

Redox Non-Innocent Ligands and Water Oxidation

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Abstract: The highly endothermic splitting of water into O₂ (oxidation) and H₂ (reduction) using an external energy source though an attractive way of energy storage is plagued by the kinetics of the 4 electron oxidation of water to dioxygen in the absence of a catalyst. [Ru₂(OH)₂(3,6-*t*Bu₂Q)₂(btpyan)]²⁺ has been shown to catalyze the oxidation of water to dioxygen at room temperature (*Angew. Chem. Int. Ed.* **2000**, *39*, 1479). Computationally, the ground electronic structure of the above complex is proposed to be $[\frac{2}{sq}, \frac{3}{sq}]^{2+}$ in water (Scheme). Although O–O bond formation is found to be thermodynamically feasible after the removal of 2 protons and 3 electrons, release of dioxygen is found to be associated with high activation barriers. Alternatively, a CE process is proposed to account for the high potential required for dioxygen release. Interestingly, this unique proposal revolves around the bidentate binding mode of quinone as well as its redox non-innocence aspect.

Scheme :

