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Synthesis and Characterization of a Novel Dimer of Di(μ-oxo)manganese Dimers with Two Coordinated Water Molecules in (III,IV,III,IV) Oxidation State

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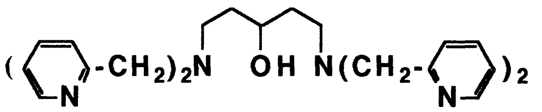
A dimer of di(μ-oxo)dimanganese(III,IV) dimers with two coordinated water molecules, $[\{Mn_2(tmdp)(O)_2(H_2O)\}_2](CF_3SO_3)_4\cdot 6H_2O$, was prepared, where Htmdp is 1,5-bis[bis(2-pyridylmethyl)amino]-3-pentanol, and its crystal structure was determined by X-ray structure analysis. The complex cation consists of two di(μ-oxo)Mn_2(III,IV) dimers which are linked by two tmdps to form a dimer of dimers with a bilayered structure.

The oxygen-evolving center (OEC) in photosystem II (PS II) in green plants and algae has been shown to contain a tetranuclear manganese center which catalytically oxidize two water molecules to molecular oxygen.1) Although the nature of the manganese center and the reaction mechanism of water oxidation are ambiguous, di(μ-oxo)dimanganese unit in the tetramer has been proposed in the S_1 and S_2 states in Kok's S state scheme2) by ESR, EXAFS, and XANES studies.3) A variety of tetranuclear manganese complexes in various oxidation states4) have been devised as structural and spectroscopic models for the S_n states in PS II. Very recently Chan and Armstrong reported an interesting dimer of di(μ-oxo)Mn_2(III,IV) dimers as a structural and spectroscopic model for S_1 state.4j)

For approaching the functional models of OEC, it is important to devise polynuclear manganese complexes that contain two water molecules as a molecular oxygen source in coordination sphere and are four-electron oxidants having enough redox potentials for water oxidation. Such functional models, however, have not been reported so far. In this study, we report the synthesis and structural characterization of a novel dimer of di(μ-oxo)-dimanganese(III,IV) dimers with two coordinated water molecules, $[\{Mn_2(tmdp)(O)_2(H_2O)\}_2](CF_3SO_3)_4\cdot 6H_2O$.



Htmdp

The complex was prepared as dark green crystals by mixing an ethanol solution (10 cm^3) of Htmdp5) (1 mmol) with an aqueous solution (10 cm^3) of $Mn(NO_3)_2\cdot 9H_2O$ (2 mmol) followed by addition of triethylamine (1 mmol) in 5 cm^3 of ethanol and CF_3SO_3Na (8 mmol). Crystals suitable for X-ray study were obtained by recrystallization from acetonitrile-water mixture (1 : 1). Found: C, 37.47; H, 4.06; N, 8.44%. Calcd. for $Mn_4C_{62}H_{82}N_{12}F_{12}O_{26}S_4$: C, 37.47; H, 4.16; N, 8.46%.

A dark green prismatic crystal with dimensions of 0.3 x 0.3 x 0.4 mm^3 was used for X-ray crystal structure analysis. Crystal data: $[Mn_4(tmdp)_2(O)_4(H_2O)_2](CF_3SO_3)_4 \cdot 6H_2O$: F.W = 1987.36, triclinic, $P\ \bar{1}$, a = 16.543(1) Å, b = 19.097(2) Å, c = 13.393(1) Å, α = 94.450(7)°, β = 90.698(6)°, γ = 84.997(7)°, V = 4202.4(6) $Å^3$, Z = 2, D_m = 1.60, D_c = 1.57 g cm^{-3}, μ(Mo-Kα) = 8.45 cm^{-1}. Intensity data were collected by a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation and corrected for Lorenz-polarization effects. A total of 16984 reflections with $2\theta < 55°$ were obtained, of which independent 5648 reflections with $|F_o| > 3\sigma|F_o|$ were used for the structure determination. The structure was solved by direct method and refined by block-diagonal least-squares method.[6] The current R (Rw) values are 0.092 (0.117).

