

Models for [Fe(CO)₂] Center in the FeS-Cluster-Free Hydrogenase Hmd

Stephen A. Koch, Doris Y. Melgarejo, and Gina M. Chiarella

Chemistry Department, State University of New York at Stony Brook

Very recently the enzyme, which had been believed to be a metal-free hydrogenase, the H₂-forming methylenetetramethanopterin dehydrogenase (Hmd), has been shown to contain a cofactor with a diamagnetic *cis*-[Fe(CO)₂] coordination center. The identity of the other ligands and the oxidation state of iron remain to be established. IR studies indicate that the inhibitors CO and CN⁻ bind to this cofactor to generate [Fe(CO)₃] and [Fe(CN)(CO)₂] centers. (Lyon et al. JACS **2004**, 126, 14239).

The [Fe^{II}(PS2')(CO)₃] and [Fe^{II}(PS2')-(CN)(CO)₂]⁻ compounds (where PS2' is a phosphinedithiolate ligand) has been synthesized and structurally characterized. The vibration spectra of the [(PS2')Fe^{II}(CO)₃] and [(PS2')Fe^{II}(CN)(CO)₂]⁻ complexes are similar to the CO and CN⁻ inhibited forms of the Hmd hydrogenase. The IR spectra of *fac*-[Fe^{II}(CO)₃] and *fac*-[Fe^{II}(CO)₂CN] complexes are sensitive to the symmetry of the compound and to the identity of the non-carbonyl ligands. It is suggested that the CO, CN⁻ inhibitors and the H₂ substrate bind to create a facial [Fe^{II}L(CO)₂] coordination. Low spin d⁶ is an attractive oxidation state for forming M(H₂) complexes. Certain M(H₂) complexes are known to show reactivity patterns which are analogous to the Hmd enzyme.

