

Iron and cobalt Complexes in Hbbpya ligand scaffold: Mechanistic investigation and spectroscopic trapping of reactive intermediates

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Fuel cells are the possible answer to the never-ending energy demand of mankind. The exact mechanism of such complex reactions within these cells is still elusive. Metal-oxo species are often proposed as the key intermediates in these reactions. We aim to study such intermediates, spectroscopically to gain better insights into such mechanisms.

Macrocyclic ligands have been used for decades to stabilise high valent transition metal-oxygen adducts in the past. However, demetallation under harsh catalytic conditions proves to be a challenge with such ligands. Therefore, we take a look into the robust bipyridyl ligand systems. Our collaborators from Netherlands have reported this bis-bipyridyl ligand system to be stable enough to withstand electrocatalytic water oxidation conditions. We therefore use this bipyridyl ligand system to trap probable intermediates using oxidising agents *ex-situ* to get a deeper mechanistic understanding of the catalytic system. Herein, we present the two bipyridyl complexes of the 3d-metal series (Fe and Co) that vary widely in their properties: reactivity with oxidising agents, and reactivity of corresponding intermediates. The iron complex is oxidised to the iron-oxo species by sPhIO and shows electrophilic reactivity while the corresponding cobalt complex forms a μ -peroxo dimer, which catalyses Oxygen Reduction Reaction (ORR) via a $2\text{H}^+/2\text{e}^-$ process.

