

MECHANISM STUDY OF 2,2'-BIPIRIDINE-6,6-DICARBOXYLATE RU CATALYSTS A WATER OXIDATION CATALYST

Jesús A. Luque-Urrutia, Miquel Solà,* and Albert Poater*

Adresses list: Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Campus Montilivi, 17003 Girona, Catalonia, Spain
e-mail: jesusantonio.luque@udg.edu

In situ production of H₂ has been a hot topic^[1] for some time now and catalysts that are able to perform this task are currently being researched,^[2] such as our Ru catalyst. The full mechanism of 2,2'-bipyridine-6,6'-dicarboxylate Ru catalyst for water oxidation catalysis (WOC)^[3] using DFT calculations. The rate determining step is found at the dimer formation while the bond cleavage for the O₂ liberation process is barrier-less. Water appears not to be involved in the cleavage process. Taking into account the recent results by Concepcion's group^[4] related to the same catalyst, where the Ru-O-Ru metallic core was proposed to be involved instead of the typical Ru-O-O-Ru one, coming from the direct interaction between the oxygens of two Ru=O moieties we report the mechanism including the possible open carboxylate and closed carboxylate structures (see Figure 1). The computational results confirm that the most common path (closed carboxylate) is strongly preferred, and consequently, the formation of such Ru-O-Ru moiety is impeded.

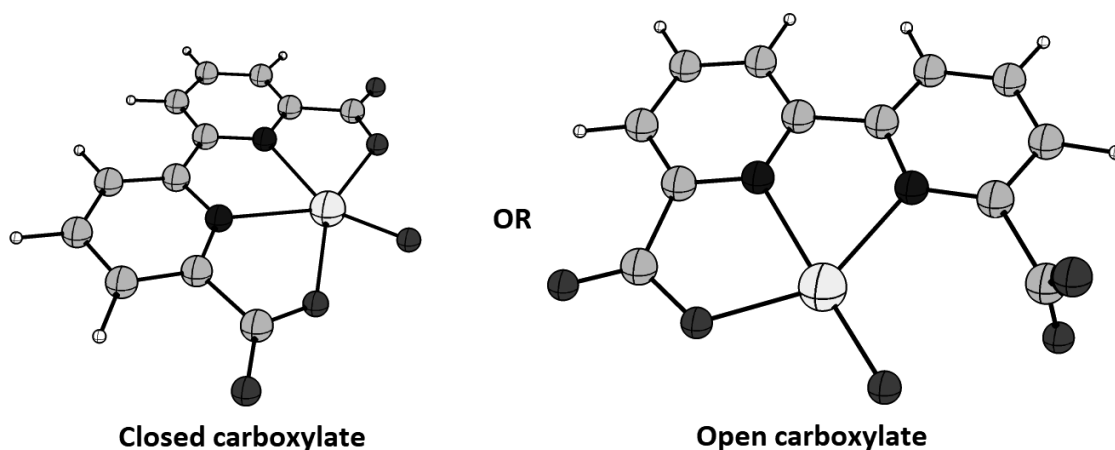


Figure 1. Closed and open carboxylate structures of our mechanism. Axial ligands omitted for clarity.

- 1) Morris, J.; Radu, M. *Int. J. Hydrog. Energy* **2010**, *35*, 7021-7023.
- 2) Kang, R.; Chen, K.; Yao, J.; Shaik, S.; Chen, H. *Inorg. Chem.* **2014**, *53*, 7130-7136.
- 3) Duan, L.; Bozoglian, F.; Mandal, S.; Stewart, B.; Privalov, T.; Llobet, A.; Sun, L. *Nat. Chem.* **2012**, *4*, 418-423.
- 4) Concepcion, J. J.; Zhong, D. K.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. *Chem. Commun.* **2015**, *51*, 4105-4108.