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Effectiveness of Optimizing Geometry for CaMn$_4$O$_5$ Cluster at 1.9 Å Resolved OEC and Proposal for Oxidation Mechanism from S$_0$ to S$_3$ States

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Based on the structure at 1.9 Å resolved OEC, which was published as PDBid=3ARC this year, the electronic structures of the CaMn$_4$O$_5$ cluster at S$_0$, S$_1$, and S$_2$ states are examined under the geometry optimization of the mixed-valence CaMn$_4$O$_5$ cluster and water molecules. It is shown that optimizing geometry purifies the spin structures of four manganese atoms, easily determining their oxidation states. It is also shown that one of two water molecules is a substrate for the oxidation to yield the oxygen molecule.

The oxygen-evolving complex (OEC) of photosystem II catalyzes four-electron oxidation to produce one oxygen molecule from two water molecules. The structure of OEC composed of a manganese cluster was observed by X-ray diffraction analyses, both the London[1] and Berlin structure[2] with resolution of 3.0–3.5 Å. This year, the structure at resolution of 1.9 Å was published by Umena and co-workers.[3] We call it the Osaka structure. The Osaka structure has a cubic-like geometry of CaMn$_3$O$_4$ similar to the London structure. The surrounding amino residues are also similar in both structures. However, the geometry of the Osaka structure is significantly different from that of the London one. The branching manganese atom in the London structure forms the geometry of Mn(μ-oxo)$_2$Mn with addition of a fifth oxygen atom in the Osaka structure, yielding a CaMn$_4$O$_5$ cluster rather than CaMn$_4$O$_4$. The amino acids, Asp170, Glu189, Glu333, Asp342, and Glu354 coordinate monodentately to manganese atoms and Ala344 coordinates bidentately to calcium ion in the London structure, while Glu333, Asp342, and Glu354 coordinate bidentately to two manganese atoms, Ala344 coordinates bidentately to manganese and calcium ions, and Asp170 coordinates monodentately to calcium ion in the Osaka structure. Thus, the CaMn$_4$O$_5$ cluster is stabilized by the bidentate amino acids. Although the manganese atoms of the London structure have room for six-coordination ligands, the empty space is not found for manganese atoms in the Osaka structure. Only one of four manganese atoms is coordinated by two water molecules. We can also find the hydrogen-bond network from the CaMn$_4$O$_5$ cluster to Tyr161 and Asp61 through water molecules. It can be then thought that the Osaka structure is superior to others and reliable. Based on this structure, theoretical examinations are expected to clarify the electronic structure and determine the oxidation mechanism.

For the Osaka structure, few theoretical studies are found among this year publications.[4–6] However, they are limited to relatively small cluster models; moreover, their geometries are fixed at the XRD structure.[3] The aim of this report is to show the first theoretical examination of a large model for the CaMn$_4$O$_5$ cluster where the surrounding amino acids and water molecules forming the hydrogen-bond network are included. The electronic structure of the high spin (HS) is first examined for the S$_0$ state of the Kok cycle and then purified by optimizing the geometry. The oxidation states of four manganese atoms at the S$_0$, S$_1$, and S$_2$ states in the low-spin (LS) state are determined, and the oxidation mechanism of water molecules is discussed.
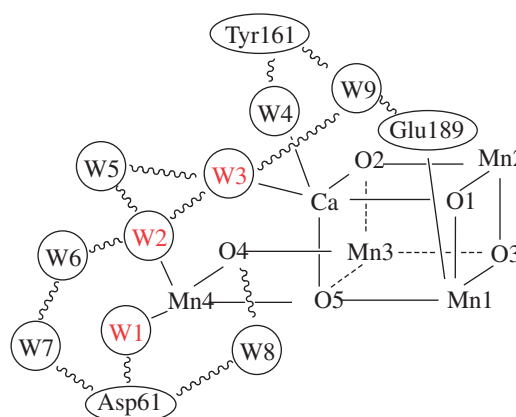

Figure 1. Schematic representation of the CaMn$_4$O$_5$ cluster and the surrounding water molecules. Waved lines mean hydrogen bonds.

