Preparation and Characterization of Different Two Types of Di-μ-oxo Dimanganese(IV) Complexes with Tetradentate Schiff Bases

Hitoshi Torayama, Tamao Nishide, Hideyuki Asada, Manabu Fujiwara, and Takayuki Matsushita*
Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-21

(Received February 5, 1996)

Novel di-μ-oxo dimanganese(IV) complexes with Schiff base ligands, *N,N'*-disalicylidene-1,2-diaminobenzene, salophenH$_2$ and *N,N'*-disalicylidene-1,4-diaminobutane, salbnH$_2$, [Mn$^{\rm IV}$(salophen)(μ-O)]$_2$ and [Mn$^{\rm IV}$(salbn)(μ-O)]$_2$ have been prepared and characterized by spectroscopies, magnetic susceptibilities and X-ray crystallography.

Manganese plays an important role in biological redox systems, which is exemplified by the oxygen-evolving center of photosystem II (PSII OEC) in green plants. The current understanding[1] is that there are four manganese atoms per OEC, although their precise arrangement has not been determined unambiguously. EXAFS spectra of the OEC indicate that the catalytic site in the system consists of a tetranuclear manganese cluster with two short Mn-Mn (2.7 Å) and two somewhat longer Mn-Mn (3.3 Å) distances. During the water oxidation cycle these are of the (II), (III), and (IV) valence states.[1] This close distance, consistent with a di-μ-oxo dimanganese core, implies a strong interaction between the manganese atoms of the substructure. In order to understand its function, manganese(IV) complexes with a di-μ-oxo structure, such as [Mn$^{\rm IV}$(salpn)(μ-O)]$_2$ (salpnH$_2$ = *N,N'*-disalicylidene-1,3-diaminopropane),[2] have been perpared by the reaction of mononuclear manganese(III) complexes with dioxygen, hydrogen peroxide, or other oxidants.

In this letter, we describe the preparation and characterization of two novel dinuclear manganese(IV) complexes with a di-μ-oxo structure. We have found that KMnO$_4$ is soluble in dry acetonitrile (MeCN) and the solution is stable for about 24 h. The tetradentate Schiff base ligands, *N,N'*-disalicylidene-1,2-diaminobenzene, salophenH$_2$, and *N,N'*-disalicylidene-1,4-diaminobutane, salbnH$_2$, were derived from salicylaldehyde and o-phenylenediamine or 1,4-diaminobutane in methanol. The manganese(IV) complexes, [Mn$^{\rm IV}$(salophen)(μ-O)]$_2$,[3] **1**, and [Mn$^{\rm IV}$(salbn)(μ-O)]$_2$,[4] **2**, were prepared by the reaction of these Schiff bases and KMnO$_4$ in MeCN with stirring at room temparature. The solution changed from purple to brown and was allowed to stand in the dark place at room temperature. Two weeks later the resulting brownish black crystals were collected on a glass filter . In the same manner, several di-μ-oxo dimanganese(IV) complexes have been prepared.[5] This synthetic method has the advantage that high-valent manganese complexes can be obtained as crystals in 50-70% yields depending on the ligands by one-step reaction, in which MnO$_4^-$ may be reduced with a part of the ligands. Single crystals of **1** and **2** have been used for X-ray crystallographic characterization.[6,7]

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

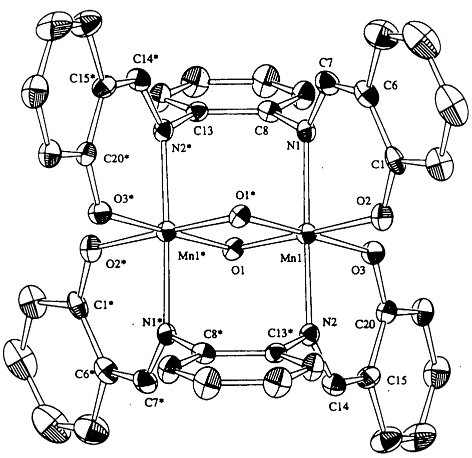

Figure 1. The moleculer structure of [Mn$^{\rm IV}$(salophen)(μ-O)]$_2$, **1**, with hydrogen atoms omitted for clarity, drawing in 30% probability. Selected interatomic distances (Å) and angles (deg) : Mn1-Mn1* 2.718(2), Mn1-O1 1.811(4), Mn1-O1* 1.822(3), Mn1-O2 1.923(4), Mn1-O3 1.934(3), Mn1-N1 2.024(5), Mn1-N2 2.015(4); Mn1-O1-Mn1* 96.9(2), O1-Mn1-O1* 83.1(2), O1-Mn1-O2 177.3(2), O1-Mn1-O3 92.8(2), O1-Mn1-N1 91.2(2), O1-Mn1-N2 91.6(2), O1*-Mn1-O2 94.2(2), O1*-Mn1-O3 175.9(2), O1*-Mn1-N1 88.7(2), O1*-Mn1-N2 90.6(2), O2-Mn1-O3 89.8(2), O2-Mn1-N1 88.7(2), O2-Mn1-N2 88.5(2), O3-Mn1-N1 90.7(2), O3-Mn1-N2 90.2(2), N1-Mn1-N2 177.1(2).

