Chemical Approaches to Complex Heterometalsulfur Sites in Biology

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Bridged metal-sulfur assemblies, consisting of two recognizable entities juxtaposed by one or more covalent bridges, are among the most complex metal sites in biology. Examples include the catalytic centers of sulfite oxidase, [Fe]-hydrogenases, [NiFe]-hydrogenases, nitrogenase, and carbon monoxide dehydrogenase (CODH). The synthesis of structural and functional analogues of these sites provides a major challenge in biomimetic inorganic chemistry. Synthetic approaches to bridged assemblies are summarized, with emphasis on the P^N $\{Fe_8S_7(S_{Cys})_2\}$ and FeMo-cofactor $\{MoFe_7S_9\}$ clusters of nitrogenase, and the A-cluster ($\{[Fe_4S_4]$-$(\mu_2$-$S_{Cys})$-$Ni[(\mu_2$-$S_{Cys})_2Gly]Ni\}$, acetylcoenzyme synthase site) and C-cluster ($\{NiFe_4S_5\}$, CO/CO_2 interconversion site) of CODH are emphasized. New reactions and structures and discussed, including realization of the P^N topology in Mo/V-FeS clusters, thiolate bridging interactions between a Fe_4S_4 and Ni^{II} and between two Fe_4S_4 clusters, and the synthesis and properties of cubanoid MFe_3S_4 clusters (M = Ni, Pd, Pt) containing planar M^{II} sites as in the C-cluster of CODH.