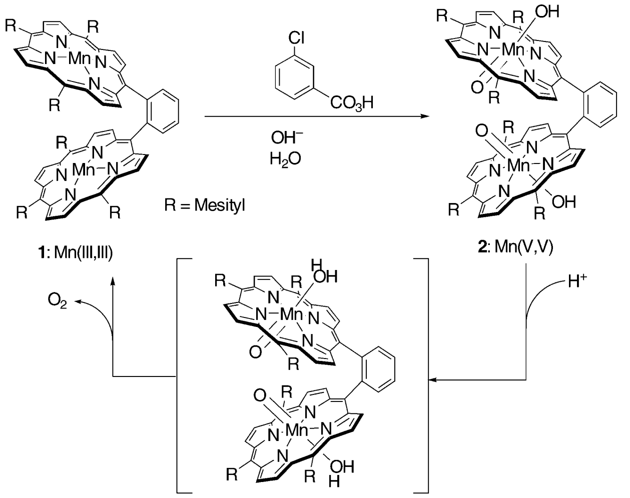
Oxygen Evolution from Water

Characterization of a Dinuclear Mn$^{\mathrm{V}}$=O Complex and Its Efficient Evolution of O_2 in the Presence of Water**

*Yuichi Shimazaki, Taro Nagano, Hironori Takesue, Bao-Hui Ye, Fumito Tani, and Yoshinori Naruta**

The oxidation of water in the process of dioxygen evolution is catalyzed by an oxygen-evolving complex (OEC) in photosynthesis, which is one of the most important and fundamental chemical processes in nature.[1–3] The active site in a photosynthetic OEC protein contains a tetramanganese cluster,[4] which adopts a Y-shaped geometry as revealed by recent X-ray structure analysis of photosystem II.[5] Though the mechanism of dioxygen evolution has not been determined, the stage of oxygen evolution would involve either a high valent terminal oxo manganese species[3,4,6] or the coupling of bridging oxo units.[2,3] Manganese complexes have been extensively studied as artificial OEC models in structural and functional investigations to understand the mechanism of oxygen evolution from water in photosynthetic OEC.[3] However, only a few Mn complexes that can catalyze homogeneous water oxidation have been reported.[7,8] We have previously reported dimanganese complexes of dimeric tetraarylporphyrins linked by 1,2-phenylene bridge (Scheme 1).[8] The anodic oxidation of an aqueous solution of acetonitrile (5% v/v H_2O in CH_3CN) with the dimanganese tetraarylporphyrin dimer evolved oxygen in the potential range > 1.20 V versus Ag/Ag$^+$. The catalyst can also oxidize olefins such as cyclooctene to form epoxide with stoichiometric amounts of *m*-chloroperbenzoic acid (*m*CPBA).[9] We proposed that the oxidation of a dimanganese(III) tetraarylporphyrin dimer could give the corresponding high valent Mn=O complex, which is the active species in these oxidation. However, the mechanisms of oxygen evolution and epoxidation, especially the formation of a high-valent Mn=O intermediate have not been fully confirmed. Herein, we report on the oxidation of the dimanganese porphyrin dimer by employing *m*CPBA as an oxidant, and the characterization of the resulting Mn$^{\mathrm{V}}$=O species by spectroscopic methods. Furthermore, oxygen evolution was observed from the Mn$^{\mathrm{V}}$=O species when a small excess of trifluoromethanesulfonic acid (CF_3SO_3H) was added. To the best our knowledge, this is the first clear example of an O–O bond formation involving a Mn$^{\mathrm{V}}$=O species.



Scheme 1. Structure of Mn_2–dimeric porphyrin complex [Mn(DTMP)]$^{2+}$ (**1**) and a reaction pathway for O_2 formation.

