Preparation and Characterization of Polynuclear Manganese(III) Complexes with SalbnH_2, *N*,*N'*-Disalicylidene-1,4-diaminobutane

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The reactions between the Schiff base ligand salbnH_2, *N*,*N'*-disalicylidene-1,4-diaminobutane and $Mn^{III}(OAc)_3·2H_2O$ have been found to give a polymer complex, $[Mn^{III}(\mu\text{-salbn})OAc]_n$ **1** or a dinuclear complex, $[Mn^{III}(\mu\text{-salbn})Cl]_2$ **2** by the addition of LiCl. In both complexes, salbn ligands act as a bridging bidentate ligand toward a manganese ion. The complex **2** has been found to decompose H_2O_2 catalytically with dioxygen evolution, cycling its oxidation states between Mn^{III}_2 and Mn^{II}_2.

The chemistry of high-valent manganese complexes is full of interest in relation to the biological redox systems involving manganese ions, such as oxygen-evolving center (OEC) of photosystem II in green plants, superoxide dismutases (SOD) and Mn-catalases (CAT).[1] In the OEC of PS II, chloride ions exist near by four manganese ions as a co-factor and their role is suspected that the chloride ion may act for proton release charge neutralization in the water splitting or as a ligand to the manganese ions and facilitates electron transfer.[2] In the case of Mn-catalases, two manganese ions are relatively close each other for the disproportionation of H_2O_2 to O_2 and H_2O.

In the past two decades, polynuclear manganese complexes have been extensively prepared and characterized as structural and functional models for the above-mentioned manganese-containing systems, and some approaches have been attempted to prepare manganese(III) and -(IV) complexes with appropriate organic ligands and chloride ions.[3]

Previously, a Schiff base ligand, salbnH_2 (*N*,*N'*-disalicylidene-1,4-diaminobutane) has been reported to act as a tetradentate ligand toward metal ions such as Ni^{2+}, Cu^{2+} and Mn^{4+}.[4] In this paper, we describe the preparation and structures of a polymer complex $[Mn^{III}(\mu\text{-salbn})OAc]_n$ **1**[5] and a dinuclear complex, $[Mn^{III}(\mu\text{-salbn})Cl]_2$ **2**,[6] and reactivities of **2** toward hydrogen peroxide (H_2O_2) and superoxide ion (O_2^-), where OAc denotes an acetate anion. In these complexes, the salbnH_2 has been found to act as a bridging bidentate ligand toward a manganese(III) ion.

The polymer manganese(III) complex **1** was prepared by the reaction of salbnH_2 (0.298 g, 1 mmol) and $Mn^{III}(OAc)_3·2H_2O$ (0.276 g, 1 mmol) in acetonitrile (MeCN, 400 mL) with stirring at room temperature for 30 min, and then the green solution was allowed to stand in the dark place. Two weeks later, the resulting green crystals were collected on a glass filter, washed with MeCN, and dried *in vacuo*. The yield was 63%. Single crystals of **1** were used for X-ray crystallographic analysis.[7] The dinuclear manganese(III) complex **2** was obtained by the reaction of salbnH_2 (1.49 g, 5 mmol) and $Mn^{III}(OAc)_3·2H_2O$ (1.38 g, 5 mmol) in the presence of LiCl(0.33 g, 7.5 mmol) in MeOH (400 mL). The solution was refluxed for 2 h and then concentrated to ca. 30 mL under reduced pressure to give a green solution. After addition of MeCN (200 mL) to it, the solution was allowed to stand for two days in the dark place to yield deep green crystals, which were collected on a glass filter, washed with MeCN, and dried *in vacuo*. The yield was 39%. Poor solubility of complex **1** in nonpolar solvents prevented molecular weight determination.

Figure 1 shows the crystal structure of complex **1** which has a spiral one-dimensional infinite chain sequence. The central manganese ion adopts a six-coordinate distorted octahedron which comprises one bidentate acetato and two salbn ligands, which coordinate to a manganese ion in *cis*-form as a bridging bidentate ligand. Two Mn–O bond lengths between the manganese ion and two oxygen donor atoms of the acetato ligand are almost equal. Moreover, two Mn–O and Mn–N bond lengths between the manganese ion and oxygen and nitrogen donor atoms of the salbn ligands are also equivalent. Since a significant Jahn–Teller distortion can not be observed in this complex, the structure of complex **1** is considered to be trigonal bipyramidal rather than octahedral. Neighboring manganese ions are separated by 8.80 Å.