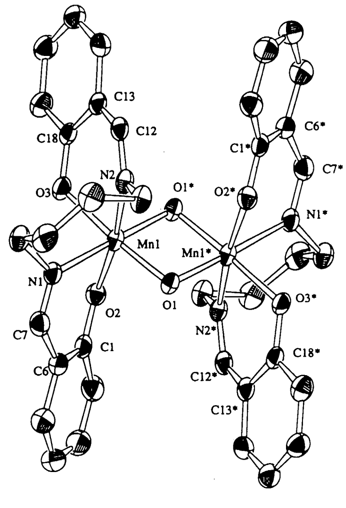

Figure 2. The moleculer structure of [Mn$^{\rm IV}$(salbn)(μ-O)]$_2$, **2**, with hydrogen atoms omitted for clarity, drawing in 30% probability. Selected interatomic distances (Å) and angles (deg) : Mn1-Mn1* 2.729(1), Mn1-O1 1.819(2), Mn1-O1* 1.826(2), Mn1-O2 1.910(3), Mn1-O3 1.940(2), Mn1-N1 2.069(3), Mn1-N2 2.008(3); Mn1-O1-Mn1* 96.9(1), O1-Mn1-O1* 83.1(1), O1-Mn1-O2 93.5(1), O1-Mn1-O3 175.2(1), O1-Mn1-N1 94.3(1), O1-Mn1-N2 90.8(1), O1*-Mn1-O2 95.6(1), O1*-Mn1-O3 92.3(1), O1*-Mn1-N1 176.6(1), O1*-Mn1-N2 91.8(1), O2-Mn1-O3 88.1(1), O2-Mn1-N1 86.8(1), O2-Mn1-N2 171.8(1), O3-Mn1-N1 90.2(1), O3-Mn1-N2 88.1(1), N1-Mn1-N2 86.0(1).

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. The temperature dependency of the magnetic susceptibilities were obtained by the Faraday method from 77 to 290 K.

The ORTEP plots of **1** and **2** are shown in Figs. 1 and 2, respectively. These structures consist of two Mn(IV) centers bridged by two oxygen atoms to yield a planar Mn_2O_2 core with Mn-Mn separation of 2.718(2) Å for **1** and 2.729(1) Å for **2**. In the structure of $[\mathrm{Mn^{IV}(salophen)}(\mu\text{-O})]_2$, **1**, two salophen ligands bridge two manganese atoms with a planar Mn_2O_2 core and bond via by one phenolic oxygen atom and one imine nitrogen atom to each manganese atom to complete the roughly octahedral coordination environment. Adoption of this binding model places two phenolic oxygen atoms of different salophen ligands trans to a bridging oxo group. In the structure of $[\mathrm{Mn^{IV}(salbn)}(\mu\text{-O})]_2$, **2**, the salbn around each manganese atom bonds via two phenolic oxygen atoms and two imine nitrogen atoms to complete the roughly octahedral coordination environment, similarly to $[\mathrm{Mn^{IV}(salpn)}(\mu\text{-O})]_2$.[2] Adoption of this binding model places one phenolic oxygen atom and one imine nitrogen atom trans to a bridging oxo group and one of each donor type in a cis position with respect to a binding oxygen atom. A distinct lengthening of the Mn-O (phenolate oxygen) and Mn-N (imine nitrogen) bond distances trans to the Mn-O (oxo) bonds is observed: Mn-O, 1.940(2) (trans) and 1.910(3) (cis) Å for **2**, and 1.934(3) (trans) and 1.923(4) (trans) Å for **1**; Mn-N, 2.069(3) (trans) and 2.008(3) (cis) Å for **2**, and 2.024(5) (cis) and 2.015(4) (cis) Å for **1**. The different coordination feature of the Schiff base ligands between **1** and **2** may arise from the difference in their flexibility.

