

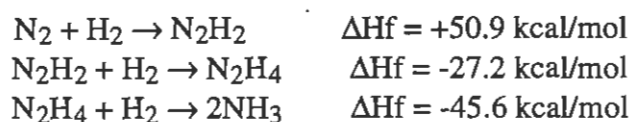
## Recent Structural Models for Dinitrogen Activation

Chris A. Wright

Literature Seminar

February 26, 1998

Dinitrogen comprises 79% of the earth's atmosphere. It is essential for the synthesis of nucleic acids and proteins which are required for all organisms.<sup>1,2</sup> Unfortunately, molecular nitrogen is highly resistant toward either oxidation or reduction, to the extent that it is commonly used as an inert atmosphere for reactive chemicals.<sup>1-5</sup> For dinitrogen to be most useful, it must be reduced to a form such as ammonia, which is currently performed effectively under ambient conditions only by the nitrogenase enzymes, and at very high temperatures and pressures by the Haber-Bosch process.<sup>2-5</sup> The primary barrier to its reduction (at least in the gaseous phase) is the first hydrogenation step, as illustrated by the enthalpies of formation which follow:<sup>3</sup>



These values show that the overall reduction is energetically favorable, if the first step is overcome.

The isolation of  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$  by Allen and Senoff in 1965 opened the door for dinitrogen coordination chemistry.<sup>7</sup> This and other advances, such as the 1960 isolation of nitrogenase extracts, and the 1964 development of transition metal compounds capable of reducing dinitrogen, spurred a tremendous interest in the field of dinitrogen activation.<sup>6</sup> A large number of dinitrogen reactions and complexes with transition metals have been discovered since 1965.<sup>1,4-6,8</sup>

Even with the amount of research on dinitrogen chemistry, no systems have been developed to compete effectively with the action of nitrogenase.<sup>1</sup> The chemistry of dinitrogen activation has expanded, providing many developments in the mechanism and structure of nitrogenase.<sup>2,3,9</sup> Perhaps most interesting to modeling efforts has been structural data reported on the metal clusters found in nitrogenases.<sup>3,10</sup> The Fe/Mo-cofactor proposed as the active dinitrogen reduction center is shown in Figure 1. While the cluster itself is known, the exact site of coordination and activation is not yet known.<sup>11</sup> Thus, synthetic efforts to model dinitrogen activation may be based on building clusters to closely model those found in nitrogenase, or in a looser sense, using structural principles learned from nitrogenase and previous dinitrogen chemistry to find a system that reduces dinitrogen but does not necessarily model nitrogenase.<sup>4</sup>

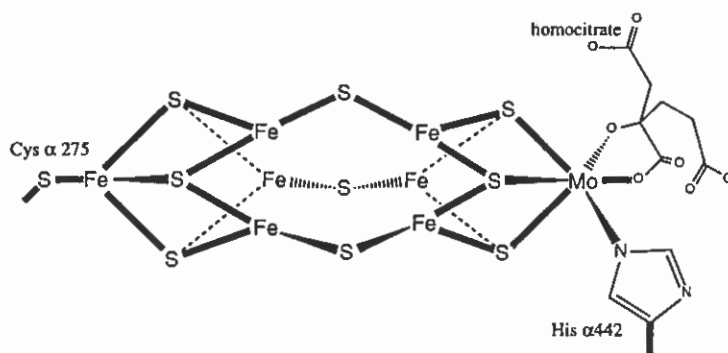


Figure 1

Efforts to closely model the clusters found within nitrogenase are based on Fe/Mo,V,Fe/S complexes.<sup>11,12</sup> Synthesis of such clusters are done in an effort to model the entire Mo/Fe-cofactor<sup>12b</sup> or structural units within the cofactor.<sup>11,12c,12d</sup> In either case, definite models for the nitrogenase cofactor have proven elusive.

Other systems have been designed to explore dinitrogen activation that do not resemble the nitrogenase cofactor quite as closely. Recent reports include a system in which N<sub>2</sub> is bound by two trinuclear gold clusters. The N-N distance of 1.475(14)Å<sup>13</sup> is longer than the single bond in hydrazine [1.454(20)Å], and significantly longer than free N<sub>2</sub> at 1.098(1)Å.<sup>14</sup> Work using low-valent early transition metals has also produced cases of elongated N-N bonding,<sup>15</sup> as well as examples of hydrogen addition to coordinated dinitrogen<sup>16</sup> and dinitrogen cleavage to form nitride complexes.<sup>17,18</sup>

