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Theory of chemical bonds in metalloenzymes XVIII. Importance of mixed-valence configurations for Mn_5O_5, $CaMn_4O_5$ and $Ca_2Mn_3O_5$ clusters revealed by UB3LYP computations. A bio-inspired strategy for artificial photosynthesis

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ABSTRACT

Full geometry optimizations of mixed-valence (MV) $Mn(II)_RMn(II)_aMn(IV)_b$ $Mn(IV)_cMn(III)_d$ (**1**), $Ca(II)_R$-$Mn(III)_aMn(III)_bMn(IV)_cMn(III)_d$ (**2**) and $Ca(II)_RCa(II)_a$ $Mn(IV)_bMn(IV)_cMn(III)_d$ (**3**) clusters by UB3LYP have been performed to elucidate possible roles of substitutions of Mn(II) with Ca(II) in parent manganese oxides. The optimized Mn–Mn and Mn–Ca distances for **1**, **2** and **3** have been compared with the EXAFS and XRD experimental structures of the oxygen evolving complex (OEC) of photosystem II (PSII) to elucidate variations of geometrical structures and valence fluctuations by the substitutions. The optimized Mn–O distances of **1**, **2** and **3** have been examined to elucidate Jahn–Teller distortions induced by the Mn(III) ions. The computational results have illuminated possible origins of the elongated Mn–Mn distances and Mn–O distances in the high-resolution XRD structure by Umena et al. Implications of the computational results have been discussed in relation to chemical modifications of multi-nuclear manganese complexes with substitutions of Mn(II) with Ca(II) for rational design of artificial catalysts for water oxidation. A new bio-inspired strategy for artificial photosynthesis is also proposed based on a guiding principle, namely use of hole- and electron-doped strongly correlated electron systems (SCES) for oxidation and reduction reactions instead of conventional semiconductor materials.

1. Introduction

Photosynthesis is one of the most important chemical processes in our planet. Extensive experimental studies on the process have revealed that oxygenic photosynthesis involves several protein–cofactor complexes embedded in the photosynthetic thylakoid membranes of plants, green algae and cyanobacteria. Among these complexes, photosystem II (PSII) has a prominent role because the oxygen-evolving complex (OEC) in PSII catalyzes the oxidation of water as shown in Eq. (1) that is the prerequisite for all aerobic life [1–4].

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

The OEC in PSII contains an inorganic cluster consisted of four manganese ions and one calcium ion that are bridged by at least five oxygen atoms: the active site is therefore expressed with the $CaMn_4O_5$ cluster. Past decades, molecular structures of the cluster have been investigated by the extended X-ray absorption fine structure (EXAFS) [5–14], X-ray diffraction (XRD) [15–22] and ENDOR [23–31] experiments of PSII. Despite these efforts, it had not been possible to derive an atomic model of the $CaMn_4O_5$ cluster because the 2.9 Å resolution [21] is not sufficient for a distinction between short and long Mn–Mn distances (in the range of 2.7–3.3 Å), and μ-oxo and di-μ-oxo bridges could not be seen.

Recently Umena et al [32,33] have reported the high-resolution XRD structure of the OEC of PSII refined to the 1.9 Å resolution, which corresponds to the dark-stable S_1-state of the catalytic cycle (the Kok cycle [3,4] as shown in the Supporting Fig. S1.)

Hereafter their XRD structure is referred to as the SP8 XRD. From Fig. S1, the $CaMn_4O_5$ cluster in OEC of PSII has five different oxidation (S_0–S_4) states for water splitting reactions. We have performed UB3LYP calculations [34–41] to elucidate variation of the electronic structures and chemical bonding on these oxidation states of the $CaMn_4O_5$ cluster of OEC of PSII, starting from the SP8 XRD (S_1) structure [32]. The computational results for the species have revealed variations of orbital, charge and spin degrees of

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freedom, illuminating the labile nature [34] of its chemical bonds that is a characteristic of strongly correlated electron systems (SCES) such as Mn oxides insulators modified by hole doping. These characteristics have been summarized as 15 selection rules for theoretical modeling of water splitting reaction in the native OEC of PSII [41]. Moreover theoretical computations [42,43] of the $CaMn_4O_5$ cluster and an artificial Ru–semiquinone catalyst (so-called Tanaka catalyst) for water oxidation have provided a common guiding principle, hole-doped Mott insulator, that is applicable for molecular design of artificial catalysts [44,45] for water oxidation.

