Dioxygen Formation by Oxo Manganese Model Complexes for Photosystem II

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Dioxygen formation is one of the most important and fundamental biological processes in nature. The oxygen-evolving center (OEC) in photosystem II (PSII) contains a μ-oxo-bridged manganese tetramer that can carry out the four-electron oxidation of water to O_2 (eq 1).[1-4] In addition, both Ca^{2+} and Cl^- are cofactors necessary for catalytic activity, but their exact structural and functional roles are not yet clear.[5]

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

Owing to the complexity of the protein and the instability of preparations of PSII, only a limited amount of information on the oxo-manganese cluster is available. EXAFS data have provided valuable structural information,[3] and recently, a crystal structure of photosystem II from *Synechococcus elongatus* was solved at 3.8 Å resolution.[6] With limited structural information, it has been a challenge to understand the mechanism of water oxidation. A number of proposals have been presented for the dioxygen formation step.[7-9]

Inorganic model complexes have played a valuable role in developing an understanding of the OEC. A number of multinuclear oxo manganese complexes have been synthesized and studied.[10] However, none of these complexes has been able to catalyze water oxidation. Recently, there have been two reports of oxo manganese model complexes that were successfully employed for dioxygen evolution.[11,12] These two model complexes are especially important in that they can provide insights into the mechanism of the dioxygen formation step in photosynthetic water oxidation. Structural and reactivity details of these two model complexes will be discussed with regard to the mechanism of O-O bond formation.

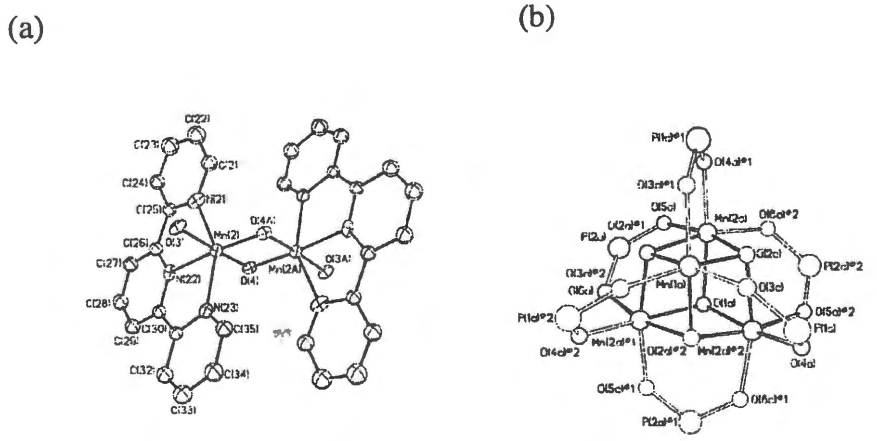

Figure 1. Structures of two functional model complexes of the OEC

Brudvig and coworkers reported that O_2 is evolved by the reaction of a the di-μ-oxo bridged manganese dimer $[Mn(terpy)(OH_2)(\mu\text{-}O)]_2^{3+}$ (Figure 1a) with a highly oxidizing oxygen atom transfer reagent, potassium peroxymonosulfate (oxone).[11(b)] This complex has d(Mn-Mn) of 2.7Å, which is close to the reported Mn-Mn distance in the native enzyme.[3] The key feature of this Mn complex is the presence of exchangeable aqua coordination sites that could provide the position for Mn(V)=O formation. Isotopic labeling studies show that dioxygen evolution proceeds via an intermediate that can exchange with water.[13] The amount of label incorporated into O_2 is dependent on the relative concentrations of oxone and the catalyst. The rate-limiting step of O_2 evolution is proposed to be formation of a Mn(V)=O species which could competitively react with either oxone or water/hydroxide to produce O_2. From this model complex study, a mechanism of dioxygen formation for the OEC was proposed that includes such a Mn(V)=O species as the active intermediate.[7]

Core conversion between cubane and butterfly structures was proposed as a possible step in the mechanism of water oxidation by Vincent and Christou in 1987.[8] A direct test of this proposal was made possible ten years later. In 1997, Dismukes and coworkers reported the synthesis and characterization of the tetramanganese complex $Mn_4O_4(O_2P(Ph)_2)_6$ (Figure 1b).[14] This cubane core reacts with the hydrogen-atom donor, phenothiazine, forming the butterfly structure and releasing two water molecules.[15] It was found that UV light absorption by the cubane core converts two of the corner oxo ligands of the cubane into an O_2 molecule which is released only if one of the bridging chelate ligands is also released.[16] The evolution of the O_2 molecule from the cubane core was corroborated by the detection of $(^{18}O)_2$ from ^{18}O labeled cubane core, where the corner oxygen atoms were replaced with ^{18}O. In this complex dioxygen evolution results from intramolecular O-O bond coupling of the oxo bridges of the cubane. This result showed that the cubane-butterfly rearrangement hypothesis cannot be excluded on the basis of the limited structural data available at the present time.

As crystallographic data of better resolution for PS II becomes available, some of the proposed mechanisms will need to be modified. However, new inorganic model complexes will be synthesized, and it is likely that they will continue to provide structural and mechanistic insights into the water oxidation process conducted by PS II.

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