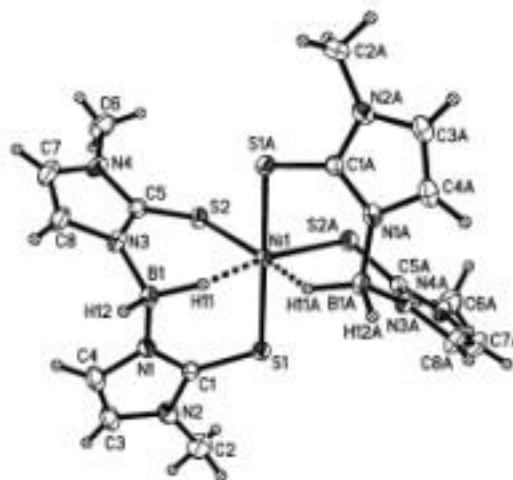
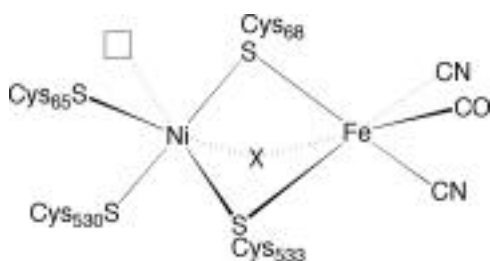
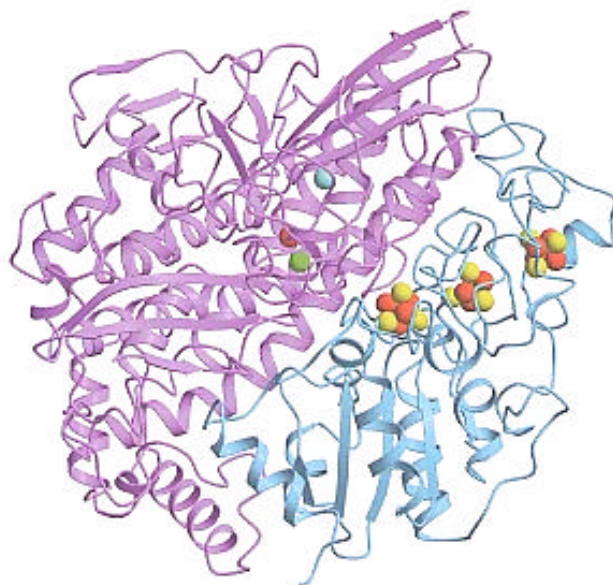


4. Model compounds for [NiFe] hydrogenases

An area of research in which we are particularly interested is in the preparation of model complexes for the nickel center in the active site of [NiFe] hydrogenases. Interest in these enzymes, which catalyze the reversible oxidation of dihydrogen to protons and thus play a key role in molecular bioenergetics, has intensified in recent years since unequivocal structural information was obtained using X-ray crystallography for the NiFe-hydrogenase extracted from *Desulfovibrio gigas* (Fontecilla-Camps, 1995).

Numerous synthetic, spectroscopic, and theoretical studies have provided valuable insight into the structure and function of [NiFe] hydrogenases and it is now clear that the active site consists of a dinuclear nickel—iron complex in a sulfur-rich environment, with the nickel atom surrounded by four cysteine groups in a geometry that has been described either as square pyramidal with a missing basal ligand or octahedral with two cis coordination vacancies. Despite these efforts, the exact nature of the catalytic cycle and the redox properties of nickel remain uncertain. We have used the BmR ligand system to prepare compounds that are unprecedented structural models for the nickel center in these enzymes, including simple $\text{Ni}(\text{Bm}^{\text{R}})_2$:



Relevant publications:

“Modeling Nickel Hydrogenases: Synthesis and Structure of a Distorted Octahedral Complex with an Unprecedented $[\text{NiS}_4\text{H}_2]$ Core” Alvarez, H. M.; Krawiec, M.; Donovan-Merkert, B. T.; Fouzi, M.; Rabinovich, D. *Inorg. Chem.* **2001**, *40*, 5736-5737.

“Poly(mercaptoimidazolyl)borate chemistry and the predominance of $\kappa^3\text{-S,S,H}$ over $\kappa^2\text{-S,S}$ or $\kappa^3\text{-S,S,S}$ coordination modes: unexpected formation of square pyramidal Ni(II) complexes” Alvarez, H. M.; Tanski, J. M.; Rabinovich, D. *Polyhedron* **2004**, *23*, 395-403.