The addition of two molar equivalents of *m*CPBA for each Mn ion to the Mn$^{\mathrm{III}}_2$ porphyrin dimer [Mn_2(DTMP)(OH)]-$NO_3{\cdot}5H_2O$ (**1**) afforded the Mn$^{\mathrm{V}}_2$ complex **2** (Scheme 1) in CH_2Cl_2/CH_3CN (1:1, v/v) solution that contained 35 equivalents of tetrabutylammonium hydroxide (Bu_4NOH) and 1.0% water at room temperature. Species **2** exhibited a very sharp Soret band centered at 423 nm (Figure 1). When one molar equivalent of 1,1-diphenyl-2-picrylhydrazine (DPPH—a one-electron reductant for each Mn ion) was added to **2**, a Mn$^{\mathrm{IV}}_2$ species **3** was rapidly formed, which has a Soret band centered at 415 nm. Complex **3** was also prepared when one molar equivalent of *m*CPBA for each Mn ion was added to **1** in CH_2Cl_2/CH_3CN (1:4, v/v) solution in the presence of five equivalents of Bu_4NOH, confirmed by UV/Vis spectrum. When the solution of **2** was left stand at room temperature, the Soret band at 423 nm gradually disappeared and a 468 nm band accordingly appeared with isosbestic points indicating

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[*] Dr. Y. Shimazaki, T. Nagano, H. Takesue, Dr. B.-H. Ye, Dr. F. Tani, Prof. Dr. Y. Naruta
Institute for Materials Chemistry and Engineering
Kyushu University, Higashi-ku, Fukuoka 812-8581 (Japan)
Fax: (+81) 92-642-2715
E-mail: naruta@ms.ifoc.kyushu-u.ac.jp

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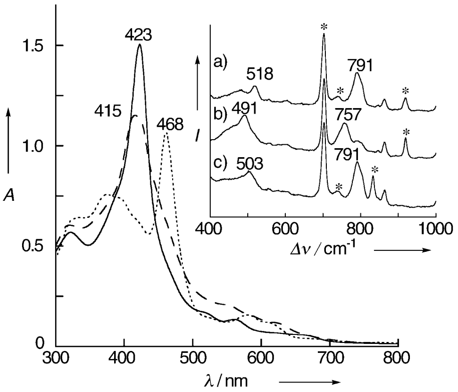

Figure 1. Comparison of the absorption spectra; **1**·NO_3, •••••; **2**, ——; **3**, – – –. Inset: resonance Raman spectra of **2** (5 °C, $\lambda_{ex} = 413.1$ nm, 20 mW). a) $Bu_4N^{16}OH$ in CH_2Cl_2/CH_3CN, b) $Bu_4N^{18}OH$ in CH_2Cl_2/CH_3CN, c) Bu_4NOD in CH_2Cl_2/CD_3CN. Incubation time of the isotopic experiment was 10 min before the Raman data was collected.

the direct reduction to an Mn^{III}_2 species. The change in absorbance over time at 423 nm at 20 °C showed that the decay of **2** is first-order. The half-life ($t_{1/2}$) of **2** was 3.1 h (the observed decay constant, $k_{obs} = 6.19 \times 10^{-5}\ s^{-1}$), thus implying that **2** was stable at 20 °C.[10–12] The Mn^{V}_2 species **2** was also stable under similar basic conditions in CH_2Cl_2/CH_3CN (1:3, v/v) solution with 10 % water ($k_{obs} = 3.38 \times 10^{-5}\ s^{-1}$). The stability of **2** is dependent upon the amount of Bu_4NOH. For example, in the presence of five equivalents of Bu_4NOH, the decay constant of **2** $k_{obs} = 5.47 \times 10^{-3}\ s^{-1}$ ($t_{1/2} = 2.1$ min) at 20 °C and furthermore, without the presence of Bu_4NOH, we did not observe the appearance of **2** under oxidation by *m*CPBA. Thus, highly basic conditions are necessary for the formation and the stabilization of **2**.