The amino acids, Asp170, Glu189, His332, Glu333, His337, Asp342, Ala344, Glu354, and Arg357 surrounding the CaMn$_4$O$_5$ cluster and Gln165, Tyr161, His190, and Asp61 are included in the model. Nine water molecules extracted from the Osaka structure are added into the model, as shown in Figure 1. His190 and Tyr161 make the hydrogen-bonding network through the water molecule (W9) toward Glu189 that is monodentately coordinated to Mn1. This network might be thought to contribute the electron transfer from the CaMn$_4$O$_5$ cluster to Tyr161. Asp161 makes two hydrogen-bonding networks; one is Asp61–W1–Mn4 and another is Asp161–W7–W6–W2–Mn4. These paths might be related to path releasing a proton from W1 or W2. W2 directly coordinated to Mn4 makes hydrogen bond to W3 that is coordinated to Ca ion. We assume that two of three water molecules, W1, W2, and W3, will be substrates of four-electron oxidation. Based on the X-ray structure, hydrogen atoms were added to make the hydrogen bond among water molecules and CaMn$_4$O$_5$ cluster. Only added hydrogen atoms were optimized, and the optimized geometry is assigned as **1**, where the coordinates of heavy atoms are the same as those of the X-ray structure.

The HS state was estimated by a usual unrestricted method. The corresponding LS state with the broken symmetry (BS) was constructed by using the orbitals of the HS state. The B3LYP method[7] was employed to estimate the electronic structures,[7–10] since it provides reliable results for the system that includes the transition metals. The Wachters DZ[11] and 6-31G*[12] basis sets were employed for Mn atoms and for other atoms, respectively. The electronic structures of the HS and LS states were confirmed by Mulliken spin densities and natural orbital analyses.[13,14]

The electronic structure of the HS state **1**, where the coordinates of heavy atoms are the same as those of the X-ray structure, is summarized in Table 1. The spin angular momentum of 65.0998 is remarkably deviated from the pure value of 63.75 obtained from the spin multiplicity of 16. The spin contamination of 1.3498 indicates

Table 1. Relative energies (E_{rel}), spin contaminations ($\langle S^2 \rangle_{SC}$), and spin densities of high-spin (HS) and low-spin (LS) states at S_0 state

	1	2	3	4	5
State	HS	HS	LS	LS	LS
E_{rel}[a]	113.75	1.64	0.00	2.94	0.94
$\langle S^2 \rangle$	65.0998	63.9632	7.8756	7.9201	7.8731
$\langle S^2 \rangle_{SC}$	1.3498[b]	0.2132[b]	7.1256[c]	7.1701[c]	7.1231[c]
Spin densities					
Mn1	3.889	3.889	3.863	3.864	−3.889
Mn2	4.058	3.935	−3.886	3.912	3.858
Mn3	3.931	3.094	−3.004	−3.040	−3.006
Mn4	4.503	3.913	3.908	−3.905	3.904
O1	−0.218	−0.028	0.029	−0.020	−0.020
O2	−0.143	−0.067	0.066	−0.022	−0.011
O3	−0.048	0.075	−0.081	0.073	0.099
O4	−0.570	−0.009	−0.023	0.007	−0.047
O5	−0.637	−0.046	0.026	0.064	0.020
Ca	0.028	0.020	−0.002	0.012	−0.014

[a]In unit of kcal mol^{-1}. [b]$\langle S^2 \rangle_{SC} = \langle S^2 \rangle - 63.75$. [c]$\langle S^2 \rangle_{SC} = \langle S^2 \rangle - 0.75$.

that the one or two pairs of antiferromagnetic spin couplings exist in the CaMn$_4$O$_5$ cluster, consistent with negative spin densities of −0.218, −0.143, −0.570, and −0.637 e on O1, O2, O4, and O5, respectively. It is not possible from the spin densities of Mn atoms, 3.889, 4.058, 3.931, and 4.503 e, to determine the oxidation states of the Mn atoms. The up-spins on the oxo atoms could be delocalized over the Mn atoms.