The Zr complex with side-on bound dinitrogen illustrated in Figure 2A has an elongated N-N bond at 1.43(1)Å. It is found to react with molecular hydrogen in toluene to give the (m-h<sup>2</sup>-N<sub>2</sub>H)(m-H) complex shown in Figure 2B, as determined by NMR data and the crystal structure of an analogous compound with a [m-h<sup>2</sup>-N<sub>2</sub>(SiH<sub>2</sub><sup>n</sup>Bu)](m-H) moiety. This reaction is unusual, as earlier complexes were noted to release N<sub>2</sub> upon reaction with H<sub>2</sub>.<sup>16</sup>

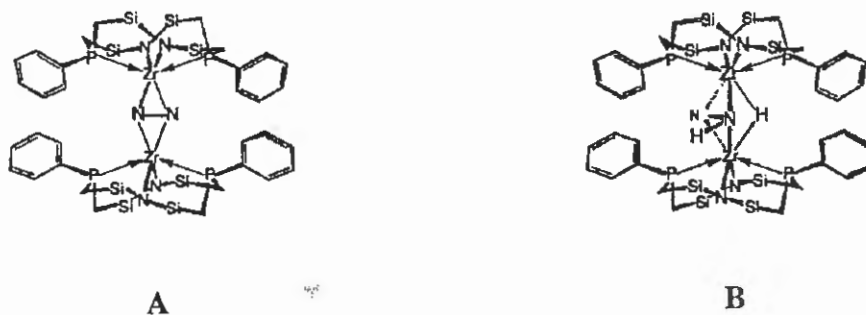


Figure 2

Dinitrogen cleavage by Mo(N(R)Ar)<sub>3</sub> (R = C(CD<sub>3</sub>)<sub>2</sub>Me, Ar = 3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>) complexes as well as very recent reports of cleavage by Nb calix[4]arene complexes have given examples of structural systems which are capable of breaking the N-N bond. Although

it has been demonstrated that coordinated  $N_2$  can be reacted with  $H_2$  and cleaved to a nitride species, well-defined catalytic systems for  $N_2$  reduction at ambient conditions have not yet been achieved. Further research to deduce the structure of the active site of nitrogenase and to produce functioning synthetic models has been stimulated by these recent advances, with substantial progress still to be made.

## References

1. Gambarotta, S., "Dinitrogen Fixation and Activation After 30 Years: A Puzzle Still Unsolved," *J. Organomet. Chem.* **1995**, *500*, 177-126.
2. Burgess, B. K.; Lowe, D. J., "Mechanism of Molybdenum Nitrogenase," *Chem. Rev.* **1996**, *96*, 2983-3011.
3. Howard, J. B.; Rees, D. C., "Structural Basis of Biological Nitrogen Fixation," *Chem. Rev.* **1996**, *96*, 2965-2982.
4. Sellmann, D.; Sutter, J., "In Quest of Competitive Catalysts for Nitrogenases and Other Metal Sulfur Enzymes," *Acc. Chem. Res.* **1997**, *30*, 460-469.
5. Hidai, M.; Mizobe, Y., "Recent Advances in the Chemistry of Dinitrogen Complexes," *Chem. Rev.* **1995**, *95*, 1115-1133.
6. Bazhenova, T. A.; Shilov, A. E., "Nitrogen Fixation in Solution," *Coord. Chem. Rev.* **1995**, *144*, 69-145.
7. (a) Allen, A. D.; Senoff, C. V., "Nitrogenopentammineruthenium(II) Complexes," *Chem. Com.* **1965**, 621-622. (b) Senoff, C. V., "The Discovery of  $[Ru(NH_3)_5N_2]^{2+}$ ," *J. Chem. Ed.* **1990**, *67*, 368-370.
8. For additional reviews see: (a) Allen, A. D.; Harris, O. R.; Loescher, B. R.; Stevens, J. R.; Whitely, R. N., "Dinitrogen Complexes of the Transition Metals," *Chem. Rev.* **1973**, *73*, 11-20. (b) Chatt, J.; Dilworth, J. R.; Richards, R. L., "Recent Advances in the Chemistry of Nitrogen Fixation," *Chem. Rev.* **1978**, *78*, 589-625. (c) Henderson, R. A.; Leigh, G. J.; Pickett, C. J., "The Chemistry of Nitrogen Fixation and Models for the Reactions of Nitrogenase," *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197-292. (d) Pelikan, P.; Boca, R., "Geometric and Electronic Factors of Dinitrogen Activation on Transition Metal Complexes," *Coord. Chem. Rev.* **1984**, *55*, 55-112. (e) Henderson, R. A., "Activation of Dinitrogen at Binuclear Sites," *Trans. Met. Chem.* **1990**, *15*, 330-336. (f) Leigh, G. J., "Protonation of Coordinated Dinitrogen," *Acc. Chem. Res.* **1992**, *25*, 177-181.
9. For additional reviews see: (a) Burgess, B. K., "The Iron-Molybdenum Cofactor of Nitrogenase," *Chem. Rev.* **1990**, *90*, 1377-1406. (b) Rees, D. C.; Chan, M. K.; Kim, J., "Structure and Function of Nitrogenase," *Adv. Inorg. Chem.* **1993**, *40*, 89-119. (c) Kim, J.; Rees, D. C., "Nitrogenase and Biological Nitrogen Fixation," *Biochem.* **1994**, *33*, 389-397. (d) Eady, R. R.; Leigh, G. J., "Metals in the Nitrogenases," *J. Chem. Soc., Dalt. Trans.* **1994**, 2739-2747. (e) Howard, J. B.; Rees, D. C., *Ann. Rev. Biochem.* **1994**, *63*, 235-264. (f) Eady, R. R., "Structure Function Relationships of Alternative Nitrogenases," *Chem. Rev.* **1996**, *96*, 3013-3030.

