Iron – Cerium adducts as intermediates in the water oxidation reaction

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Water oxidation (WO) reaction is one of the biggest scientific and technological challenges towards realization of artificial photosynthesis.[1,2] Since water is abundant and its oxidation produces O_2 as by product, light-driven oxidation of water is arguably the most attractive source of electrons to be used in multi-ton scale. Therefore, WO may be ideally coupled with very important reduction reactions such as generation of H_2 or the reduction of CO_2.

Scientists have been trying to imitate and understand Nature creating biomimetic Mn-based water oxidation catalysts[3] and, in the last years, other first row transition metals (Co,[4] Fe[5]) have been also found catalytically active in water oxidation. However, understanding the details of the WO mechanism is under debate.

Our group recently reported the first example of a well-characterized inner-sphere complex to be formed in cerium(IV)-mediated water oxidation, based on the non-haem iron complex α-[$Fe^{II}(CF_3SO_3)_2$(mcp)] (mcp = (N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-cis-diaminocyclohexane).[6] The identified Fe^{IV}-O-Ce^{IV} intermediate represents an iron-based analog of the oxygen evolving complex in photosystem II, in which the proposed Lewis acid role of cerium may be benificial for the O-O bond formation event. To unravel the key aspects of the iron catalyzed oxidation of water, we have carried a DFT study to elucidate the structure and WO reactivity of this unprecedented Fe^{IV}-O-Ce^{IV} adduct.[7] This computational study explores the involvement of cerium in the WO mechanism, opening the way for the development of new and more efficient heterodinuclear iron based WO catalysts.

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