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Regular Article

DFT Study on the Mechanism of Water Oxidation Catalyzed by a Mononuclear Copper Complex

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Abstract: This work employed DFT calculations to elucidate the mechanism of water oxidation reaction catalyzed by a mononuclear pyridine-based copper complex, which was reported to be a homogeneous water oxidation catalyst in a pH=11.84 buffer solution. The coordination of one water molecule with the Cu^{II} center leads to the generation of the Cu^{II}-OH_2 (**1-H_2O**). The active species (Cu^{IV}=O, **3**) is generated after two subsequent proton-coupled electron transfer processes from **1-H_2O**. **3** triggers the O-O bond formation via water nucleophilic attack mechanism. The triplet O_2 can be released after following two oxidation processes. The formation of the O-O bond is the rate-determining step for the catalytic cycle associated with a total barrier of 19.3 kcal/mol.

Key words: water oxidation, density functional calculations; reaction mechanism, copper complex.

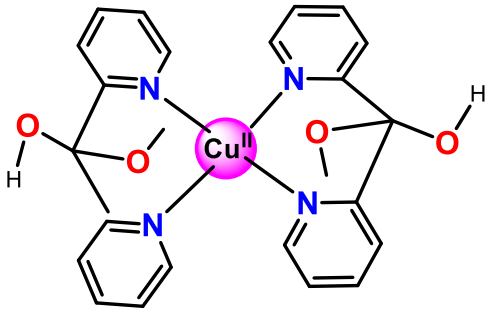
1. Introduction

Solar energy is an ideal source of energy. However, obtaining and utilizing solar energy is a challenge. Inspired by nature, a promising approach is to construct artificial photosynthetic systems [1]. The water oxidation reacti on, consisting of the releasing of four protons and four electrons as well as the O-O bond formation process (equation **1**), lies at the heart of this system. The oxidation potential of the water oxidation reaction is 1.23 V at pH 0. This oxidation reaction is both thermodynamically and kinetically very difficult. It is necessary to develop efficient water oxidation catalysts (WOCs).

$$2H_2O\,(aq) \longrightarrow O_2(gas) + 4e^- + 4H^+(aq) \quad (E_0 = 1.23\ V - 0.059\ pH) \quad (1)$$

Homogeneous WOCs have the advantages of mechanism study and tunable ligand design [2]. The development of WOCs dates back to the design of the "blue dimer" in 1982 [3]. Since then, some Ru and Ir-based WOCs have been reported [4-7]. However, non-noble and earth-abundant metal-based complexes [8], such as Fe [9,10], Co, [11-14] Ni [15], Cu [16], V [17], Mn [18,19] based complexes, have

been drawing more and more attention in terms of the application in industry. Computational chemistry is useful for detailed mechanism research, which is beneficial for the design of more efficient WOCs. Great progress has been made in the computational community for the mechanism study of water oxidation reaction, [20-28] including the theoretical mechanism study of Cu-based WOCs [29-33].



Scheme 1. Schematic structure of the copper complex.

In 2021, a copper complex (**Scheme 1**) was reported to be a water oxidation catalyst in sodium acetate buffer solution at the pH of 11.84 with a reported TOF of 9.20 s^{-1}.[34] The complex adopts a square-planar geometry, and four pyridyl nitrogen atoms coordinate with the Cu^{II} center. Two oxygens from the OCH_3 groups occupy axial positions above and below the plane but do not directly coordinate with the copper center. The linear relationship between the concertation of the catalyst and the catalytic current peaks was disclosed, which indicates a first-order reaction.[34] The reaction mechanism remains unclear. In the present work, DFT calculations were used to investigate the reaction mechanism of water oxidation catalyzed by the copper complex. The oxidation process, O-O bond formation and the release of the O_2 were calculated.

2. Theoretical method

The Gaussian 16 program was used to do all calculations [35]. B3LYP-D3 functional was employed to do geometrical optimizations [36,37]. 6-31G(d,p) basis set was used to describe non-mental elements, while SDD pseudopotential was employed for Cu element [38]. The analytic frequency calculations were carried out to confirm the nature of all structures at the same level. Single-point calculations with the SMD implicit solvation model were carried out to obtain the final energy, where 6-311+G(2df,2p) was used to describe all non-mental elements [39].