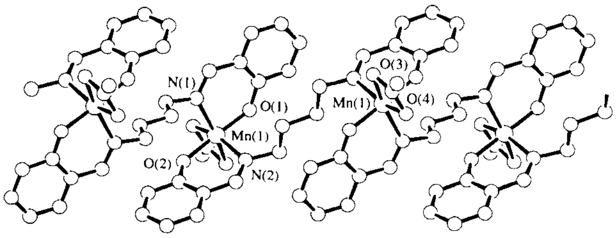

Figure 1. Crystal structure of $[Mn^{III}(\mu\text{-salbn})OAc]_n$, **1**, with hydrogen atoms omitted for clarity. Selected bond length (Å) and angles(°): Mn1-O1 1.860(4), Mn1-O2 1.846(4), Mn1-O3 2.225(7), Mn1-O4 2.215(10), Mn1-N1 2.134(9), Mn1-N2 2.128(5), Mn1-Mn1’ 8.80; O1-Mn1-O2 178.4(3), O3-Mn1-O4 58.0(3), N1-Mn1-N2 105.8(3)

Figure 2 shows a perspective view of complex **2**. Because crystals of complex **2** have a disordered structure, which may be caused by a disorder of disposition of the molecules, its precise molecular structure could not be refined completely.[8] However, the results suggested that manganese ions have a five-coordinate square-pyramidal configuration bridged by two salbn ligands, in which a N_2O_2 donor set occupies an equatorial plane and a chloride ion an apical position. Adoption of this configuration places all the N_2O_2 donor atoms to *trans*-position each other. Two manganese ions are separated by roughly 5.2 Å. This dinuclear structure is supported by the ESI-MAS measurements.[9] The magnetic moments of complexes **1** and **2** measured at room temperature by the Gouy method are 4.75 and 4.69 μ_B per manganese ion, respectively, which are close to the spin-only value of 4.95 μ_B expected for a magnetically diluted high-spin d^4 manganese(III) ion. These results are consistent with the relatively long Mn–Mn distances mentioned above.

The reactivity of complex **2** toward H_2O_2 was studied by UV–vis and EPR spectroscopies, cyclic voltammetry, and a

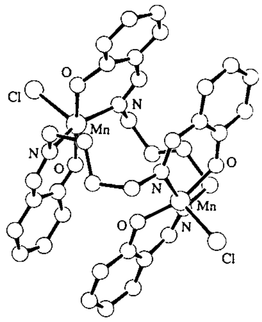

Figure 2. A perspective view of $[Mn^{III}(\mu\text{-salbn})Cl]_2$, **2**.

volumetric measurement of evolved dioxygen. Figure 3 shows absorption spectral changes of a MeCN solution of complex **2** during the reaction with H_2O_2 at 23 °C. An addition of H_2O_2 diluted with MeCN to a MeCN solution of complex **2** changed its brownish green color to yellow immediately. The intensities of the absorption bands around 300, 400, and 700 nm are decreased with a slight increase in the intensity of the absorption band around 500 nm. A frozen solution of complex **2** was EPR silent at 213 K, but showed an EPR spectrum of 6-line signal typical for a manganese(II) ion after the addition of H_2O_2.[10] These results indicate that the manganese(III) ions of complex **2** react with H_2O_2 to be reduced to manganese(II) ions. The cyclic voltammograms measured in MeCN supported these results: a peak current due to a Mn(III) ↔ Mn(II) redox couple of complex **2** $\{E_{1/2} = -0.04$ V(vs SCE)$\}$ was significantly decreased with appearance of a large cathodic peak due to evolved dioxygen ($E_{c,p} = -0.75$ V) by the addition of H_2O_2. It is noteworthy that the resulting yellow solution changed to the original brownish green gradually by allowing to stand, which was observed in the absorption spectral changes (Figure 3) and cyclic voltammograms. This means that the reduced manganese(II) complex is reoxidized to the original manganese(III) complex. Moreover, decomposition rates of H_2O_2 were studied by a stopped-flow spectroscopy and a volumetric measurement of evolved dioxygen. As shown in Figure 4, nearly one-third amounts of added H_2O_2 can be decomposed quickly within 10 sec and then the remaining H_2O_2 gradually until 10 min, under the conditions (H_2O_2/Mn: 100, a solution volume: 10 ml). These results indicate that complex 2 can decompose excess amounts of H_2O_2 by cycling its oxidation states between Mn^{III}_2 and Mn^{II}_2.