Past decades a number of manganese oxides complexes [46–55] have been synthesized and their molecular structures have been determined by the EXAFS and XRD techniques [4–22]. Magnetic measurements and related spectroscopic methods [23–31] have also been applied for elucidation of electronic and spin structures of these species that are origins of single molecular magnetism and other interesting magnetic behaviors. Thus, a number of single molecular magnets and single chain magnets have been reported and characterized in past decades [46–55]. On the other hand, chemical reactivity of these manganese oxide clusters have not been investigated thoroughly in relation to water oxidation, though Christou and co-workers [56,57] have performed the pioneering work toward this direction. Recently several manganese oxides such as binuclear Mn_2 and tetranuclear Mn_4 oxide complexes have been investigated as active catalysts for water oxidation [58–69]. However, stability of the Dismukes Mn_4O_4 complex [62] was found to be not sufficient enough for catalytic water-oxidation processes [70], indicating the necessity of developments of appropriate ligands and search of other robust Mn complexes. In fact, renewed interest has been coming for modifications of single Mn molecular magnets and chain magnets [46–57] for developments of water oxidation catalysts. However, little is known for modification procedures of these magnetic materials for the purpose. As a theoretical effort toward the goal, we here perform UB3LYP computations of parent Mn_5O_5 (**1**) and Ca-substituted $CaMn_4O_5$ (**2**) and $Ca_2Mn_3O_5$ (**3**) clusters that are iso-structural species for OEC of PSII. The full geometry optimizations of **1**, **2** and **3** have been performed to elucidate the optimized Mn–Mn, Ca–Mn and Mn–O distances. Implications of the computational results have been discussed in relation to concepts of theoretical modeling, a guiding principle for design of water-oxidation catalysts and a new bio-inspired strategy for artificial photosynthesis.

2. Computational models for the catalytic site in OEC of PSII

The $CaMn_4O_5(H_2O)_4$ core in OEC of PSII revealed by the SP8 XRD structure [32] consists of a cuboidal cluster $CaMn_3O_4$ with an extra Mn ion linked by a μ-oxo and μ-X (X = hydrooxo, or oxo) bridges as shown in Fig. 1. The magnetic manganese cluster is essentially regarded as an inorganic cubane structure found in nature as inorganic crystals of ranciete or hollandite $Mn(IV)_4Ca(II)O_9(H_2O)_3$ where manganese ions have the uniform valence Mn(IV) structure [71]. It is confined with protein environments in OEC of PSII. The protein ligands lining in the cluster-binding site, mainly glutamates and asparates [32,33], have carbonate anions that coordinate hard Mn ions. For surrounding proteins and ligands, we take all amino acid residues within the first coordination sphere of the SP8 XRD structure [32–35]. But in order to reduce the computational complexity, Ala344, Asp342, Asp170, Glu333, Glu189, Glu354 residues were modeled by acetate anions, and His332 residue by an imidazole that coordinates to a manganese ion (Mn_d). Each Mn ion in the core has a distorted octahedral ligand field [37,41]. Thus we have constructed simple model clusters [34–41] of the catalytic site for water oxidation in OEC of PSII in Fig. 1.

The $Mn_5O_5(H_2O)_4$ cluster (**1**) in Fig. 1 may be regarded as a parent cluster for the $CaMn_4O_5(H_2O)_4$ cluster (**2**) where one of five Mn ions in the cubane structure is replaced with a Ca(II) ion. The outside Mn ion linked with the cubane skeleton $CaMn_3$ of **2** is replaced with one-more Ca(II) ion, affording a model cluster $Ca_2Mn_3O_5(H_2O)_4$ cluster (**3**). The valence state of the Ca ion in **2** and **3** remains divalent throughout the photo-induced oxidation processes (Kok cycle in Fig. S1), as has been elucidated by UB3LYP calculations [34–41] of **2**. Deprotonations of water molecules in **2** are important processes for the O–O bond formation. Here we assume no change of water molecules with replacement(s) of Mn ion with Ca ion except for the $O_{(5)}$ site where water molecule is deprotonated, affording hydroxide anion (the $O_{(5)}$ site = $HO_{(5)}$: notation (**a**) in the S_0 site. One more deprotonation of the $HO_{(5)}$ site affords the oxygen dianion, the $O_{(5)}$ site = $O_{(5)}$; notation (**b**) as illustrated in Fig. 1.)

