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Computational study of the Copper-catalyzed water oxidation catalytic cycle using macrocyclic ligands: unraveling the role of HPO_4^{2-}

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Highlights

- The catalytic cycle of copper-catalyzed water oxidation with a macrocyclic N-donor ligand was computationally investigated based on previous experimental studies
- The reaction intermediates and transition states were computed using quantum chemical calculations, in which the energy profile of the catalytic cycle reproduces well the experimental turnover overall frequency (TOF).
- Computational analysis reveals that HPO_4^{2-} facilitates O–O bond formation.

Resumo/Abstract

The oxidation of water is a key reaction in both natural and artificial photosynthesis mechanisms. This process is thermodynamically challenging, and therefore, the development of efficient water oxidation catalysts (WOCs) is crucial for achieving industrial-scale applications [1]. Specifically, Yu *et al.* [2] reported an efficient electrocatalytic water oxidation using a Cu-based catalyst with the 1,4,8,11-Tetramethylcyclam (TMC) ligand. A TOF of 30 s^{-1} was achieved under neutral pH conditions (0.1 M phosphate buffer), demonstrating excellent electrocatalytic water oxidation activity. However, the catalytic cycle remains poorly understood. We computationally investigated the electrochemical transformations, including the role of HPO_4^{2-} , possible intermediates and transition states of the water oxidation mechanism with Cu-TMC complexes. Specifically, when the O–O bond formation transition state by a single water molecule was calculated (Fig. 1a), the barrier was found to be 40 kcal/mol. However, in the presence of HPO_4^{2-} as a proton acceptor with H_2O (Fig. 1b) lowered this barrier to 17 kcal/mol, highlighting the important role of phosphate in enhancing the catalytic efficiency of water oxidation.

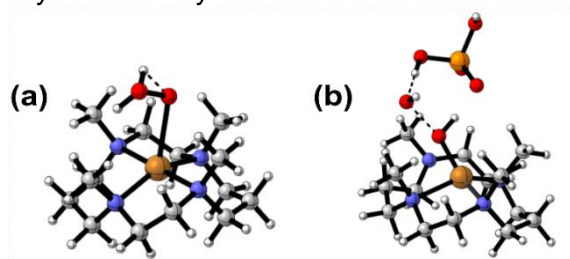


Figura 1: O-O bond formation transition states of the catalyst with: (a) a single water molecule; (b) a phosphate and a water molecule

All calculations were carried out using the B3LYP-D3 density functional, associated with the LANL2TZ(f) and def2-SVP basis sets for copper and lighter atoms, respectively. The solvent effects were considered implicitly using the SMD model.

[1] Marenich *et al.* *Angewandte Communications*, 51, 12810-12814. **2012**; [2] Yu *et al.* *Chemical Communications*. 52, 10377-10380. **2016**.

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