

Exploratory Inorganic Synthesis Inspired by the Iron-Molybdenum Cofactor of Nitrogenase

Miriam V. Bennett¹, Sebastian Stoian², Emile L. Bominaar², Eckard Munck², and R. H. Holm¹.

¹Department of Chemistry and Chemical Biology, Harvard University,
and ²Department of Chemistry, Carnegie Mellon University.

The recent discovery of a light interstitial atom in the iron-molybdenum cofactor of nitrogenase has prompted us to investigate the synthesis of high nuclearity ferrous and ferric nitride clusters. A facile method has been developed for the incorporation of nitride into ferric molecules through a self-assembly process. Initial results include $[\text{Fe}_4\text{N}_2\text{X}_{10}]^{4-}$ and $[\text{Fe}_{10}\text{N}_8\text{X}_{12}]^{5-}$ ($\text{X} = \text{Cl}^-, \text{Br}^-$). These compounds are unique structurally and electronically and represent a new class of molecular transition-metal clusters. Additional studies targeting molecules which contain ferrous nitride moieties have yielded unprecedented coordination compounds with unusual geometries about the metal center. Synthetic methods for incorporating sulfide into iron nitride clusters, as well as attempts to incorporate nitride into iron-sulfur clusters, will be presented. The relevance of these studies to the iron-molybdenum cofactor of nitrogenase will be discussed.