

# ISOLATION AND CHARACTERIZATION OF AN ELUSIVE $\eta^2$ -[Ru<sup>IV</sup>-OO]<sup>2+</sup> INTERMEDIATE AFTER THE O-O BOND FORMATION IN RU CATALYSED WO: THE MISSING LINK

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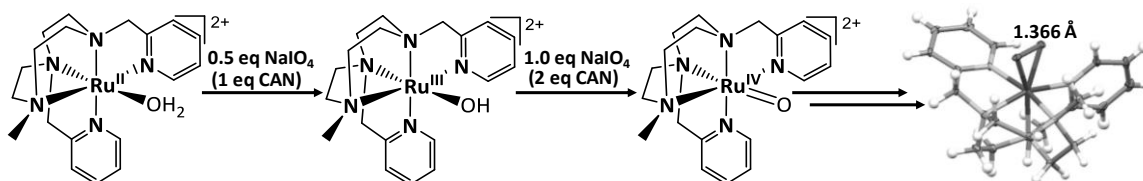
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The application of artificial photosynthesis to store solar energy into chemical bonds is one of the major challenges of our society.<sup>[1]</sup> Since water is abundant and its oxidation produces O<sub>2</sub> as by-product, it is the most attractive source of electrons to be used in large scale. However, WO has been identified as the bottleneck, because it requires very high redox potentials only bearable by few species. Therefore, to design more efficient and robust WOC it is necessary to understand the intermediates involved in either the activation of water and the O-O bond formation.



**Figure 1.** Generation of the intermediates involved in the WO catalytic cycle and the peroxo species formed after the O-O.

We recently reported a catalytic and mechanistic study of a Ru-WOC based on an aminopyridyl ligand,<sup>[2]</sup> which pointed towards a high valent [Ru<sup>V</sup>=O]<sup>3+</sup> as the active species responsible for the O-O bond formation. DFT studies showed that after the O-O bond formation a [Ru<sup>III</sup>-OOH]<sup>2+</sup> is formed, yielding a closed shell  $\eta^2$ -[Ru<sup>IV</sup>-OO]<sup>2+</sup> intermediate after a PCET, which would finally release O<sub>2</sub>. There has been an extended discussion about the electronic and coordination nature of such postulated species.<sup>[3]</sup> Herein we report the isolation and characterization of this elusive  $\eta^2$ -[Ru<sup>IV</sup>-OO]<sup>2+</sup> intermediate under catalytic conditions: the missing link after the O-O formation that has not been reported so far. Characterization of the isolated  $\eta^2$ -[Ru<sup>IV</sup>-OO]<sup>2+</sup> intermediate by means of X-ray, EXAFS, NMR, IR, HRMS and DFT shows a closed-shell heptacoordinated structure with a side-on coordination of the peroxo moiety.

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- 2) C. Casadevall, Z. Codolà, M. Costas, J. Lloret-Fillol, *Chem. Eur. J.* **2016**, 22, 10111.
- 3) J. J. Concepcion *et. al.*, *J. Am. Chem. Soc.* **2010**, 132, 1545; E. Garand *et. al.*, *Angew. Chem. Int. Ed.* **2016**, 55, 4079.