A Model for the Bimetallic Active Site of [NiFe] Hydrogenase Enzymes

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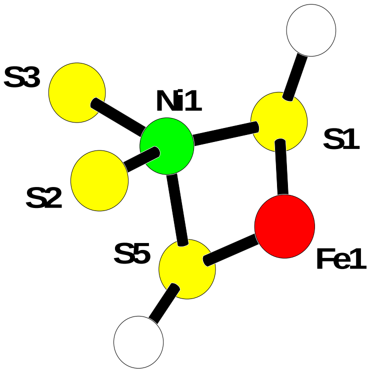
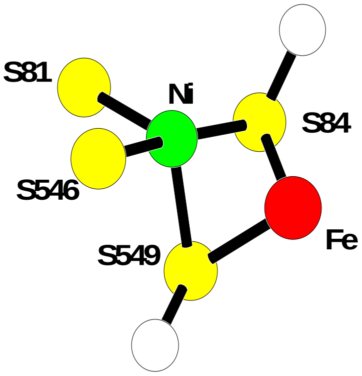
In efforts to understand the nature of the Ni-Fe center in hydrogenases, attention has focused on the observation that the coordination geometry at the nickel center is highly contorted, leading to the idea that it is this unique geometry that enhances the reactivity of the Ni-Fe center. By using the multidentate *tris*-(2-Phenyl-thiolate)phosphine [PS3] ligand and appropriate synthetic strategy, we have been able to construct a compound with a mixed-metal center that replicates the “distorted” $[(RS)_2Ni\text{-}(\mu_2\text{-}SR)_2\text{-}Fe]$ unit found in the hydrogenases. However, there is the stipulation that analog compounds contain the biologically unfamiliar phosphine center. Via this submission, we report the construction and characterization of a redox active [Ni-Fe] dimer $[NiFe(PS3)_2]^{1-}$ (#**1**) and its mixed valence $[Fe^{II}Fe^{III}]$ analog $[Fe_2(PS3)_2]^{1-}$ (#**2)**. Both compounds have acutely folded $[M(\mu_2\text{-}SR)_2M]$ bridging units with short M-M distances of ~2.5 Å. Compound #**2** is a rare example of a structurally characterized mixed valence iron dimer with a predominately sulfur donor ligands. Moreover, both compounds show reversible one-electron oxidations and reductions. Examination and comparison of the $[(RS)_2Ni\text{-}(\mu_2\text{-}SR)_2\text{-}Fe]$ unit in **#1** and in the reduced hydrogenases show remarkably similar geometries (See below.) The ramifications of the chemistry associated with the metal-metal centers in **#1** and **#2** and in the analogous centers in the hydrogenases will be presented.



$[NiFe(PS3)_2]^{1-}$



[NiFe]-Hydrogenase