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Role of Arg (357) in Water Oxidation in Photosystem II

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Abstract: In the new structure of the PSII OEC, the guanidinium side-chain of CP43-Arg357, straddling the active face of the metal-oxo cluster. However there are a few proposal roles of Arg357. In this study three roles of Arg357 are proposed by studying model complexes: First, deprotonation of water molecules ligated to calcium and manganese (4). Second increasing positive charge on water ligated to manganese (4). Third, postulated hydrogen bonding interactions with the substrate water.

Key words: Arg (357), photosystem II, manganese complex, water oxidation complex

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INTRODUCTION

Photosystem II is a dimeric, multi-subunit, transmembrane protein complex, of molecular weight ca. 650 kDa, that is found in the thylakoid membrane of plant chloroplasts and in cyanobacteria. It catalyzes photosynthetic water oxidation and is therefore responsible for the presence of oxygen in the earth's atmosphere. PSII's primary role in the photosynthetic chain is to use energy obtained from sunlight to produce a charge separation, leading to reduction of the membrane quinone pool. This reducing power, augmented by further photonic energy in photosystem I, is used to assimilate carbon dioxide in the dark reactions of photosynthesis. The ultimate source of these low-potential electrons is water, which is oxidized to dioxygen in the oxygen-evolving complex of PSII according to the four-electron reaction given in Eq. (1):

$$2H_2O \rightarrow O_2 + 4H^+ + 4\,e^- \qquad (1)$$
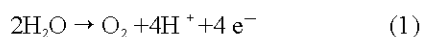
This reaction is responsible for nearly all of the dioxygen on our planet and conceptually is the reverse reaction of respiration where dioxygen is converted back to water. Plants use an expansive airay of photopigments in photosystem II, four manganese ions, calcium and chloride to carry out these reactions. The arginine sidechain is a well-known, important and versatile component of hydrogen-bonding networks in proteins. Cytochrome c oxidase, for instance, contains a hydrogen-bonded network incorporating two highly-conserved arginines which are important in optimizing both electron and proton transfer around the active site (Puustinen and Wikstrom, 1999; Qian, 2004). In the new structure of the PSII OEC, the guanidinium side-chain of CP43-Arg357, straddling the active face of the metal-oxo cluster, is positioned to hydrogen bond not only to the two putative substrate waters (ligated respectively to Ca^{2+} and Mn (4)), but also to the putative non-substrate ligands (probably water or hydroxide) of Mn (3) and Mn (4). In this study three roles of Arg357 are proposed by studying model complexes.

RESULTS AND DISCUSSION

In the recent 3.5 A° resolution XRD-deduced model depicted in Fig. 1, the authors (Ferreira et al., 2004) describe the electron density attributed to the Mn$_4$Ca cluster in its resting oxidation state as "capped tetrahedral" with four metal atoms in the large end and one in a connected small end. The latter density has been assigned to a single Mn based on comparing the anomalous scattering of X-rays that are preferentially absorbed by Mn. A series of difference Fourier omit maps accommodate a tetrahedral array of four metal ions (MN$_3$Ca) in the large end and one Mn in the small end. A Ca atom is located in one of the corners of the tetrahedron based upon anomalous diffraction data taken at the Ca absorption edge. The presence of Ca at ~3.4 A° to Mn is supported also by compelling evidence from three types of EXAFS measurements obtained at the Mn, Ca and Sr edges (Ferreira et al., 2004). The Mn-Mn intermetal
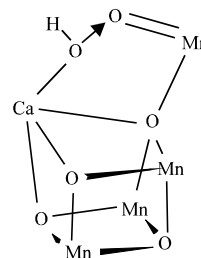

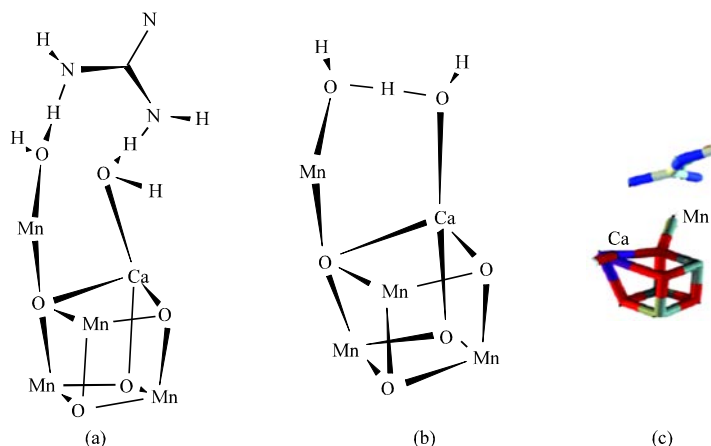Fig. 1: XRD model of the Water-Oxidizing Complex (WOC)

