Mixed Valence Fe Thiolate Dimers with CO and CN^- Ligation Model for Di-Iron Centers in [FeFe]-Hydrogenase Enzymes

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Environmental and energetic concerns have helped drive studies of [FeFe]-hydrogenase enzymes, capable of hydrogen production. Searching for mimics for the binuclear Fe-Fe active center, Iron complexes containing carbonyl, cyanide and thiolate (PS2') ligands have been synthesized.

The precursor $[Fe^{II}(PS2')(CO)_3]$ is prepared using $Fe(CO)_4Br_2$ and PS2' ,a bis-thiophenyl-phenyl phosphine. It dimerizes into a brown dimer, $[Fe_2(PS2')_2(CO)_4]$, and a green asymmetric dimer $[Fe_2(PS2')_2(CO)_3]$

The cyanation of $[Fe_2PS2')_2(CO)_3]$ yields $[Fe^{II}Fe^{II}(PS2')_2CN(CO)_2]^{1-}$ which mimics the Fe-Fe active center of H_2-ases. Irons are bridged by PS2' ligands, one Fe attaches CO and CN^-, the other Fe completes its hexacoordination with a single CO.

The H_2-ase catalysis implies redox transformations at the Fe sites. Electrochemical and chemical oxidation of the mimic reveals a catalytic prospect.

The structure of the oxidized $[Fe^{II}Fe^{III}(PS2')_2(CN)(CO)_2]$ shows a shortened Fe-Fe distance. Fe-CO, Fe-CN lengths change accordingly to a delocalized mixed valence compound, also revealed by shifts in IR spectra. Characterization includes X-ray crystallography, FTIR, NMR, and Mass spectroscopy.