Two crystallographically independent tetranuclear complexes are present in the unit cell, whose structures are slightly different from each other. Figure 1 shows one of molecular structures of the complex cations. The complex cations consist of two di(μ-oxo)Mn_2 dimers which are linked by two tmdp bridges to form a dimer of dimers with a bilayered structure. Two $\mathrm{Mn}<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{Mn}$ planes are not faced directly, but slid as shown in Fig. 1b. Two di(μ-oxo)Mn_2 dimers in tetranuclear structure are crystallographically equivalent, since the complex cation possesses an inversion center. All manganese ions are in distorted octahedron. The oxidation states of Mn1 and Mn2 ions in the dimer can be assigned to be three and four, respectively, by considering the total charge of complex cation and comparing the bond distances around manganese atoms. The bond distances around Mn1 and Mn2 atoms are comparable to those of the di(μ-oxo)Mn_2(III,IV) complexes.[7] The most striking

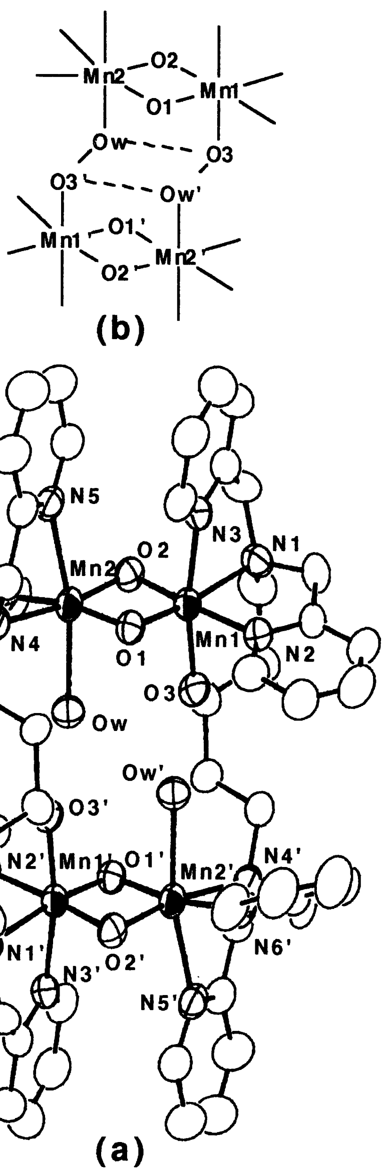


Fig. 1. Molecular structure (a) and schematic drawing (b) of one of the complex cations. The selected bond length (l/Å) and angles (ϕ/°) are as follows ; Mn1-O1 1.778(6), Mn1-O2 1.789(6), Mn1-O3 1.876(6), Mn1-N1 2.094(7), Mn1-N2 2.054(7), Mn1-N3 2.030(8), Mn2-O1 1.841(6), Mn2-O2 1.825(6), Mn-Ow 2.285(7), Mn2-N4 2.169(8), Mn2-N5 2.249(8), Mn-N6 2.065(8), Mn1-Mn2 2.644(2), Mn1···Mn2' 5.864(2), O3···Ow 2.865(9), O3···Ow' 2.682(9), Ow···Ow' 3.333(9), Mn1-O1-Mn2 93.9(3), Mn1-O2-Mn2 94.0(3).

feature of the complex is that it has two water molecules coordinated to manganese(III) ions. Those two water molecules are separated only by ca. 3.3 Å. This is the first example of a tetranuclear complex which contains two di(μ-oxo)Mn_2(III,IV) dimers and two coordinated water molecules in close proximity. Such coordinated water molecules must be of a key importance for modelling of OEC in PS II. The four oxygen atoms, Ow, Ow', O3, and O3', form a rhomboidal plane, where the distances of Ow···O3 and Ow···O3' are 2.865(9) and 2.682(9) Å, respectively, and the angle of O3···Ow···O3' is 106°. These distances and angle probably suggest the presence of network of hydrogen bondings between four oxygen atoms.

