



Molecular modeling as a tool for the design of ligands in artificial photosynthesis studies

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Abstract

The potential of ruthenium complexes as water oxidation catalysts is already known, thereby the necessity for compounds of the first transition series emerges, that are more affordable due to its higher abundance. The biggest challenge is the lability of these species when compared to the analogs of other series. In this way, the project aims to contribute in the research of alternative chelating ligands from a theoretical perspective, in order to reduce the number of experimental studies necessary to achieve our goal.

Key words:

Water oxidation catalysis, artificial photosynthesis, macrocyclic ligands.

Introduction

The energy demands are usually supplied by fossil fuels. The artificial photosynthesis emerges as a promising alternative, combining H_2 and O_2 in a clean and sustainable fuel cell. The reaction limitation is the water oxidation step, a highly endergonic process with a large potential barrier. Thus, this reaction becomes the main point of studies by inorganic chemists, as well as the development of its catalysts.

In nature, the oxidation of two water molecules is coupled to a flux of electrons induced by the photon absorption within the chloroplasts. The process occurs at the photosystem II (PS2) with a transfer of four electrons to the oxygen-evolving complex, which the active site is a cluster of manganese and calcium.

Results and Discussion

The study was performed with three distinct ligands and iron centers. The calculations varied the oxidation number, the multiplicity of the complex, and the deprotonation in the water molecule. The DFT (Density Functional Theory) results were utilized to the achievement of pKa values and oxidation potentials by a method of

thermodynamic cycles. Briefly, the values are obtained interpolating data in a calibration curve, composed by species with known pKa values¹.

Figure 1 presents the theoretical Pourbaix diagram along with the structure of the complex in the lowest oxidation state. It is possible to verify that the higher the oxidation state, the lower the pKa, as expected by similar experimental studies, indicating that our theoretical strategy succeeded. The potential values for consecutive oxidations increase too.

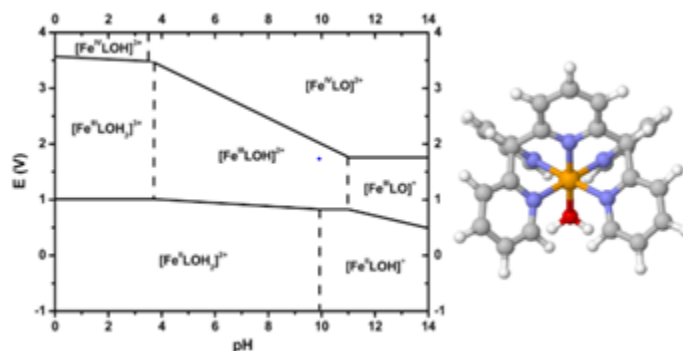


Figure 1. Pourbaix diagram next to the initial optimized structure $[Fe^{II}(\text{ligand1})(OH_2)]^{2+}$.

It is worth noting that the Fe(IV) oxidation state is only stabilized by the hydroxo (-OH) and

oxo (=O) ligands, with a larger range by the oxo. This species is fundamental in the catalytic cycle (analogously to ruthenium complexes) when it is considered the four major steps of WOC (water oxidation catalysis): water oxidative activation, O-O bond formation, oxidative activation of peroxide intermediates and O₂ evolution. At pH 7, the applied potential required for the formation of this species is approximately 2.75 V (vs. Ag/AgCl).

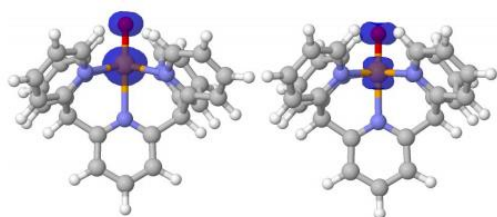


Figure 2. Spin density representation of [Fe^{III}(ligand1)O]⁺ and [Fe^{IV}(ligand1)O]²⁺.

From **Figure 2**, it is clear that the spin density is distributed among the two atoms, indicating a covalent bond between the iron center and the oxygen atom in this high oxidation state. In the first case, the complex presents a high spin with approximately 4 unpaired electrons on iron and 1 on oxygen (from Mulliken population analysis, 4.06 and 0.78, respectively). Otherwise, after oxidation, the complex features a low spin with 1 electron on iron and 1 on oxygen (from Mulliken population analysis, 1.17 and 0.89, respectively). The reactivity of the complex must increase with the number of unpaired electrons

on oxygen. Looking at the deprotonation states, the behavior is low spin in -OH₂ species and high spin on -OH and =O, it influences the strength of the covalent bond, evidenced by the bond lengths of 1.92 Å, 1.81 Å and 1.71 Å respectively for the Fe^{III} oxidation state.

Conclusions

From the Pourbaix diagrams it was possible to map the existing species in a pH range from 0 to 14. The spin population analysis is an important parameter since it can indicate the mechanism to be followed². Future studies intend to calculate the energies associated with the ligands deprotonations, making possible a deeper electronic state analysis.

Acknowledgement

The authors acknowledge CNPq for the financial support and CENAPAD-SP for computational time.

¹ Guerra, R. B.; Huamaní, L. S. C.; Tenorio, J. C.; Guimarães, W. M.; Bonacin, J. A.; Barboza Formiga, A. L. Analysis of Solvent-Accessible Voids and Proton-Coupled Electron Transfer of 2,6-Bis-(1H-Imidazol-2-Yl)Pyridine and Its Hydro-chloride. *Acta Cryst C* 2019, 75 (10), 1359–1371.

² Shaffer, D. W.; Xie, Y.; Concepcion, J. J. O–O Bond Formation in Ruthenium-Catalyzed Water Oxidation: Single-Site Nucleophilic Attack vs. O–O Radical Coupling. *Chem. Soc. Rev.* 2017, 46 (20), 6170–6193.