Our previous theoretical investigations [38,40,41] have revealed three possible geometrical structures for **2**: right-elongated (R; Mn_a–X···Mn_d), central (C; Mn_a–X–Mn_d) and left-elongated (Mn_a···X–Mn_d) ones. If the potential surface has a single-valley structure, the central (C) structure may become the true minimum as illustrated in Fig. 1B: the R- and L-type trial structures provide the same converged structure (C). On the other hand, the R-and L-type structures may become true local minima in the case of the double-well potential in Fig. 1C. Here we perform full geometry optimizations of several intermediates in Fig. 1 in order to elucidate geometrical variations with replacement of Mn ion with Ca(II) ion. The total high-spin (HS) (↑↑↑↑) UB3LYP solution [72,73] has been employed for the purpose because the optimized geometrical parameters are not so dependent on the spin configurations [38]. The basis sets used are, respectively, the LANL2DZ [74,75] for Mn and Ca atoms, and 6-31G(d) for C, H, O and N atoms [76]. Table 1 summarizes the optimized Mn–Mn, Ca–Mn and Mn–O distances obtained by UB3LYP calculations of **1**, **2** and **3**. Table 2 summarizes spin populations on heavy atoms obtained by the same procedure.

3. Computational results

3.1. Mixed-valence configurations of *1*, *2* and *3* in the S_0 state

First of all, we examine the clusters **1**, **2** and **3** in the S_0 (the $O_{(5)}$ site = $HO_{(5)}$ = **a**) state. Total positive charge of the parent uniform-valence $Mn(III)_5$ cluster (**0a**) is 3 × 5 = 15. However, the optimized geometrical structure of **1a**(S_0) has provided non-uniform spin populations, 4.81, 4.82, 2.75, 2.98 and 3.84 for Mn_R, Mn_a, Mn_b, Mn_c and Mn_d, respectively, as shown in Table 2. The spin populations clearly indicated that the mixed-valence (MV) state of **1a**(S_0) is qualitatively assigned as $Mn(II)_RMn(II)_a$ $Mn(IV)_b$ $Mn(IV)_c$-$Mn(III)_d$. Total sum (Q_M) of the calculated spin densities on the Mn sites are 19.2(0.5) where the sum of spin densities on the oxygen atoms is given in parentheses. Therefore the total spin density (19.7) is approximately 20 (=5 + 5 + 3 + 3 + 4). This means that the spin polarization of the Mn–O bonds of **1a**(S_0) is negligible. The spin density populations (Q_M = 14.4) for **2a**(S_0) are −0.01(0.00), 4.82(3.90), 2.77(3.84), 2.97(2.98) and 3.82(3.81) for Mn_R, Mn_a, Mn_b, Mn_c and Mn_d, respectively, indicating a mixed-valence (MV) configuration, $Ca(II)_RMn(II)_aMn(IV)_bMn(IV)_c$ $Mn(III)_d$: the spin populations for the other geometrical isomer **2a**′(S_0) are given in parentheses. Judging from the spin populations, the MV configuration of **2a**′(S_0) is assigned to be $Ca(II)_RMn(III)_aMn(III)_b$-$Mn(IV)_cMn(III)_d$ where Q_M = 14.5. As shown previously, **2a**′(S_0) is more stable than **2a**(S_0) in the S_0 state [38]. Thus the local MV-pair, $Mn(II)_aMn(IV)_b$, in **2a**(S_0) is converted into a uniform valence pair, $Mn(III)_aMn(III)_b$, in **2a**′(S_0) by replacing $Mn(II)_R$ with $Ca(II)_R$. Further replacement of $Mn(II)_a$ with Ca(II) affords the iso-structural isomer **3a**(S_0) that exhibits the spin populations, 0.00, 0.01, 2.69,