From magnetic susceptibility measurements on powdered samples of **1** and **2** in the temperature range 77-290 K, using the Faraday method, temperature-dependent magnetic moments of 1.74 μ_B at 77 K and 3.09 μ_B at 290 K for **1** and 1.21 μ_B at 77 K and 2.85 μ_B at 290 K for **2** per dimeric unit were calculated. These results indicate that there is intramolecular antiferromagnetic coupling between the two Mn(IV) ions (d^3).

References and Notes

1 V. L. Pecoraro, "Manganese Redox Enzymes", VCH Publishers, Inc., New York (1992); V. K. Yachandra, V. J. DeRose, M. J. Latimer, I. Mukerji, K. Sauer, and M. P. Klein, *Science*, **260**, 675 (1993).

2 E. J. Larson and V. L. Pecoraro, *J. Am. Chem. Soc.*, **113**, 3810 (1991); J. W. Gohodes and W. H. Armstrong, *Inorg. Chem.*, **31**, 368 (1992); E. J. Larson, M. S. Lah, X. Li, J. A. Bonadies, and V. L. Pecoraro, *Inorg. Chem.*, **31**, 373 (1992); R. Manchanda, G. W. Brudvig, R. H. Crabtree, and *Coord. Chem. Rev.*, **144**, 1 (1995).

3 Physicochemical data for **1**: UV-visible spectra (MeCN): λ_{max} = 488 nm (logε = 3.71). IR spectra (KBr): 630 cm^{-1} (ν Mn-O). Cyclic voltammogram (DMSO): $E_{1/2}$ = -0.17 V (vs. SCE). Magnetic moment per dimer: 3.16 μ_B (297 K). Anal. Found (%): C, 60.43; H, 3.99; N, 9.76; Mn, 12.50. Calcd (%) for $Mn_2O_6N_6C_{44}H_{33}$: C, 61.98; H, 4.02; N, 9.86; Mn, 12.89.

4 Physicochemical data for **2**: UV-visible spectra (MeCN): λ_{max} = 495 nm (logε = 3.58). IR spectra (KBr): 615 cm^{-1} (ν Mn-O). Cyclic voltammogram (DMSO): $E_{1/2}$ = -0.34 V (vs. SCE). Magnetic moment per dimer: 2.91 μ_B (297 K). Anal. Found (%): C,58.65; H,5.70; N,10.37; Mn,13.40. Calcd (%) for $Mn_2O_6N_6C_{40}H_{42}$: C,59.11; H,5.21; N,10.34; Mn,13.50.

5 $[\mathrm{Mn(X\text{-}salen)(O)}]_2$ (X = H, 5-Br), $[\mathrm{Mn(X\text{-}salpn)(O)}]_2$ (X = H, 3-MeO, 5,6-Benzo, 5-Br), $[\mathrm{Mn(X\text{-}salbn)(O)}]_2$ (X = H, 3-MeO, 5-Br), $[\mathrm{Mn(X\text{-}salophen)(O)}]_2$ (X = H, 5-Br), $[\mathrm{Mn(X\text{-}salchxn)(O)}]_2$ (salchxnH_2 = *N,N'*-disalicylidene-*trans*-1,2-diaminocyclohexane) (X = H, 3-MeO, 5,6-Benzo, 5-Br).

6 Crystal data for **1**·CH_3CN: $Mn_2O_6N_5C_{42}H_{30}$, M = 810.60, monoclinic, space group $P2_1/n$, a = 8.937(2), b = 12.382(2), c = 17.736(2) Å, β = 95.98(1) °, V = 1951.9(5) $Å^3$, Z = 2, D_{calc} = 1.379 g/cm^3, μ(Mo-Kα) = 7.00 cm^{-1}, T = 298 K, crystal size 0.10 × 0.07 × 0.30 mm. A total of 4983 reflections were measured on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation; 2012 with I > 3.00σ(I) were observed. The structure was solved by direct method (MITHRIL84) and refined by the full-matrix least-squares method. The refinement converged at R = 0.052, R_W = 0.044.

7 Crystal data for **2**·CH_3CN: $Mn_2O_6N_5C_{38}H_{39}$, M = 771.63, triclinic, space group $P\bar{1}$, a = 10.003(3), b = 10.740(4), c = 9.972(2) Å, α = 95.24(2), β = 100.48(2), γ = 64.84(2) °, V = 953.3(5) $Å^3$, Z = 1, D_{calc} = 1.344 g/cm^3, μ(Mo-Kα) = 7.12 cm^{-1}, T = 298 K, crystal size 0.45 × 0.20 × 0.35 mm. A total of 4623 reflections were measured on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation; 2799 with I > 3.00σ(I) were observed. The structure was solved by direct method (SHELX86) and refined by the full-matrix least-squares method. The refinement converged at R = 0.043, R_W = 0.034.