Fig. 2: Arginine's postulated hydrogen bonding interactions with the substrate waters are significant because these waters are prevented from hydrogen-bonding to one another (a, b). Real position of Arg (357) in photosystem II(c)

distances within the cube are not adequately resolved in the XRD data and have been set equal for simplicity, yielding a symmetrical trigonal prism of $CaMn_3$. The authors postulate four bridging oxides (not directly observable in their measurements) linking the tetrahedral array of $CaMn_3$ atoms, with one of these oxides (u_4-oxo) bridging to the fourth Mn atom external to the cube. The resulting $CaMn_4O_4$ cluster can be classified also in terms of the two types of oxide bridges (u_3-oxo)$_3$(u_4-oxo) that make up the core. Both Mn EXAFS and EPR methods had previously predicted eight possible Mn_4O_x core geometries, one of which has the same topology as the XRD model (Robblee *et al.*, 2002).

These methods also show that a lower symmetry cluster must exist in S_1 and S_2. This asymmetry could be accommodated if some of the postulated oxide bridges are hydroxide or water molecules. The Mn EXAFS derived inter-manganese distances are 2.7 A° and 3.3 A° and in S_1 and 3.4 A° for Mn-Ca The photosynthetic $CaMn_4O_4$ core is novel; No exact structural analogs have been synthesized. However, structurally homologous synthetic Mn_4O_4 core complexes are known that produce dioxygen from the corner oxos (Ruettinger *et al.*, 2002). The O = O bond formation is proposed to occur by a nucleophilic attack from a second-substrate water molecule ligated to Ca^{2+} (McEvoy *et al.*, 2004), where this metal ion may also act in part as a weak Lewis acid, possibly aided by the Mn (3) cluster and by a Cl^- ligand.

Role of Arg (357): Arg357 (Fig. 1), may provide hydrogen bonds for stabilizing intermediates prior to O = O bond formation. Indeed, mutation of Arg357 to a serine totally inhibited the evolution of oxygen and prevented photoautotrophic growth.

It is proposed (McEvoy *et al.*, 2004) that the nearby Arg357 side-chain is central in organizing the flow of protons from the OEC during the later part of the catalytic cycle. It is only with the publication of the recent crystal structure that this residue's proximity to the OEC has emerged: the terminal nitrogens of the Arg357 side-chain are each a little over 4A° from the active face of the cluster. it helps to organize the hydrogen-bonding network of metalligated waters and hydroxides around the OEC cluster.

Both of the substrate water ligands, bound respectively to Ca^{2+} and Mn (4), may plausibly be fitted into the structure within a few angstroms of the terminal nitrogens of the arginine side-chain, which points almost directly at these spaces in the structure. Arginine's postulated hydrogenbonding interactions with the substrate waters are significant because these waters are prevented from hydrogen-bonding to one another (McEvoy *et al.*, 2004). Such a bond would fix a hydrogen between the two oxygen atoms, preventing their close approach in the O-O bond-forming step (Fig. 2).

Other proposal role of Arg (357) in water oxidation in photosystem II is deprotonation of water molecules ligated to calcium and manganese (4), increasing oxidation number manganese atom(s) also help to deprotonate of water molecules ligated to calcium and manganese (4) (Fig. 3).