The HS state **2** was obtained, after the geometries of W1–W9 and CaMn$_4$O$_5$ moiety was optimized by sixty cycles. As can be found in Table 1, the spin densities on the oxo atoms disappear and are essentially localized on the Mn atoms. The Mn3 atom has the spin density of 3.094 e close to three, while three other Mn atoms have the spin densities of 3.889, 3.935, and 3.913 e nearly equal to four. Accordingly, we can easily assign the oxidation states of four Mn atoms as (Mn1, Mn2, Mn3, Mn4) = Mn$_4$(III, III, IV, III). For problem whether the oxidation states of the S_0 state is Mn$_4$(III, III, III, IV) or Mn$_4$(II, III, IV, IV), the Osaka structure clearly gives the answer that the oxidation states of the S_0 state is Mn$_4$(III, III, III, IV) not Mn$_4$(II, III, IV, IV), in good agreement with our proposal from a small binuclear model.[13,14]

The geometry of **2** is shown in Figure 2, and the selected interatomic distances are summarized in Table 2. It can be seen from Figure 2 that W1 coordinated to Mn4 is hydrogen-bonded to Asp61 and W2 coordinated to Mn4 is also hydrogen-bonded to Asp61 through W6 and W7. W3 coordinated to Ca ion is hydrogen-bonded to W2 with the O–O distance of 2.928 Å. These networks of the hydrogen bonds are anticipated to aid the proton transfer from the CaMn$_4$O$_5$ cluster to Asp61. W9 makes the hydrogen bond to both Tyr161 and Glu189 with the O–O distances of 2.874 and 2.638 Å, respectively. The path of Mn1–Glu189–W9–Tyr161 will be a strong candidate for the electron transfer from the CaMn$_4$O$_5$ cluster.

From Figure 2, it can be seen that the cuboidal geometry of the CaMn$_3$O$_4$ moiety is maintained. From Table 2, the distances of Mn3–O4, Mn3–O5, Mn4–O4, and Mn4–O5 are remarkably reduced to 1.812–1.886 Å, while the distances of Mn1–Mn4 and Mn3–Mn4 are slightly reduced. The formed Mn3(III)–μ(O4,O5)–Mn4(IV) has very similar geometry to our small model.[13,14] This structure is probably originated by large movement of O5, though the Mn1–Mn4 distance remains almost intact. These changes might be due to the hydrogen-bond network of H$_2$Os and the surrounding amino acids.

When the BS solution of the LS state is constructed from the unrestricted solution of the HS state, the Mn3(IV) atom must be
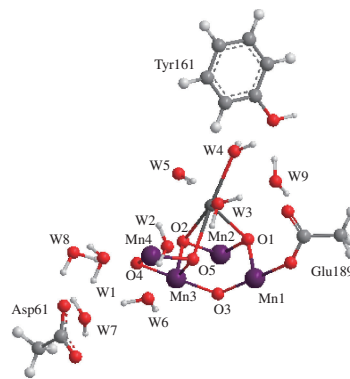
Figure 2. Geometry of the CaMn$_4$O$_5$ cluster and the surrounding water molecules in the HS state **2**.

Table 2. Selected interatomic distances (Å) of **1** and **2**

	Mn1–Mn4	Mn3–Mn4	Mn3–O4	Mn3–O5	Mn4–O4	Mn4–O5
1[a]	4.998	2.972	2.085	2.383	2.110	2.497
2	4.816	2.747	1.844	1.858	1.812	1.886

[a]Same as distances observed by the X-ray crystallographic analysis.

apparently chosen as down spins. The constructed **3**, **4**, and **5** have negative spin densities for Mn2, Mn4, and Mn1, respectively, maintaining the oxidation states of Mn$_4$(III, III, IV, III). The $\langle S^2 \rangle_{SC}$ values of three states are nearly equal to seven, consistent with seven pairs of antiferromagnetic spin couplings. The HS and LS states are isoenergetic, indicating that the LS states of the CaMn$_4$O$_5$ cluster are in strong correlation region.[4] The transitions among **3**, **4**, and **5** do not easily occur because of spin flipping.

