Models for [Fe(CN)(CO)] Centers in [NiFe] Hydrogenase Enzymes

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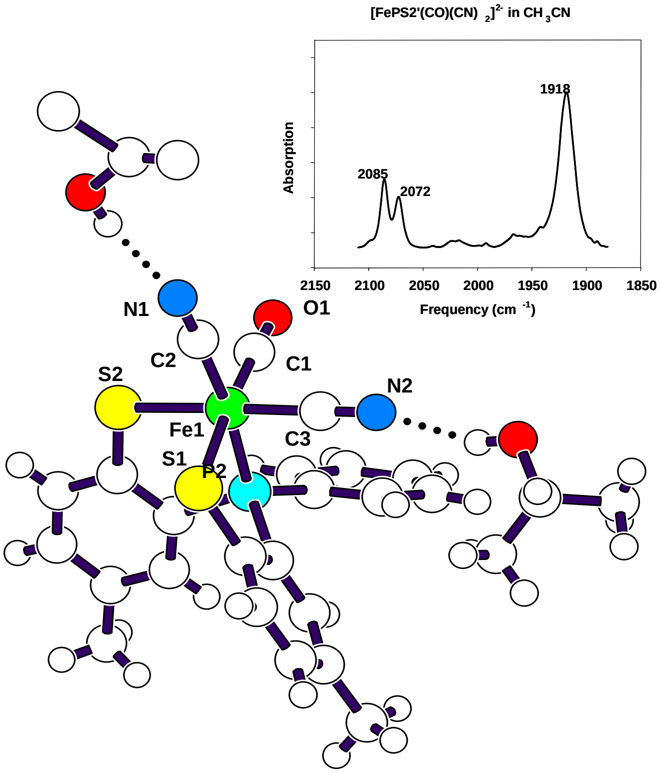
A series of iron cyanide carbonyl mimic complexes for iron moiety of nickel-iron hydrogenase active center have been synthesized and characterized: $[Fe^{II}(PS2')(CN)(CO)_2]^-$ C_1 symmetry, $[Fe^{II}(PS2')(CN)(CO)_2]^-$ C_s symmetry, $[Fe^{II}(PS2')(CN)_2(CO)]^{2-}$ and $[Fe^{III}(PS2')(CN)_3]^{2-}$. PS2' = *bis*[5-Methyl-2-thiophenyl]phenyl phosphine.



These carbonyl cyanide compounds were obtained by the reaction of $[Fe^{II}(PS2')(CO)_3]$ with cyanide salts and also by reaction of $FeCl_2$ with CO, CN^- and PS2'. The two isomers of the monocyanide complex, $[Fe^{II}(PS2')(CN)(CO)_2]^-$, were isolated. The C_1 symmetry isomer was prepared at room temperature in the dark while the C_s isomer was obtained when the reaction mixture was exposed to light. $[Fe^{II}(PS2')(CN)_2(CO)]^{2-}$ was prepared by cyanation of the former compound, and $[Fe^{III}(PS2')(CN)_3]^{2-}$ was obtained by oxidation and cyanation of the dicyanide compound and also reacting $FeCl_2$, PS2' and CN^- with later oxidation.

The crystal structures of these compounds were obtained, showing hydrogen bonding between nitrogen atom from cyanide ligand and the solvent. The compounds were further characterized by mass spectroscopy, FTIR and NMR studies. Electrochemical studies showed reversible oxidation of $[Fe^{II}(PS2')(CN)_2(CO)]^{2-}$ and reversible reduction of $[Fe^{III}(PS2')(CN)_3]^{2-}$.