Diferrous Structural and Functional Models of the Iron-only Hydrogenases

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The Fe-only hydrogenases catalyze the interconversion between protons and dihydrogen. The H₂-binding center (H-cluster) in the Fe-only hydrogenases adopts a face-shared bi-octahedral structure (Figure 1). The entire complement of ancillary ligands are unusual in the biological context. Cyanide and CO are rarely observed in Nature, although they are also found in the NiFe hydrogenases. Other unusual features include the dithiolate cofactor, the sulfur atoms of which bridge the iron atoms, and an Fe₄S₄(SCys)₄ cluster that is linked to the active site via a cysteinyl thiolate bridge. The oxidized, active form (Hox, see below) of the binuclear active site can be described as [Fe₂(SCH₂)₂X](CN)₂(µ-CO)(CO)(SR₂)(L)]', where SR₂ represents the thiolato-bridged Fe₄S₄ ligand, X is speculated to be NH, and L is the Hₙ-binding site (n = 1, 2) that can also be occupied by CO (Hox CO) or possibly H₂O.

![Figure 1. Hydrogenase active site, Hox(left) and [HFe₂(S₂C₃H₆)(CN)₂(CO)₄] (right).](image)

Oxidations of sub-ferrous compounds afford a new family of diferrous dithiolates. Low temperature oxidation of Fe₂(S₂C₆H₁₈)₃(CNMe)₁₀(CO)₆ (n = 2, 3; x = 2, 3) affords a family of mixed carbonyl-isocyanides of the type [Fe₂(S₂C₆H₁₈)(CO)₆(CNMe)₇-I₃]. The degree of substitution is controlled by the RNC/Fe ratio as well as the degree of initial substitution at iron, with tricarbonyl derivatives favoring more highly carbonylated products. The structures of the monocarbonyl derivatives [Fe₂(S₂C₆H₁₈)(µ-CO)(CNMe)₆]PF₆ (n = 2, 3) established crystallographically and spectroscopically, are quite similar, with Fe-Fe distances of ca. 2.5 Å, although the µ-CO is unsymmetrical in the propanedithiolate derivative. In the dicarbonyl species, [Fe₂(S₂C₃H₆)(µ-CO)(CO)(CNMe)₃]PF₆, the terminal CO ligand is situated at one of the basal sites, not trans to the Fe-Fe vector.

Oxidation of (Et₄N)₂[Fe₂(S₂C₂H₄)(CN)₂(CO)₄] in the presence of cyanide and tertiary phosphines and of Fe₂(S₂C₂H₄)(PMe₃)₂(CO)₄ in the presence of cyanide affords a series of diferrous cyanide derivatives (Scheme 1) that bear a stoichiometric, structural, and electronic relationship to the Hox state of the Fe-only hydrogenases. With PPh₃ as the trapping ligand, we obtained an unsymmetrical isomer of Fe₂(S₂C₂H₄)(µ-CO)(CN)(PPh₃)₂(CO)₂, which was confirmed crystallographically. This diferrous cyanide features the *semi*bridging CO ligand with
Fe-μC bond lengths of 2.15 and 1.85 Å. Four isomers of Fe₂(S₂C₂H₄)(μ-CO)(CN)₂(PMe₃)₂(CO)₂ were observed, the initial product again being unsymmetrical but more stable isomers are symmetrical. DFT calculations confirm that the most stable isomers of Fe₂(S₂C₂H₄)(μ-CO)(CN)₂(PMe₃)₂(CO)₂ have cyanide trans to μ-CO. Oxidative decarbonylation also afforded the new tetracyanide [Fe₂(S₂C₂H₄)(μ-CO)(CN)₄(CO)₂]. Insights into the oxidative decarbonylation mechanism of these syntheses comes from the spectroscopic characterization of the tetracarbonyl [Fe₂(S₂C₂H₄)(μ-CO)(CN)₄(CO)₃]. This species reacts with PEt₃ to produce the stable adduct [Fe₂(S₂C₂H₄)(μ-CO)(CN)₃(CO)₂(PEt₃)]⁺.

Scheme 1. Oxidative decarbonylation methodology for (Et₄N)₂[Fe₂(S₂C₂H₄)(CN)₂(CO)₄].

The protonation of (Et₄N)₂[Fe₂(S₂C₂H₄)(CN)₂(CO)₄] has been further characterized. Low temperature IR spectroscopic studies show that the protonation of (Et₄N)₂[Fe₂(S₂C₂H₄)(CN)₂(CO)₄] with HOTs gave Et₄N[Fe₂(S₂C₂H₄)(CN)(CNH)(CO)₄]. The species, Et₄N[Fe₂(S₂C₂H₄)(CN)(CNH)(CO)₄], undergoes an approximate first-order decay to the hydride Et₄N[Fe₂(S₂C₂H₄)(CNH)(CO)₄] (Figure 1). Addition of a second equiv of H⁺ to Et₄N[Fe₂(S₂C₂H₄)(CN)(CO)₄] resulted in protonation at the CN⁻ ligand to give [Fe₂(S₂C₂H₄)(CNH)(CO)₄]. [Fe₂(S₂C₂H₄)(CN)(CO)₄] was shown to catalyze the reduction of protons at -1.5 V vs Ag/AgCl. Decarbonylation of Et₄N[Fe₂(S₂C₂H₄)(CN)(CO)₄] in the presence of PPh₃ resulted in Et₄N[Fe₂(S₂C₂H₄)(CN)(CO)₃(PPh₃)] followed by Et₄N[Fe₂(S₂C₂H₄)(CN)(CO)₃(PPh₃)], which exist as multiple isomers. MeCN solutions of Et₄N[Fe₂(S₂C₂H₄)(CN)(CO)₄] in the absence of PPh₃ gave the solvolysis product, Et₄N[Fe₂(S₂C₂H₄)(CN)(MeCN)(CO)₃], which reacts with PMe₃ and CN⁻ to produce Et₄N[Fe₂(S₂C₂H₄)(CN)(MeCN)(CO)] and (Et₄N)₂[Fe₂(S₂C₂H₄)(CN)₃(CO)₃], respectively.
References