For $S_0 \rightarrow S_1$ transition, one electron and one proton are released from the reaction system. It is reasonable to assume that one proton is released from W1, W2, and W3 shown in Figures 1 and 2. For W1 and W2, the proton transfers through the hydrogen-bond network from Mn4 to Asp61, while the proton from W3 transfers through the hydrogen-bond network proposed in the Osaka structure.[3] The state **6** shown in Table 3 corresponds to the singlet LS state where the proton is released from W2, the state **7** is release from W1 and the state **8** is release from W3. The left OH was optimized for **6**, **7**, and **8**. It is obvious from Table 3 that the left OHs of **6** and **7** are anions without spin densities. The spin densities on Mn1, Mn2, and Mn3 do not change from those in the LS state **3**, while the spin density on Mn4 changes from four to three, indicating that the only Mn4 is oxidized from Mn4(III) to Mn4(IV). This oxidation is not caused by direct release of one electron from the Mn4 atom. At the stage of light irradiation, Tyr161 is first one-electron oxidized, followed by the electron transfer from Mn1 to Tyr161 through the path of Mn1–Glu189–W9–Tyr161. Subsequently the up-spin on Mn4 transfers to occupy the d orbital on Mn1 through O5 by double exchange (spin delocalization). This shows that the oxidation state of the Mn atom coordinated by the OH$^-$ ion is Mn(IV) not Mn(III), consistent with our proposal obtained by small model.[13,14] The LS states **6** and **7** are isoenergetic and meaningfully lower in energy than the LS state **8**, showing the possibility that at the S_1 state, one proton is released from H$_2$O coordinated to the Mn4 atom not from H$_2$O on Ca^{2+} ion. Obviously, the oxidation states of Mn atoms at the S_1 state are Mn$_4$(III, III, IV, IV). It is also interesting that the geometry of the CaMn$_4$O$_5$ cluster at S_0 state gives clear oxidation states of Mn atoms of the S_1 state.

The LS state **8** where one proton is released from W3 gives significantly different electronic structure for the CaMn$_4$O$_5$ cluster.

Table 3. Relative energies (E_{rel}), spin contaminations ($\langle S^2 \rangle_{SC}$), and spin densities of high-spin (HS) and low-spin (LS) states at S_1 and S_2 states

|	**6**	**7**	**8**	**9**	**10**
State	LS	LS	LS	LS	LS
$E_{rel}{}^a$	2.19	0.00	12.05		
$\langle S^2 \rangle_{SC}$	7.1909	7.1579	7.9806	6.3990	6.2293
Spin densities					
Mn1	3.849	3.852	3.851	3.873	3.891
Mn2	−3.885	−3.885	−3.886	−3.426	−3.092
Mn3	−3.015	−3.036	−2.991	−3.014	−3.021
Mn4	3.004	2.889	3.813	2.961	3.003
O1	0.042	0.043	0.042	0.050	0.004
O2	0.010	0.016	0.013	0.214	0.093
O3	−0.050	−0.047	−0.048	0.054	0.019
O4	0.072	0.045	−0.032	0.047	−0.031
O5	0.020	0.098	0.002	0.106	0.061
Ca	0.001	−0.001	0.007	0.000	−0.001
OH(W1)		0.110			
OH(W2)	0.057			0.070	0.081
OH(W3)			−0.804		

^{a}In unit of kcal mol^{-1}.

The left OH is a neutral radical with negative spin density of $-0.804\,e$, definitely not OH$^-$ ion, with retaining the same oxidation states of Mn atoms as those of **3** at S_0 state. From the natural orbital analysis, the down-spin on OH is antiferromagnetically coupled with the up-spin on the Mn4 atom, indicating electron transfer from OH on Ca^{2+} ion to the Mn4 atom.