The ESR spectrum of **3** at 77 K showed $g = 4.5$ and 2.2 (g = the g factor), signals characteristic of a high-spin d^3 Mn^{IV} complex.[13,14] On the other hand, **2** was ESR inactive at 5 K. Though an oxo-bridged dinuclear Mn^{IV} porphyrin complex is ESR inactive,[15] the Mn centers of **1** could not be bridged intra/intermolecularly by an oxo or hydroxo group, because of the steric hindrance of the *meso* mesityl groups.[16] However, some examples of monomeric $Mn^{V}=O$ complexes have been reported to be diamagnetic species.[10–12] On the basis of these chemical and magnetic studies, we assign the Mn centers of **2** as low-spin, d^2 Mn^{V} ions.

The resonance Raman spectrum of **2** exhibited two isotope-sensitive intense bands at 791 and 518 cm^{-1} (Figure 1, inset). By replacing $Bu_4N^{16}OH$ in $H_2{}^{16}O$ with $Bu_4N^{18}OH$ in $H_2{}^{18}O$, these bands shifted to 757 and 491 cm^{-1}, respectively. Furthermore, by replacing $Bu_4N^{16}OH$ in $H_2{}^{16}O$ with $Bu_4N^{16}OD$ in $D_2{}^{16}O$, the 518 cm^{-1} band shifted to 503 cm^{-1}, while the 791 cm^{-1} band did not shift. The observed isotopic shifts of 34 and 27 cm^{-1} with ^{18}O-substitution and 15 cm^{-1} with OD-substitution are in good agreement with the calculated values (^{18}O, 35 and 22 cm^{-1}; OD, 11 cm^{-1}) from the harmonic oscillator approximation of $Mn^{V}=O$ and $Mn^{V}-OH$ stretching vibrations. Therefore, the 791 and 518 cm^{-1} bands are assigned to $\nu(Mn^{V}=O)$ and $\nu(Mn^{V}-OH)$, respectively, thus indicating that each Mn center of **2** is six-coordinate $HO-Mn^{V}=O$. The observed $Mn^{V}=O$ stretching frequency is higher than that of $[Mn^{IV}(O)(OH)(TMP)]^{-}$ (712 cm^{-1}; TMP = tetramesitylporphyrin),[14] thus indicating the $Mn^{V}=O$ bond is stronger than $Mn^{IV}=O$. On the other hand, $\nu(Mn^{V}\equiv O)$ of a Mn tetraamide complex (979 cm^{-1}) is much higher than the present value,[12] which shows that the manganese–oxo bond of **2** is much weaker than that of the tetraamide complex, presumably because of the effect of the *trans*-hydroxo ligand in **2**. Although ^{16}O-*m*CPBA was used as an oxidant in the ^{18}O-labeled experiment, the isotopic shifts were observed, because of facile exchange of the oxo and hydroxo oxygen atoms with oxygen atoms of H_2O and OH^{-}. Oxo–hydroxo tautomerism, that is, conversion of oxo to the hydroxo moiety, would proceed through a hydrogen-bonded water molecule in a concerted fashion.[17] Consequently, oxo and hydroxo groups could exist both inside and outside of the cavity in the tautomeric process.

The monomeric $Mn^{V}=O$ porphyrin species can exist only for a few seconds or minutes, whereas **2** is stable for several hours.[10–12] Actually, we could not observed a stable $Mn^{V}=O(TMP)$ complex under the same conditions used for **2**. The higher stability of **2** than that of $Mn^{V}=O(TMP)$ complex is due to its characteristic structure.[16] The present dimeric complex has a hydrophobic cavity surrounded by the porphyrin rings and the bulky *meso* mesityl groups, which could protect the inside oxo groups.

