Assembly of a Tetranuclear Mixed-Valence Manganese(II,III) Complex from a Binuclear Manganese(II) Complex by Photo-Irradiation

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A tetranuclear mixed-valence manganese(II,III) complex, $[Mn_2(O)(Ph_2MeCCOO)_2(phen)_2]_2(PF_6)_2\cdot 10H_2O$ (2), has been assembled from a binuclear manganese(II) complex, $[Mn(Ph_2MeCCOO)(phen)_2]_2(PF_6)_2\cdot 2MeCN$ (1) by use of a photo-induced oxidation reaction.

In recent years, numerous tetranuclear manganese complexes with μ-oxo bridges have been reported as a structural model of the active site of photosystem II (PS II).[1] To the best our knowledge, however, no synthetic reports on tetranuclear manganese complexes using a photo-induced oxidation reaction are known. In this paper, we report on the syntheses and characterization of a binuclear manganese(II) complex, $[Mn(Ph_2MeCCOO)(phen)_2]_2(PF_6)_2\cdot 2MeCN$ (1), and on assembly of a tetranuclear mixed-valence manganese(II,III) complex, $[Mn_2(O)(Ph_2MeCCOO)_2(phen)_2]_2(PF_6)_2\cdot 10H_2O$ (2), from 1 using a photo-irradiation procedure, where $Ph_2MeCCOO$ is 2,2-diphenylpropionate ion and phen is 1,10-phenanthroline.

Complexes 1 and 2 were obtained as follows. Complex 1: The $Mn(Ph_2MeCCOO)_2\cdot(CH_3)_2SO$ complex (1 mmol), which was prepared by using a method similar to that described in the literature,[2] was dissolved in 6 cm^3 of methanol. To this solution, a solution of phen$\cdot H_2O$ (2 mmol) and tetrabutylammonium hexafluorophosphate (1 mmol) in 6 cm^3 of acetonitrile was added under stirring. The reaction mixture was allowed to stand for one week at room temperature. Yellow crystals were precipitated, and dried in air (yield 0.78 g, 49.3%).[3] Complex 2: A yellow solution of 1 (1 mmol) in 10 cm^3 of a methanol/acetonitrile mixture was exposed to the sun for two days. Yellow precipitates were filtered off, and the filtrate was allowed to stand for two weeks at room temperature. The color of the solution changed from yellow to brown, and brown crystals were obtained, and dried in air (yield 0.27 g, 25.0%).[3] The complex can be prepared even to irradiate with light of a super-high-pressure mercury lamp.

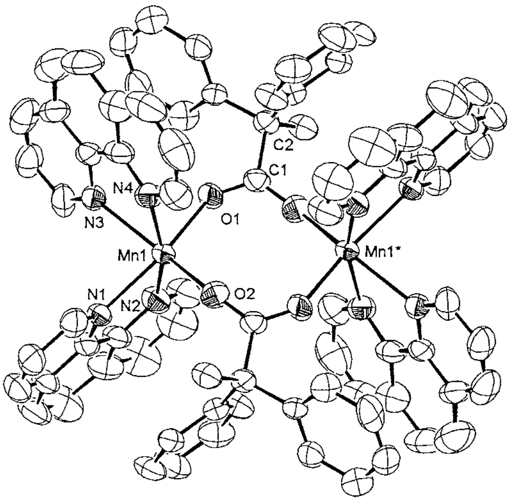

Figure 1. An ORTEP drawing for the complex cation of **1**. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mn1$\cdots$Mn1* 4.632(5), Mn1-O1 2.105(8), Mn1-O2 2.078(8), Mn1-N1 2.267(9), Mn1-N2 2.28(1), Mn1-N3 2.340(9), Mn1-N4 2.26(1), O1-Mn1-N1 160.2(4), N2-Mn1-N4 162.8(4), O2-Mn1-N3 158.8(4).

The crystal structure[4] for the complex cation of 1 is shown in Figure 1. Complex 1 has a crystallographic inversion center. The two manganese(II) ions are linked by two bidentate bridging carboxylates of a *syn-anti* mode. The coordination environment of Mn is a distorted octahedral geometry with two oxygen atoms of two bridging carboxylates and four nitrogen atoms of two terminal phen ligands. The average distance of the Mn–N bonds (2.30 Å) is longer than that of the Mn–O bonds (2.09 Å). The Mn$\cdots$Mn distance in 1 (4.632(5) Å) is slightly longer than those found in the dimangane(II) complexes with two carboxylato *syn-anti* bridges; $[Mn_2(PhCOO)_2(bpy)_4](ClO_4)_2$ (4.509 Å)[5] and $[Mn_2(MeCOO)_2(tpa)_2](TCNQ)\cdot 2MeOH$ (tpa = tris(2-pyridylmethyl)amine) (4.125 Å)[6].

