The First Acive-Site Analogue for the All-Ferrous Iron Protein of Nitrogenase

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The enzyme nitrogenase consists of two metalloproteins: the Fe protein and the MoFe protein. The discovery of the all-ferrous Fe protein through use of strong reductants has posed a challenge to the current understanding of the nitrogen fixation mechanism. However, the stabilization of a protein $[Fe_4S_4]^0$ analogue has proven to be difficult due to the extreme air-sensitivity of the $[Fe_4S_4]^0$ cluster outside of the polypeptide environment. In as early as 1974, an all-ferrous cluster $[Fe_4S_4(SR)_4]^{4-}$ was detected electrochemically in solution, but the all-ferrous species has never been isolated or fully characterized despite substantial efforts toward the goal. Most recently, we have synthesized an $[Fe_4S_4(CN)_4]^{3-}$ cluster, whose $[Fe_4S_4]^{0/1+}$ redox potential (-1.16 versus NHE) implies a feasible reduction to the all-ferrous state. In this presentation we wish to report the synthesis, crystal structure, and spectroscopic studies of the first protein analogue for the active site of the all-ferrous Fe protein of nitrogenase.