A reference potential of 1.5 V (vs. SHE) was used to construct the Gibbs energy diagram since the controlled potential electrolysis experiment was tested at the potential of 1.5 V [34]. The absolute potential of 4.281 V of SHE was token as a reference [40]. The pK_a values of various intermediates were calculated to study the proton-releasing process. The proton solvation energy of -264.0 kcal/mol in water from the experimental study was used. The pK_a values were used to determine whether the oxidation process involved proton release. For an oxidation process, the high oxidation intermediate prefers to be deprotonated if its pK_a is lower than the pH of the reaction solution. Under such conditions, the oxidation process is coupled with the release of a proton. The solvation energy (-6.3 kcal/mol) of water in aqueous was used [41]. A concentration correction value of 1.9 kcal/mol (RTln24.5) at 298.15K was applied to all species to account for the standard state changes arising from the use of the SMD solvation model. This correction originates from the calculation of the solvation energy in aqueous solution that defined as the free energy of transfer of the solute from the gas phase (24.5 L mol^{-1}) to the aqueous phase (1 mol L^{-1}). Meanwhile, water has a concentration correction term of 4.3 kcal/mol. The SCF convergence was set to 10^{-8}. The computational methodology employed in the present work has been validated for mechanistic investigations of water oxidation reactions.

3. Results and discussion

3.1 The oxidation process

The DFT calculations commenced from the geometry optimization of the Cu catalyst (**1**). The optimized structure is displayed in **Figure 1**. **1** is a doublet state. The copper center is in a +2 oxidation state. Four nitrogen atoms from pyridines coordinate with the Cu^{II} center at a distance of 2.04 Å, which is consistent with the reported value of 2.007/2.000 Å [34]. Two oxygen atoms of the two methanol groups have distances of 2.51 Å away from the metal center. The spin density on Cu is 0.62. To initiate the water oxidation reaction, at least one water molecule must coordinate with the Cu^{II} center. The coordination of one water with the Cu^{II} leads to the generation of **1-H_2O** (**Figure 1**.) This step was calculated to be endergonic by 7.0 kcal/mol (**Figure 2**). The coordination of the water with the copper center resulted in the release of one N atom from the metal coordination sphere. The Cu-O1 distance was calculated to be 2.00 Å in **1-H_2O**. The second water combined with the metal in **1-H_2O** is thermodynamically unfavorable, as the coordination of the second water to **1-H_2O** is endergonic by 11.3 kcal/mol (**Figure S1**). In addition, the one-electron oxidation of **1** has a calculated redox potential of 2.2 V, suggesting the oxidation of **1** is unlikely (**Figure S1**).

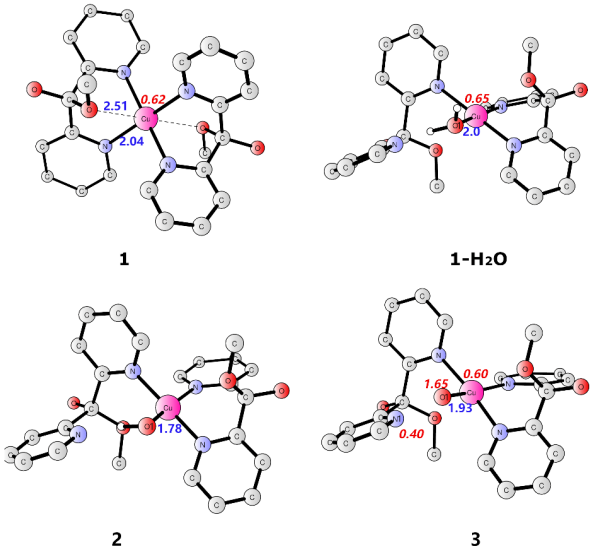


Figure 1. Optimized structure of **1** (doublet), **1-H_2O**(doublet), **2**(singlet) and **3**(quartet). Spin densities on selected atoms are shown in red in italics. Distances are shown in blue in Å. Unimportant H atoms are not shown.

The pK_a of $\mathbf{2_{pt}}$ (the protonation state of **2**, Cu^{III}-OH_2, Figure **S1**) was calculated to be 3.3, suggesting that the deprotonation state domains in the pH=11.84 solution. Therefore, the first oxidation of **1-H_2O** is associated with a proton release from the water ligand. This is