrm{Mn^{IV}}(N\text{-R-sal})_2(\mu\text{-O})]_2$ (R = Pr, Bu, Hx, Oct, Dod, and Octd) at room temperature, 2.28(Pr), 2.28(Bu), 2.19(Hx), 2.23(Oct), 2.41(Dod) and 2.66(Octd) μ_B per dimeric unit were calculated. These results indicate that there is intramolecular antiferromagnetic coupling between the two Mn(IV) ions (d^3).

These dimanganese(IV) complexes having linear-alkyl groups possess good solubility in organic solvents and relatively lower melting points with (without) some decomposition compared to those of the corresponding manganese(IV) complexes with tetradentate Schiff base ligands. Thus, the thermal properties of the present manganese(IV) complexes have been studied. The DSC curve of $[\mathrm{Mn^{IV}}(N\text{-Octd-sal})_2(\mu\text{-O})]_2$ measured over the temperature range of 25 to 250 °C shows both endothermic (110.8 ℃) and exothermic peaks (118.8 ℃), which can be assigned to melting and partial decomposition of the complex, respectively. However, the DSC curves of the other complexes show only exothermic peak at 124.1(R = Dod), 131.2(Oct), 145.7(Hx), 149.7(Bu) and 168.8 °C(Pr). This means that some thermal decomposition of these complexes took place prior to their melting. The TG-DTA curves of $[\mathrm{Mn^{IV}}(N\text{-Pr-sal})_2(\mu\text{-O})]_2$ shown in Figure 2 exhibit a clear weight loss of 4.2% at 174 °C, accompanying an exothermic reaction, which corresponds to the calculated value (4.05%) expected for the release of two μ-oxo oxygen atoms from the complex. A similar result was obtained for the complex of R = Bu, but the corresponding weight losses for the other complexes were slightly less than the calculated values for the release of two oxygen atoms: this may be caused by the difficulty in diffusion of dissociated oxygen atoms from the molten state of the complexes under the thermal analysis conditions in a stream of air. In fact, when the complexes were heated in a vacuum oven for 1 h at higher temperatures by 10 °C than those of their exothermic peaks, the weight losses have been found to correspond to the amount of two oxygen atoms per di-μ-oxo dimanganese complex.

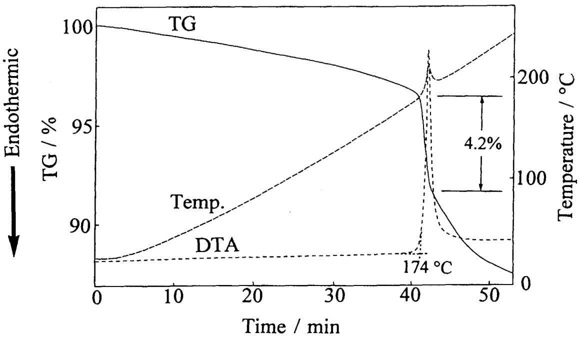

Figure 2. TG-DTA curves of $[\mathrm{Mn^{IV}}(N\text{-Pr-sal})_2(\mu\text{-O})]_2$. Heating rate : 5 °C / min in flowing air (60 ml / min).

In the IR spectrum of the product obtained by heating $[\mathrm{Mn^{IV}}(N\text{-Dod-sal})_2(\mu\text{-O})]_2$ at 137 °C for 1 h in vacuo, the intense band (632 $\mathrm{cm^{-1}}$) due to ν(Mn-O) characteristic for the $\mathrm{Mn_2O_2}$ core disappeared without significant changes in other peaks. These results suggest that the bridging oxygen atoms were released from the di-μ-oxo dimanganese(IV) complexes by heating.

References and Notes

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4 Physicochemical data for $[\mathrm{Mn^{IV}}(N\text{-Hx-sal})_2(\mu\text{-O})]_2$: UV-visible spectra ($\mathrm{CH_2Cl_2}$): λ_{max} = 406 nm (log ε = 4.13), 475 nm (log ε = 3.97), 693 nm (log ε = 2.81). IR spectra (KBr): 631cm^{-1} ν(Mn-O). Cyclic voltammogram ($\mathrm{CH_2Cl_2}$): $E_{1/2}$ = -0.29, -0.58 V (vs. SCE). Anal. Found (%): H, 7.61; C, 64.42; N, 5.81; Mn, 11.21. Calcd (%) for $\mathrm{Mn_2O_6N_4C_{52}H_{72}}$: H, 7.57; C, 65.12; N, 5.84; Mn, 11.46.

5 Crystal data for $[\mathrm{Mn^{IV}}(N\text{-Hx-sal})_2(\mathrm{O})]_2$: $\mathrm{Mn_2O_6N_4C_{52}H_{72}}$, M = 959.04, monoclinic, space group $P2_1$, a = 12.280(4), b = 13.828(3), c = 15.336(3) Å, β = 107.59(2) °, V = 2482(1) Å^3, Z = 2, D_{calc} = 1.283 g/cm^3, μ(Mo-Kα) = 5.60 cm^{-1}, T = 298 K, crystal size 0.35 × 0.20 × 0.05 mm. A total of 6143 reflections were measured on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation; 2641 with I > 3.00σ(I) were observed. The structure was solved by direct method (SHELXS86) and refined by the full-matrix least-squares method. The refinement converged at R = 0.047, R_W = 0.052.

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