The importance of H-bonding in regulating metal ion reactivity is exemplified by metalloproteins. Several metalloproteins have active sites that contain either H-bond donors or acceptors that interact with external ligands that are covalently bonded to a metal center (Hom *et al.*, 1996; Springer *et al.*, 1994). Efforts to mimic this multimode binding in synthetic complexes have
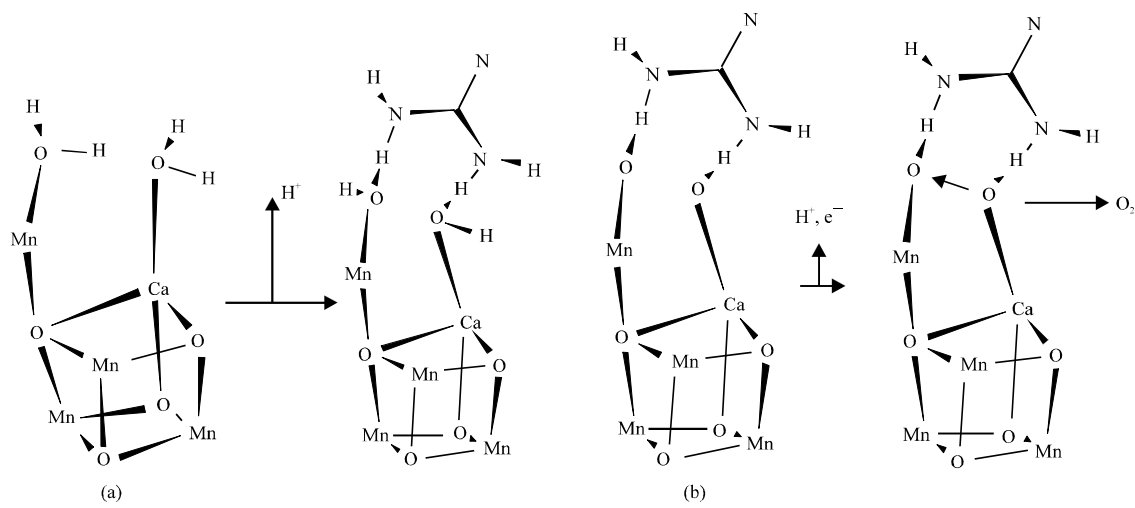
Fig. 3: a) one of the proposal role of Arg (357) in water oxidation in photosystem II is deprotonation of water molecules ligated to calcium and manganese (4) b) Increasing oxidation number manganese atom(s) help to deprotonate of water molecules ligated to calcium and manganese (4)
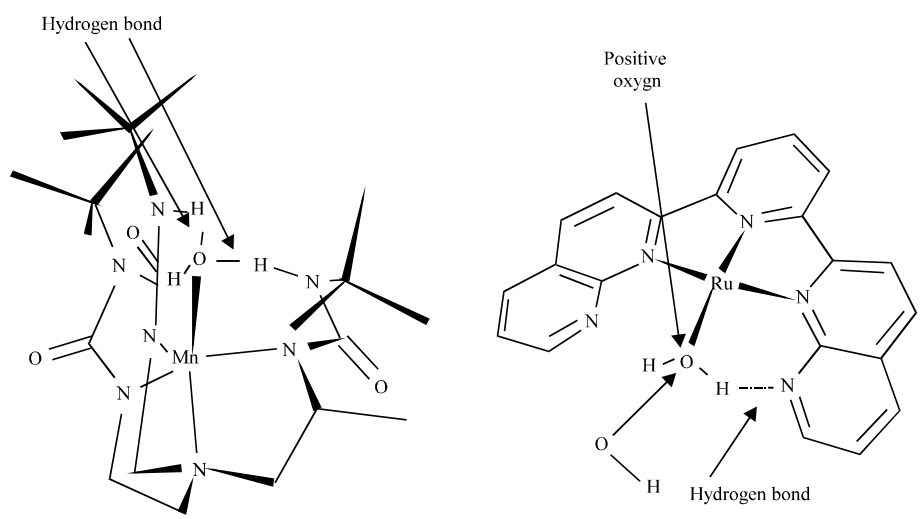

Fig. 4: a) H-bonding cavity around vacant coordination sites b) Ruifa Zong and Randolph P. Thummel's complex

involved both heme and non-heme systems. However, duplicating these desirable effects in synthetic systems has proven difficult, in part because of the inability of synthetic complexes to correctly position H-bonding groups near the metal center.

Cora *et al.* (2004) have recently developed a urea-based tripodal ligand that, when bonded to a metal ion, creates a H-bonding cavity around vacant coordination sites. This cavity is formed by the planar urea groups of each tripodal arm and is large enough to accommodate external ligands. Intramolecular H-bonding between the cavity N-H groups and the atom coordinating to the metal center is probable because thermodynamically favored sixmembered rings are formed

when these interactions occur (Fig. 4a). This example can show role of hydrogen bond in deprotoning of water ligated to manganese.

Third proposal role of Arg (357) in water oxidation in photosystem II is increasing positive charge on water ligated to manganese. In this condition, Mn = O is more electrophilic to react with the calcium-bound substrate water.

Zong and Thummel (2005) have reported a new family of Ru complexes for water oxidation. These complexes are unique in water oxidation. In these complexes the water molecule is H-bonded to an uncomplexed naphthyridine nitrogen on ligand (Fig. 4b). Ru-O is more electrophilic (than other Ru-O with out H-bond) to react with water.

ACKNOWLEDGMENTS

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