The effective magnetic moments of the tetranuclear complex at 300 and 80 K are 3.50 and 2.51 B.M., respectively, which are smaller than the spin only value (8.83 B.M. : S=2•S=3/2•S=2•S=3/2), indicating the presence of antiferomagnetic interaction between manganese ions. Since two di(μ-oxo)Mn_2(III,IV) dimers are separated by ca. 5.9 Å and there is no bridging group providing the super-exchange interaction between dimers, it is reasonable to assume that the exchange interaction between two dimers is negligible. Temperature dependence of magnetic susceptibilities (300 K - 80 K) was analyzed by the isotropic exchange interaction model ($H=-2JS_1 \cdot S_2$: $S_1=2$ and $S_2=3/2$), where exchange interaction between two dimers in the tetranuclear complex is assumed to be zero (Fig. 2) The data were well interpreted in terms of the following parameters : J = -142 cm^{-1} and g = 2.00. The J value is comparable to those of di(μ-oxo)Mn_2(III,IV) complexes.$^{7)}$

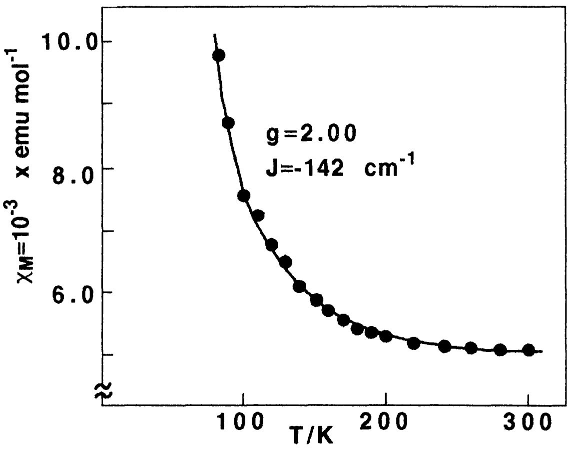


Fig. 2. Temperature dependence of magnetic susceptibilities of $[\{Mn_2(tmdp)(O)_2(H_2O)\}_2](CF_3SO_3)_4 \cdot 6H_2O$.

It is well known that the di(μ-oxo)Mn_2(III,IV) dimers exhibit an ESR signal at g = 2.0 with a so called 16-hyperfine pattern.$^{8)}$ The complex shows two broad signals at g = 4.5 and 2.0 (Fig. 3). No significant spectral change was observed at 77 K and 13 K. As mentioned above, since the exchange interaction between the dimers is negligible, only dipolar interaction may be present in this system. The dipolar interaction between di(μ-oxo)Mn_2(III,IV) dimers (assuming $S_1 = 1/2 \cdot S_2 = 1/2$ couple) gives rise to S = 1 and S = 0 states. The signal at g = 2.0 may be assigned to $\Delta M_S = 1$ transition within the S = 1 states. Disappearance of ^{55}Mn hyperfine splittings in this signal seems to be attributable to the dipolar interaction

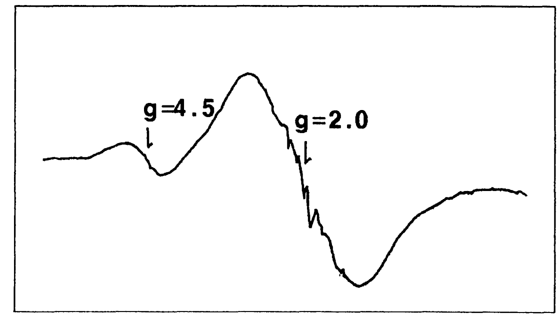


Fig. 3. ESR spectrum of $[\{Mn_2(tmdp)(O)_2(H_2O)\}_2](CF_3SO_3)_4 \cdot 6H_2O$ in acetonitrile : ethanol : toluene (2 : 1 : 1) at 77 K.$^{9)}$

between two dimers. Although the origin of the low field signal at g = 4.5 is not clear, one of possibilities is due to a $\Delta M_S = 2$ transition.

The cyclic voltammogram of the complex in acetonitrile showed a reversible wave at ca. 1.0 V vs. SCE which corresponds to Mn_4(III,IV,IV,IV)/Mn_4(III,IV,III,IV) redox couple and an irreversible oxidation wave at ca. 1.2 V vs. SCE. Further study of the electrochemistry is in progress.

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