On the other hand, the reaction of complex **2** with superoxide ion (O_2^-) in DMSO has been found to produce a di-μ-oxo dimanganese(IV) complex, $[Mn^{IV}(salbn)(\mu\text{-}O)_2]$.[11]

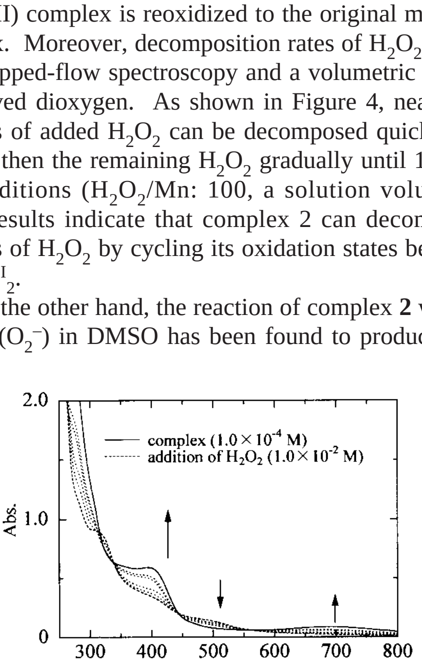

Figure 3. Absorption spectra during the reaction of complex 2 in MeCN (solid line), and addition of H_2O_2 (dotted line). Arrows indicate the spectral changes after allowing to stand the resulting yellow solution.

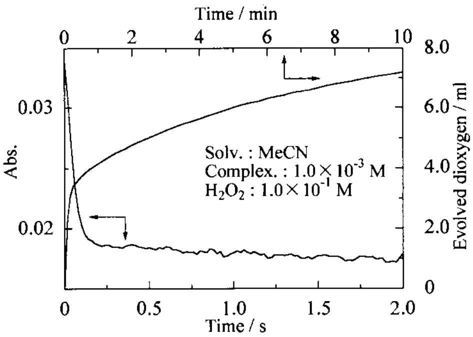

Figure 4. Time courses of dioxygen evolution in the disproportionation of H_2O_2 by complex **2** and changes in absorbance at 686 nm.

In conclusion, the polymer manganese(III) complex **1** has been found to have a spiral one-dimensional infinite chain structure and the dinuclear manganese(III) complex **2** to exhibit a reactivity toward H_2O_2 like Mn-catalases.

References and Notes

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5 Physicochemical data for **1** : UV–vis spectra (MeOH) : λ_{max} = 380 nm (log ε = 3.76), 610 nm (log ε = 2.62) (per Mn unit). Cyclic voltammogram (MeOH) : $E_{1/2} = -0.06$ V (III↔II), 0.44 V (IV↔III) (vs SCE). Magnetic moment per Mn : 4.75 μ_B (297 K). Anal. Found. C, 60.81; H, 5.29; N, 8.07; Mn, 13.21%. Calcd for $C_{20}H_{21}N_2O_4Mn$: C, 61.02; H, 5.49; N, 7.97; Mn, 13.45%.

6 Physicochemical data for **2** : UV–vis spectra (MeCN) : λ_{max} = 394 nm (log ε = 4.08), 686 nm (log ε = 3.25). Cyclic voltammogram (MeCN): $E_{1/2} = -0.04$ V (III↔II), 0.44 V (IV↔III) (vs SCE). Magnetic moment per Mn: 4.69 μ_B (297 K). Anal. Found. C, 55.98; H, 4.68; N, 7.22; Mn, 14.98%. Calcd for $C_{36}H_{36}N_4O_4Cl_2Mn_2$: C, 56.19; H, 4.72; N, 7.28; Mn, 14.28%.

7 Crystal data for **1** : $C_{20}H_{21}N_2O_4Mn$, M_W = 408.33 (per Mn unit), triclinic, space group $P\bar{1}$, a = 10.264(3) Å, b = 11.729(3) Å, c = 10.239(2) Å, α = 115.87(1)°, β = 119.92(2)°, γ = 67.51(1)°, V = 939.5(4) $Å^3$, Z = 2, D_c = 1.443 g/cm^3, R (R_W) = 0.055 (0.083) for 1604 reflections ($I > 3.00\sigma(I)$).

8 Crystal data for **2** : $C_{36}H_{36}N_4O_4Cl_2Mn_2$, M_W = 769.49, monoclinic, space group $P2_1$, a = 14.029(6) Å, b = 12.645(3) Å, c = 19.805(4) Å, β = 98.51(1)°, V = 3474(1) Å^3, Z = 4, D_c = 1.471 g/cm^3, R (R_W) = 0.173 (0.163) for 4709 reflections ($I > 3.00\sigma(I)$). Because its crystals have a disordered structure, the structure was refined anisotropic for Mn and Cl atoms and isotropic for C, N and O atoms. H atoms could not be fixed. A possibility of existence of two isomers having different configurations can not be ruled out as a cause of disorder.

9 ESI-MAS spectra exhibited two strong peaks which can be attributed to $[Mn^{III}_2(\mu\text{-salbn})_2Cl]^+$ and $[Mn^{III}_2(\mu\text{-salbn})_2]^{2+}$ species.

10 EPR spectra of a frozen MeCN solution of complex **2** and after addition of 100 fold amounts of H_2O_2 over it were measured at 213 K.

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