Low Coordinate Iron Complexes for Modeling FeMo Nitrogenase

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The reduction of dinitrogen to ammonia is carried out on the industrial scale by the Haber-Bosch process, at high temperatures and pressures, and by nitrogenase enzymes, under ambient conditions. The three types of nitrogenases include FeMo, FeV, and Fe, based on the metals found in the active site. Nitrogen reduction occurs at an eight-metal cofactor, which for the most common enzymes is a $MoFe_7S_9X$ cluster, in which X= C, N, or O. Six high spin iron centers have pseudotetrahedral geometries, with iron bound to three sulfides and X (Figure 1). The proposed oxidation states in the resting state of the enzyme are as follows: $(Fe^{3+})_3(Fe^{2+})_4(Mo^{4+})$, but in order to bind N_2, the active site must be reduced by three to four electrons.

Two proposed pathways for N_2 reduction are illustrated in Scheme 1. In the "distal mechanism" (D) the uncoordinated N atom is protonated and released prior to protonation of the metal-bound N atom. In the "alternating mechanism," (A) protonation alternates between the two N centers, until NH_3 is released. The N_2 ligand initially binds a single Fe atom, but multiple iron centers may be involved in later steps.[1]
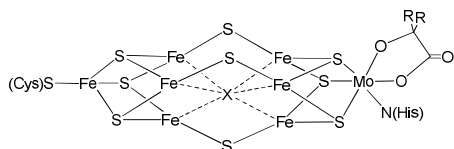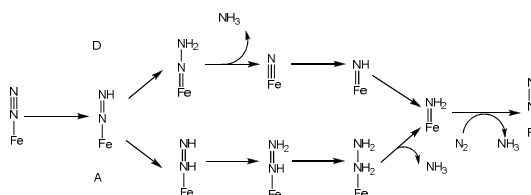

Figure 1

Scheme 1

Intense efforts have been made to model the FeMo cofactor. One approach toward this goal is to synthesize complexes in which iron has both a low coordination number and high spin electron configuration, as seen in the enzyme. The proposed reduction cycle implies that low coordinate iron complexes can adopt a range of oxidation states and bind both π acidic and π basic ligands.

One approach to modeling involves the use of sterically bulky ligands that enforce low coordination numbers on the iron centers (Figure 2). Holland and coworkers have synthesized complexes of the type $L^RFeNNFeL^R$, where L^R are β-diketiminate ligands. These compounds exhibit weakening of the N-N triple bond, as evidenced by the lengthened N-N bond length and decreased N_2 stretching frequency. Based on high level quantum chemical calculations on a simplified diiron dinitrogen compound, orbitals with N-N π antibonding character and Fe-N π bonding character are occupied, resulting in strong Fe-N bonds and weak N-N bonds.[2]

Although these complexes do not exhibit reactivity with protons, they can reduce sulfur to form $L^RFeSFeL^R$, R=Me, which contains low coordinate Fe centers bound to sulfide, reminiscent of those in the cofactor. The bridging sulfide complex forms pseudotetrahedral

adducts with alkyl hydrazines and ammonia, whose geometries resemble those proposed for the enzyme. The bridging sulfide complex can also cleave the N-N bond in phenylhydrazine, forming the Fe(II)Fe(III) adduct shown in Figure 3 and releasing ammonia and phenyl amine.[3] Although the iron β-diketiminates are good structural models of the iron atoms in the FeMo cofactor, they lack the reactivity with protons that is exhibited by the enzyme.
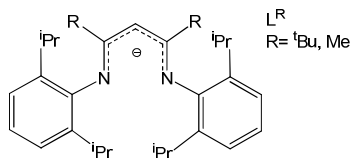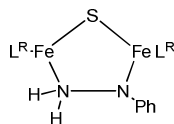

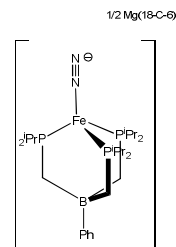**Figure 2**   **Figure 3**   **Figure 4**

Another approach to nitrogenase modeling has been the use of tripodal phosphine ligands that impose four coordinate geometry. Peters and coworkers have synthesized a pseudotetrahedral iron dinitrogen complex supported by the ligand $[PhB(CH2PR_2)_3]$ ($[PhBP^R_3]$) (Figure 4). The activation of N_2 is apparent from the reduced N-N stretching frequency, 1884 cm^{-1}.[4] The iron tris(phosphino)borate complex can also support imido, diazenido, amido, and nitride ligands, in which the oxidation states of iron match those of the proposed intermediate.[4,5,6]

A   **B**

Figure 5

The common trend in the complexes discussed so far has been low coordination number at iron. Two examples of trigonal bipyramidal iron complexes with weakly bound terminal dinitrogen ligands have been synthesized. The Peters group uses a tris(phosphino)silyl ligand, $[(2-R_2PC_6H_4)_3Si]^-$ (SiP^R_3), and the Field group the $P(CH_2CH_2P^iPr_2)_3$ (PP^i_3) (Figure 5A, B).[7,8] Both ligands enforce trigonal bipyramidal geometry. The dinitrogen ligand binds in an axial position, trans to a strong trans effect ligand, resulting in weak binding of the nitrogen ligand and weak N_2 activation.

In the enzyme, initial N_2 binding likely occurs at a single iron site, but diiron intermediates may be involved in later steps. A model for this pattern has been developed by the Peters group in the form of a Fe(II)Fe(II) μ-nitrido complex, which reacts with acid to form ammonia.[9] An alternating diiron pathway for nitrogen reduction would involve hydrazine, hydrazido, diazine, amide, and imide bound intermediates, and such complexes have been prepared synthetically, using tris(phosphino)borate supported iron sites.[10]

Based on ligand field splitting for pseudotetrahedral, trigonal planar, and trigonal bipyramidal complexes, the three and four coordinate complexes feature high energy d_{xy} and d_{yz} orbitals that can interact with π orbitals on the ligand. In the trigonal bipyramidal complexes, the d orbitals that can π bond with ligand orbitals are relatively low energy. Therefore, the low coordinate complexes are more capable of engaging in π interactions, which are required for binding and subsequent reduction of N_2 at an iron center.

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