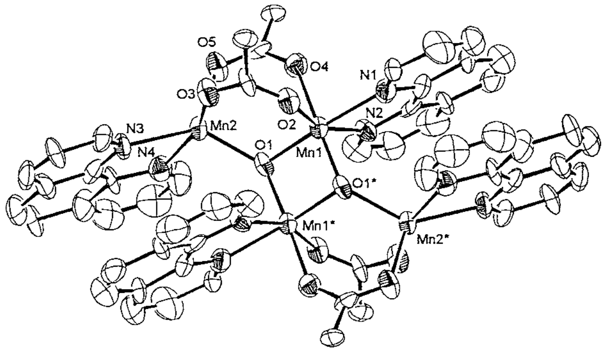

Figure 2. An ORTEP drawing for the complex cation of **2**. The phenyl and methyl carbon atoms and all hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Mn1$\cdots$Mn1* 2.770(6), Mn1$\cdots$Mn2 3.255(4), Mn1$\cdots$Mn2* 3.578(4), Mn2$\cdots$Mn2* 6.255(6), Mn1-O1 1.88(1), Mn1-O1* 1.86(1), Mn1-O2 2.17(1), Mn1-O4 1.97(1), Mn1-N1 2.14(2), Mn1-N2 2.26(2), Mn2-O1 2.04(1), Mn2-O3 2.09(1), Mn2-O5, 2.08(1), Mn2-N3, 2.23(1), Mn2-N4 2.26(2), O1-Mn1-N1 174.0(6), O1*-Mn1-O4 175.8(5), O2-Mn1-N2 159.5(5), O3-Mn2-N4 159.6(6), Mn1-O1-Mn1* 95.7(5), Mn1-O1-Mn2 112.2(5), Mn1*-O1-Mn2 132.8(6).

Complex 2 has a crystallographic inversion center. Four manganese atoms in 2 are bridged by two μ_3-oxo atoms (O1, O1*) (Figure 2). Further, the Mn1 and Mn2 atoms are bridged by two carboxylates of a *syn-syn* mode. As a consequence, the tetranuclear manganese core in 2 consists of two μ-oxo-bis(μ-carboxylato)dimanganese units making a dimer-of-dimers structure. The coordination environment of Mn1 is a distorted octahedral geometry with O2–Mn1–N2 (159.5(5)°) as an axial axis. The Mn2 atom has a fairly distorted trigonal bipyramidal geometry. The valence of the central manganese atoms (Mn1, Mn1*) and the terminal manganese atoms (Mn2, Mn2*) are assigned to +3 and +2, respectively, on the basis of the following structural characters. (i) The average of the Mn1–N bonds (2.20 Å) is shorter than that of the Mn2–N bonds (2.25 Å). (ii) The central manganese atoms to μ_3-oxo distances (1.86(1)–1.88(1) Å) are significantly shorter than the terminal manganese atoms to μ_3-oxo distances (2.04(1) Å). (iii) A Jahn-Teller axial elongation is observed around Mn1.

There are three types of Mn···Mn separation in **2**. The central Mn1···Mn1* separation (2.770(6) Å), the intra-unit Mn1···Mn2 separation (3.255(4) Å), and the inter-unit Mn1*···Mn2 separation (3.578(4) Å) are comparable to those previously reported for $\mathrm{Mn^{II}{}_2Mn^{III}{}_2(\mu_3\text{-}O)_2}$ core,[7] however, the inter-unit Mn1*···Mn2 separation bridged by only one oxo is longer than that bridged by one oxo and one carboxylato in $\mathrm{[Mn_4O_2(O_2CMe)_6(bpy)_2]\cdot 2CHCl_3}$ (3.481(1) Å).[8] The longer Mn1*···Mn2 separation is probably attributable to the existence of only one oxo bridge between Mn1* and Mn2. The dimer-of-dimers structure in **2** is stabilized by oxo bridging and π-π stacking[9] of phen as a terminal ligand.