10. (a) Peters, W. J.; Stowell, M. H. B.; Sotis, S. M.; Finnegan, M. G.; Johnson, M. K.; Rees, D. C., "Redox-Dependent Structural Changes in the Nitrogenase P-Cluster," *Biochem.* **1997**, *36*, 1181-1187. (b) Schindelin, H.; Kisker, C.; Schlessman, J. L.; Howard, J. B.; Rees, D. C., "Structure of ADP·AlF<sub>4</sub><sup>-</sup> Stabilized Nitrogenase Complex and its Implications for Signal Transduction," *Nature* **1997**, *387*, 370-376.
11. Demadis, K. D.; Malinak, S. M.; Coucouvanis, D., "Catalytic Reduction of Hydrazine to Ammonia with MoFe<sub>3</sub>S<sub>4</sub>-Polycarboxylate Clusters. Possible Relevance Regarding the Function of the Molybdenum-Coordinated Homocitrate in Nitrogenase," *Inorg. Chem.* **1996**, *35*, 4038-4046.
12. (a) Holm, R. H., "Trinuclear Cuboidal and Heterometallic Cubane-Type Iron-Sulfur Clusters: New Structural and Reactivity Themes in Chemistry and Biology," *Adv. Inorg. Chem.* **1992**, *38*, 1-71. (b) Huang, J.; Mukerjee, S.; Segal, B. M.; Akashi, H.; Zhou, J.; Holm, R. H., "Molybdenum-Iron Sulfide-Bridged Double Cubanes," *J. Am. Chem. Soc.* **1997**, *119*, 8662-8674. (c) Demadis, K.; Coucouvanis, D., "Synthesis, Structural Characterization, and Properties of New Single and Double Cubanes Containing the MoFe<sub>3</sub>S<sub>4</sub> Structural Unit and Molybdenum-Bound Polycarboxylate Ligands," *Inorg. Chem.* **1995**, *34*, 436-448. (d) Tyson, M. A.; Coucouvanis, D., "New Fe/Mo/S Clusters with MoFe<sub>3</sub>S<sub>3</sub> Cuboidal Cores Similar to the One in the Fe/Mo Cofactor of Nitrogenase," *Inorg. Chem.* **1997**, *36*, 3808-3809.
13. Shan, H.; Yang, Y.; James, A. J.; Sharp, P. R., "Dinitrogen Bridged Gold Clusters," *Science* **1997**, *275*, 1460-1462.
14. Leigh, G. J., "A Fixation With Fixation," *Science* **1995**, *268*, 827-828.
15. Ferguson, R.; Solari, E.; Floriani, C.; Osella, D.; Ravera, M.; Re, N.; Chiesi-Villa, A.; Rizzoli, C., "Stepwise Reduction of Dinitrogen Occurring on a Divanadium Model Compound," *J. Am. Chem. Soc.* **1997**, *119*, 10104-10115.
16. (a) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G., "Transformation of Coordinated Dinitrogen by Reaction with Dihydrogen and Primary Silanes," *Science* **1997**, *275*, 1445-1447. (b) Cohen, J. D.; Fryzuk, M. D.; Loehr, T. M.; Mylvaganam, M.; Rettig, S. J., "Synthesis and Structure of a Zirconium Dinitrogen Complex with a Side-On Bridging N<sub>2</sub> Unit," *Inorg. Chem.* **1998**, *37*, 112-119.
17. (a) Laplaza, C. E.; Cummins, C. C., "Dinitrogen Cleavage by a Three-Coordinate Molybdenum(III) Complex," *Science* **1995**, *268*, 861-863. (b) Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J., "Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data," *J. Am. Chem. Soc.* **1996**, *118*, 8623-8638.
18. Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C., "Stepwise Reduction of Dinitrogen to Nitride Assisted by Niobium Bonded to Oxygen Donor Atoms: The Potential of Reduced Forms of Niobium Calix[4]arene," *J. Am. Chem. Soc.* **1998**, *120*, 437-438.