

Manganese Imidazole Complexes: Electrocatalytic Hydrogen Production

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Abstract : Hydrogen is one of the most abundant elements present on earth's crust and considered to be the simplest element in existence. It is not found naturally as a gas on earth and thus has to be manufactured. Hydrogen can be produced from a variety of sources, i.e., water, fossil fuels, or biomass and it is a byproduct of many chemical processes. It is also considered as a secondary source of energy commonly referred to as an energy carrier. Though hydrogen is not widely used as a fuel, it still has the potential for greater use in the future as a clean and renewable source of energy. Electrocatalysis is one of the important source for the production of hydrogen which could contribute to this prominent challenge. Metals such as platinum and palladium are considered efficient for hydrogen production but with limited applications. As a result, a wide variety of metal complexes with earth abundant elements and varied ligand environments have been explored for the electrochemical production of hydrogen. In nature, [FeFe] hydrogenase enzyme present in *Desulfovibrio desulfuricans* and *Clostridium pasteurianum* catalyses the reversible interconversion of protons and electrons into dihydrogen. Since the first structure for the enzyme was reported in 1990s, a range of iron complexes has been synthesized as structural and functional mimics of the enzyme active site. Mn is one of the most desirable element for sustainable catalytic transformations, immediately behind Fe and Ti. Only limited number manganese complexes have been reported in the last two decades as catalysts for proton reduction. Furthermore, redox reactions could be carried out in a facile manner, due to the capability of manganese complexes to be stable at different oxidation states. Herein are reported, four μ_2 -thiolate bridged manganese complexes $[\text{Mn}_2(\text{CO})_6(\mu\text{-S}_2\text{N}_4\text{C}_{14}\text{H}_{10})]$ 1, $[\text{Mn}_2(\text{CO})_7(\mu\text{-S}_2\text{N}_4\text{C}_{14}\text{H}_{10})]$ 2, $\text{Mn}_2(\text{CO})_6(\mu\text{-S}_4\text{N}_2\text{C}_{14}\text{H}_{10})]$ 3 and $[\text{Mn}_2(\text{CO})(\mu\text{-S}_4\text{N}_2\text{C}_{14}\text{H}_{10})]$ 4 have been synthesized and characterized. The cyclic voltammograms of the complexes displayed irreversible reduction peaks in the range - 0.9 to -1.3 V (vs. Fc^+/Fc in acetonitrile at 0.1 Vs^{-1}). The complexes were catalytically active towards proton reduction in the presence of trifluoroacetic acid as seen from electrochemical investigations.

Keywords : earth abundant, electrocatalytic, hydrogen, manganese

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