Magnetic susceptibility measurements for **1** and **2** were carried out in the temperature range of 80–300 K. The μ_{eff} values per Mn for **1** gradually decrease with decreasing temperature from 5.84 B.M. at 293.1 K to 5.70 B.M. at 81.3 K. These results indicate that a weak antiferromagnetic interaction is operative between two $\mathrm{Mn^{II}}$ ions in **1**. The μ_{eff} values per $\mathrm{Mn_4}$ of **2** gradually decreases from 8.33 B.M. at 293.6 K to 7.10 B.M. at 81.6 K. This magnetic behavior of **2** suggests that an antiferromagnetic interaction is operative in the $\mathrm{Mn^{III}\cdots Mn^{III}}$ pair and the $\mathrm{Mn^{II}\cdots Mn^{III}}$ pairs. The interaction in the $\mathrm{Mn^{II}\cdots Mn^{II}}$ pair can be considered to be negligible because the $\mathrm{Mn^{II}\cdots Mn^{II}}$ distance is so long (Mn2···Mn2* = 6.255(6) Å).

The oxidation reaction of **1** in a methanol/acetonitrile (1:1) mixture (10 mmol dm^{-3}) has been investigated by means of a photo-irradiation procedure using an USHIO USH-500D super-high-pressure mercury lamp (500 W). The solution of **1** gradually changes from yellow to dark brown with the passage of irradiation time. This behavior was confirmed by spectrophotometric measurement. The methanol/acetonitrile solution of **1** has no absorption in the visible region, whereas the spectrum of the solution after photo-irradiation shows a new intense broad band at about 20×10^3 cm^{-1}. This band is corresponding to a d-d transition for the $\mathrm{Mn^{III}}$ ions with an elongated octahedral geometry in **2**.[10] The oxidation reaction is induced most effectively by the light near 365 nm, because the reaction occurs when the solution of **1** is irradiated by the mercury lamp through a Toshiba UV-D35 filter (about 75% transmittance at 365 nm) and no reactions occur using a Toshiba L-42 filter to eliminate light shorter than 400 nm. The reaction is accelerated when a few drops of water are added to the yellow solution. The irradiation-time is less than one fifth of that for no addition of water till **2** is precipitated. No color change is observed when the photo-irradiation for a dried solution of **1** is carried out under a nitrogen atmosphere. Judging from the marked acceleration of the reaction, the bridging oxo ions in **2** probably originate from water molecules contained as an impurity in solvents. To certify the origin of the oxo ions, further investigations using water-^{18}O are currently under way.

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References and Notes

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3 The solvated acetonitrile in **1** and the crystal water in **2** were lost upon dring of the crystals, so that the moleculer weights of the samples employed in elemental analyses and magnetic susceptibility measurements were calculated as one acetonitrile solvation in **1** and the anhydride of **2**. Anal. Found (**1**): C, 59.69; H, 3.94; N, 8.14%. Calcd for $\mathrm{C_{80}H_{61}F_{12}Mn_2N_9O_4P_2}$: C, 59.60; H, 3.81; N, 7.82%.Anal. Found (**2**): C, 60.55; H, 4.11; N, 5.06%. Calcd for $\mathrm{C_{108}H_{84}F_{12}Mn_4N_8O_{10}P_2}$: C, 59.96; H, 3.91; N, 5.18%.

4 Crystal data for **1**: $\mathrm{C_{82}H_{64}F_{12}Mn_2N_{10}O_4P_2}$, M = 1623.28, triclinic, space group $P\bar{1}$, a = 12.825(8) Å, b = 13.337(7) Å, c = 12.742(6) Å, α = 90.11(5)°, β = 99.98(5)°, γ = 62.66(3)°, U = 1899(2) Å^3, Z = 1, μ = 4.44 cm^{-1}, T = 293 K, $R1$ = 0.064 and $wR2$ = 0.066 for 2071 observed reflections with $I > 3.0\sigma(I)$. Crystal data for **2**: $\mathrm{C_{108}H_{104}F_{12}Mn_4N_8O_{20}P_2}$, M = 2307.70, triclinic, space group $P\bar{1}$, a = 14.044(5) Å, b = 14.999(7) Å, c = 13.491(5) Å, α = 103.15(4)°, β = 93.72(4)°, γ = 109.28(3)°, U = 2582(2) Å^3, Z = 1, μ = 5.79 cm^{-1}, T = 293 K, $R1$ = 0.075 and $wR2$ = 0.077 for 2355 observed reflections with $I > 3.0\sigma(I)$.

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