

G003 SULFIDO BRIDGED FE/S AND FE/MO/S CLUSTERS. A NEW PROPOSED MODEL FOR THE FE/MO/S CENTER IN NITROGENASE. D. Coucouvanis P.R.Challen, Sang-Man Koo, S. Al Ahmad and W.R Dunham, Dept of Chemistry The Univ. of Michigan, Ann Arbor MI, 48109, USA.

A new model is proposed for the core of the Fe/Mo/S center in nitrogenase. The model is an octanuclear cluster that contains the already known Fe_4S_4 and Fe_3MoS_4 units coupled via a $\mu\text{-S}^{2-}$ bridge. We report on the first doubly $\mu\text{-S}^{2-}$ bridged, double cubanes. The new clusters contain the $[\text{MoFe}_3\text{S}_4(\text{Cl})_2(\text{Cl}_4\text{cat})]^-$ units bridged by two $\mu\text{-S}^{2-}$ ligands in the $\{[\text{MoFe}_3\text{S}_4(\text{Cl})_2(\text{Cl}_4\text{cat})]_2(\text{S})\}^{6-}$ anion and by a S^{2-} and a OH^- ligands in the $\{[\text{MoFe}_3\text{S}_4(\text{Cl})_2(\text{Cl}_4\text{cat})]_2(\text{S})(\text{OH})\}^{5-}$ anion. The X-ray structures and properties of these clusters will be discussed. The synthesis and characterization of the latest analog for the nitrogenase Fe/Mo/S center, with the $[[\text{Fe}_4\text{S}_4]\text{S}[\text{Fe}_3\text{MoS}_4]$ core, will be presented.

G004 THE MECHANISM OF LONG DISTANCE ELECTRON TRANSFER IN PHOTOSYNTHETIC REACTION CENTERS. Steven G. Boxer, Dept. of Chemistry, Stanford University, Stanford, CA 94305 USA.

Eight or more electron transfer reactions take place in photosynthetic reaction centers. The mechanisms of the initial ps charge separation reaction and the slower recombination between the primary electron donor and reduced quinone have been examined using electric fields. Insights into the mechanism of charge separation and recombination will be discussed along with more general implications for long distance electron transfer reactions in proteins.

G005 QUINONE SUBSTITUTED MONOMETALATED PORPHYRIN DIMERS: EVIDENCE FOR "SUPEREXCHANGE" MEDIATED ELECTRON TRANSFER IN MULTICOMPONENT PHOTOSYNTHETIC MODEL SYSTEMS. Jonathan L. Sessler and Martin R. Johnson, Department of Chemistry, University of Texas, Austin, Texas 78712 USA.

The optical properties of two pairs of selectively monometalated, zinc-containing, quinone substituted 1,3-phenyl linked "gable" and 1,4-phenyl linked "flat" porphyrin dimers will be described. These compounds contain the key biomimetic components, metalloporphyrin, free-base porphyrin, and quinone, arranged in several different but well-defined configurations and provide a unique "matched set" of photosynthetic models suitable for studying intermacrocycle orientation and energetic effects in multistep photoinduced electron transfer reactions. Optical studies of the more elaborate of these models, which contain a built-in energy barrier, have revealed the presence of a long-range "superexchange" mediated electron transfer process involving the central porphyrin moiety.