

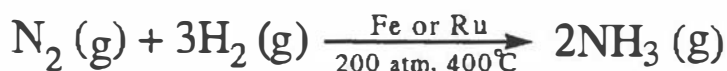
New Insights into Dinitrogen Activation and Fixation

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Dinitrogen surrounds us as the major component of Earth's atmosphere. It is the initial source of all nitrogen in organisms and an essential element in the chemistry of life. The Haber-Bosch process, which is a very successful commercial process, reacts dinitrogen gas with three equivalents of hydrogen gas over a metal catalyst to produce ammonia.¹ But in order to activate dinitrogen in this process, harsh, energy intensive conditions are required.²



The first dinitrogen complex $[(\text{H}_3\text{N})_5\text{Ru}(\text{N}_2)]^{2+}$ was identified in 1965 by Allen and Senoff.³ However, it was not until 1972 that the first reaction of coordinated dinitrogen to give a well-defined complex product was announced by Chatt.⁴

In 1995, Cumunins and coworkers were the first to report that a simple inorganic complex (see Figure 1) can split the triple bond of dinitrogen to yield a known nitrido complex without the need for any other reagent.^{5,6} Recently, by using a similar system, Floriani accomplished the same result by using light for activation.⁷

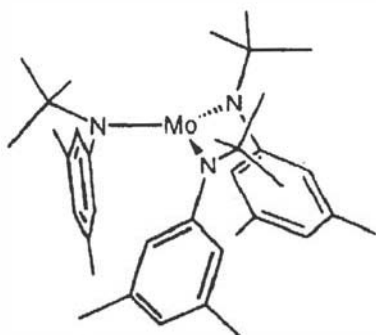


Figure 1

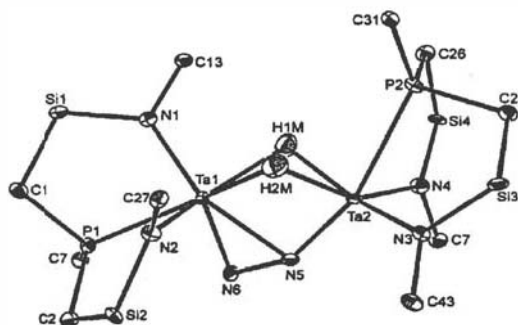


Figure 2

Recent reports have depicted new coordinated dinitrogen reactivities and bonding modes. Fryzuk reported that coordinated dinitrogen could be induced to react stoichiometrically with hydrogen and silanes.^{8,9} Hidai showed that cationic dihydrogen complexes could be used as the acid in the stoichiometric production of ammonia via a protonation sequence.^{10,11} Recently Fryzuk also reported a new bonding mode for the coordinated dinitrogen complex, which is both side-on and end-on.¹² (see Figure 2)

In marked contrast with the Haber-Bosch process, a similar chemical process requiring only atmospheric temperature and pressure is carried out by nitrogen-fixing bacteria, many of which live in symbiotic association with legume plants. The secret of their success is the enzyme nitrogenase, which transforms dinitrogen in the atmosphere into ammonia that plants can then use for growth.¹³

Nitrogenase consists of two essential metalloproteins: one, the iron protein, is a very specific ATP-activated electron donor to the other, the molybdenum-iron protein. (see Figure 3) The MoFe protein contains two unique metal-sulfur clusters: the P-cluster [8Fe-7S] and the FeMo-cofactor [Mo-7Fe-9S].¹⁴ A very similar model compound for the P-Cluster has been synthesized recently by Holm and coworkers.¹⁵ The protein level dinitrogen reduction mechanism for nitrogenase is relatively clear, but the mechanism on the molecular level is still a secret.^{16,17}

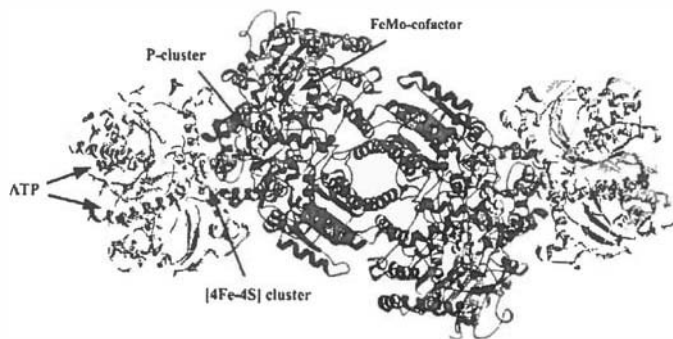


Figure 3

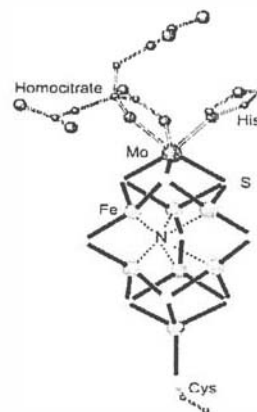


Figure 4

Rees and co-workers report the structure of the MoFe protein of bacterial nitrogenase at an improved resolution of 1.16 angstroms. They interpret their data in terms of a model that includes an interstitial hexacoordinate light atom within the FeMo-cofactor cluster that is bonded to each of the six iron atoms. (see Figure 4) Furthermore, they argue that the light atom is most likely to be nitrogen. Carbon or oxygen cannot be ruled out, but sulfur is unlikely.^{18,19}

In conclusion, many new insights into dinitrogen activation and fixation have been developed recently. A simple inorganic complex can split the dinitrogen triple bonds. New coordinated dinitrogen reactivities and bonding modes have been discovered. The high-resolution structure of the FeMo cofactor of nitrogenase will force scientists to think again about how the enzyme is biosynthesized and how it catalyzes the production of ammonia from dinitrogen.

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