Studies of Low-Coordinate Iron Models of Nitrogenase

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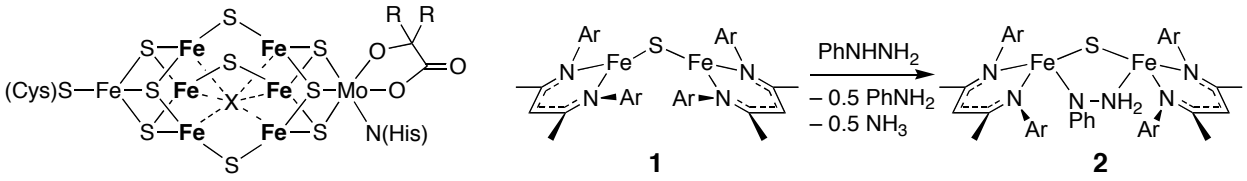
Molybdenum-dependent nitrogenase enzymes bind and reduce N_2 at the iron-molybdenum cofactor (FeMoco), which is illustrated below (X is probably N^{3-}). The mechanism is unknown, but kinetic and spectroscopic studies of mutants indicate that the central iron "waist" atoms are the most likely sites for binding of N_2 and other substrates. The most detailed characterization of substrate adducts in the mutants has come from electron-nuclear double resonance (ENDOR) spectroscopy, which specifically detects nuclei coupled to the FeMoco [1].

In an effort to create small synthetic compounds with some of the coordination characteristics of the iron "waist" sites on the FeMoco, we synthesized the sulfide-bridged diiron complex **1** [2]. This complex has two trigonal-planar Fe^{2+} ions bridged by a biomimetic μ-sulfido ligand. Compound **1** binds a number of nitrogenase substrates and substrate analogues. Some hydrazines are reduced by the iron(II) ions to ammonia with cleavage of the N-N bond. One mixed-valence iron(II)-iron(III) product (**2**) has a bridging hydrazido ligand, and the S = ½ ground state is amenable to characterization by ENDOR spectroscopy. ENDOR studies of the ^{15}N and ^{2}H labeled isotopomers of **2** have been performed and compared with the corresponding ENDOR spectra of a trapped hydrazine reduction intermediate of nitrogenase [3].



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