For $S_1 \rightarrow S_2$ transition, only one electron is released from the reaction center. The LS state **9** shown in Table 3 is a singlet state which has the same geometry as the LS state **6**. The spin densities of Mn1, Mn3, and Mn4 do not change for the $S_1 \rightarrow S_2$ transition, while the spin density of Mn2 atom remarkably changes from -3.885 to $-3.426\,e$. $\langle S^2 \rangle_{SC} = 6.3390$ indicates strong six antiferromagnetic spin couplings and weak one in the CaMn$_4$O$_5$ cluster. It is, then, expected that the electron is released from Mn2. The electronic structure after optimized geometry of **9** by sixty cycles is shown as **10** in Table 3. The spin density of the Mn2 atom is given as $-3.092\,e$, apparently indicating that the oxidation state of the Mn2 atom is Mn2(IV) with release of one electron from Mn2(III) at the S_1 state. The hydrogen-bonding network of Mn2–Ala344–W4–Tyr161 is formed at the S_2 state, although it is not shown in Figure 1. This network is expected to be a path that the electron is released.

Present computational results for the S_0–S_2 states have elucidated a possible mechanism for water-splitting reaction. Figure 3 shows our proposal of the oxidation mechanism of the H$_2$O molecule at 1.9 Å resolved CaMn$_4$O$_5$ cluster. Apparently the reaction point is the Mn4 atom with changing from Mn4(III)–OH$_2$ to Mn4(IV)–OH$^-$. For the $S_1 \rightarrow S_2$ transition, Mn2(III) is oxidized to Mn2(IV). At the S_3 state, the Mn4(IV)–O$^{\bullet-}$ bond is formed from the Mn4(IV)–OH$^-$ bond. We have previously proposed the oxidation mechanism based on the small model of Mn–(μO)$_2$–Mn and shown the formation of Mn(IV)–O$^{\bullet-}$ bond. The oxidation mechanism proposed from 1.9 Å resolved structure perfectly matches the previously proposed mechanism.

Based on the geometry of the 1.9 Å resolved CaMn$_4$O$_5$ cluster of OEC, under the geometry optimization of the CaMn$_4$O$_5$ cluster and water molecules, we clarified the electronic structures of the CaMn$_4$O$_5$ cluster at the S_0, S_1, and S_2 states and proposed the oxidation mechanism of water molecule from the S_0 to S_3 states. At the S_0 state, the 1.9 Å resolved structure gives the electronic structure where the spins are delocalized over μ-oxo atoms from the Mn atoms. However,
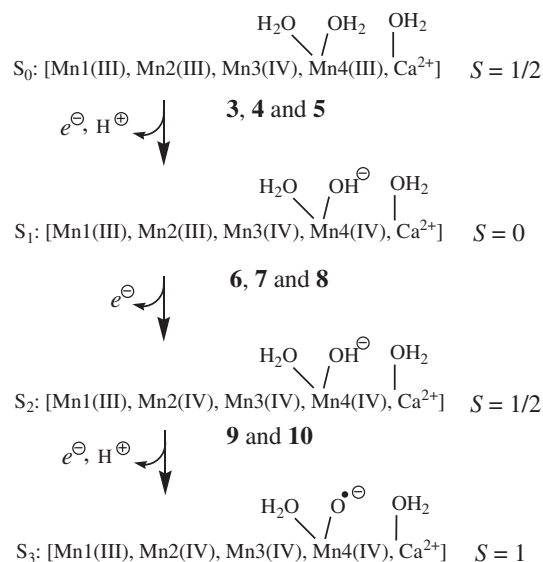
Figure 3. Proposal for oxidation mechanism of water molecule from S_0 to S_3 states in OEC.

the optimization of the CaMn$_4$O$_5$ cluster and water molecules sharply gives the distinguishable spin densities of four Mn atoms to easily assign the oxidation states of four Mn atoms. The optimization does not largely change the 1.9 Å resolved structure with retaining the cubic geometry. It is obviously necessary to optimize the CaMn$_4$O$_5$ cluster and water molecules at least in order to extract the clear spin structures. In analyzing the reaction with the QM/MM method, the CaMn$_4$O$_5$ cluster and surrounding water molecules must be included in the QM region. Although the 1.9 Å resolved structure is needed to slightly adjust the geometry at each state of the Kok cycle, it is highly reliable and superior to the London and Berlin structures.

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