When 40 equivalents of CF_3SO_3H for each manganese ion was added to the $HO-Mn^{V}=O$ species **2** in CH_2Cl_2/CH_3CN (1:3, v/v) solution that contained 10 % water, the Mn^{V} species was spontaneously reduced to Mn^{III} within a few seconds and O_2 evolution was observed under an Ar atmosphere. The yield of the evolved O_2 was determined by mass spectrometry to be 92 % with respect to complex **2**, based on the assumption that each $[Mn^{V}=O]_2$ complex gives one O_2 molecule (Figure 2). Upon ^{18}O-substitution of water and hydroxide, $^{18}O_2$ was observed to evolve in a yield greater than 90 %. Furthermore, the mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ was observed in a statistical distribution, when the mixture of $^{16}OH^{-}$ in $H_2{}^{16}O$ and $^{18}OH^{-}$ in $H_2{}^{18}O$ was employed. The ratio of $^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2$ was in good agreement with the calculated value from the applied isotopic ratio of ^{16}O:^{18}O in water and hydroxide anion (for example, the observed ratio of $^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2{}^{16}O = 4$:42:54, the calculated ratio of

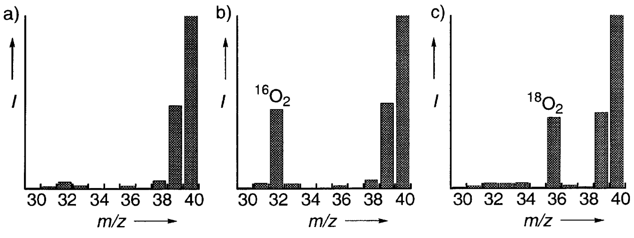

Figure 2. Mass spectrometric gas analysis upon the addition of CF_3SO_3H to **2** under an Ar atmosphere. a) Before addition of CF_3SO_3H to **2**, b) addition of 40 equiv CF_3SO_3H to **2** in $H_2{}^{16}O/{}^{16}OH^{-}$, c) addition of 40 equiv CF_3SO_3H to **2** in $H_2{}^{18}O/{}^{18}OH^{-}$.

$^{16}O_2{:}^{16}O^{18}O{:}^{18}O_2{}^{16}O = 9{:}42{:}49$ from the applied isotopic ratio of $^{16}O{:}^{18}O = 3{:}7$ in water and hydroxide anion). These results indicated quantitative incorporation of oxygen atoms from H_2O and OH^- into the evolved O_2. On the other hand, no O_2 evolution was detected on the controlled experiment with a $Mn^{IV}{}_2$ species **3**. It was reported that $H_2O{-}Mn^{V}{=}O$ can oxidize halide anion through an oxo-transfer reaction.[11] Indeed, upon protonation, **2** quantitatively oxidized Cl^- into ClO^- by an attack of the $Mn^{V}{=}O$ moiety on Cl^-, whereas without protonation, Cl^- oxidation could not be observed. Thus, the protonation on **2** could form a transient intermediate, such as $(H_2O{-}Mn^{V}{=}O)_2$. The O–O bond formation would occur by the attack of the $H_2O{-}Mn^{V}{=}O$ group on water, or by a coupling reaction between the oxo groups of each $Mn^{V}{=}O$ unit. Furthermore, as decomposition of the Mn complex was not detected in the stoichiometric reaction presented herein, the interconversion between **1** and **2** can be extended to a catalytic cycle.

In conclusion, we have characterized the $Mn^{V}{=}O$ porphyrin dimer as a key intermediate of the O_2 evolution in detail. The reaction of the $Mn^{III}{}_2$ complex **1** with *m*CPBA under strong basic conditions gave the stable diamagnetic $Mn^{V}{}_2$ intermediate **2**, which has oxo and hydroxo axial ligands derived from water and/or hydroxide ions. Addition of a small excess amount of acid to **2** rapidly afforded a $Mn^{III}{}_2$ species, and dioxygen was evolved quantitatively. Further studies on the mechanism of this oxygen evolution catalyzed by the dimanganese tetraarylporphyrin dimer are in progress in our laboratory.

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