

What is important about N₂ chemistry, practically speaking?

N₂ is 78.1% of atmosphere (by volume)¹
Nitrogen is *ca.* 15 wt% of proteins

⇒ Plentiful source of N atoms
Important synthetic goals

Some physical constants for dinitrogen:

$d(\text{N-N})$: 1.094 Å

mp 63.1 K

bp 77.3 K

Heat of dissociation is very large:

No appreciable dissociation at 3000 °C and ordinary pressure²

$\text{N}_2(\text{g}) = 2\text{N}(\text{g})$

$\Delta H = 944.7 \text{ kJ mol}^{-1}$

Study Questions: What is the electronic configuration of N (what orbitals are the electrons in)? In its ground state, is the nitrogen atom a singlet, doublet, triplet, quartet, etc.? Draw the Lewis structure for N₂. Draw the molecular orbital diagram for N₂.³

Nitrogenase

In 1886, atmospheric nitrogen was shown to be fixed by organisms (*rhizobium*) in root nodules.⁴ The protein that accomplishes this is nitrogenase.⁵ Nitrogenase is made up of two metalloproteins, both of which have been recently characterized structurally by X-ray crystallography (see the next two items).

- Doug Rees, *et al.* *Science*, **1992**, 257, 1653.⁶ Abstract:

The nitrogenase enzyme system catalyzes the ATP (adenosine triphosphate)-dependent reduction of dinitrogen to ammonia during the process of nitrogen fixation. Nitrogenase consists of two proteins: the iron (Fe)-protein, which couples hydrolysis of ATP to electron transfer, and the molybdenum-iron (MoFe)-protein, which contains the dinitrogen binding site. In order to address the role of ATP in nitrogen fixation, the crystal structure of the nitrogenase Fe-protein from *Azotobacter vinelandii* has been determined at 2.9 Å resolution. Fe-protein is a dimer of two identical subunits that coordinate a single 4Fe:4S cluster. Each subunit folds as a single α/β -type domain, which together symmetrically ligate the surface exposed 4Fe:4S cluster through two cysteines from each subunit. A single bound ADP (adenosine diphosphate) molecule is located in the interface region between the two subunits. Because the phosphate groups of this nucleotide are approximately 20 Å from the 4Fe:4S cluster, it is unlikely that ATP hydrolysis and electron transfer are directly coupled. Instead, it appears that interactions between the nucleotide and cluster sites must be indirectly coupled by allosteric changes occurring at the subunit interface. The coupling between protein conformation and nucleotide hydrolysis in Fe-protein exhibits general similarities to the H-Ras p21 and recA proteins that have been recently characterized

¹ N.N. Greenwood; A. Earnshaw. *Chemistry of the Elements*, 2nd edn., pp. 406-472, Butterworth-Heinemann, Boston, 1997. This book is in the Hayden Reserve Book Room.

² F. A. Cotton; G. Wilkinson. *Advanced Inorganic Chemistry*, 5th edn., pp. 305-381, John Wiley & Sons, New York, 1988. This book is in the Hayden Reserve Book Room.

³ For help on molecular orbital diagrams if you have not taken 5.03, please see the following reference (this book is on reserve in the Hayden Reserve Book Room) or one of your TAs: G.L. Miessler; D.A. Tarr. *Inorganic Chemistry*, 2nd edn., chapter 5, Prentice Hall, New Jersey, 1999.

⁴ J.B. Lawes; J.H. Gilbert. *Philosophical Transactions of the Royal Society of London. B*, **1889**, 180, 1. J.B. Lawes; J.H. Gilbert. *Proceedings of the Royal Society of London*, **1889 – 1890**, 47, 85.

⁵ For a description of the inorganic chemistry of nitrogenase, see the following: N.N. Greenwood; A. Earnshaw. *Chemistry of the Elements*, 2nd edn., pp. 1035-1037, Butterworth-Heinemann, Boston, 1997. This book is in the Hayden Reserve Book Room.

⁶ This article is available online: <http://www.jstor.org/>

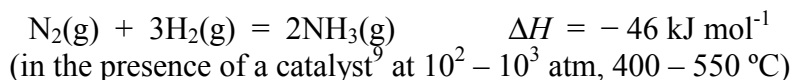
structurally. The Fe-protein structure may be relevant to the functioning of other biochemical energy-transducing systems containing two nucleotide-binding sites, including membrane transport proteins.

- James Howard, *et al.* *Nature*, **1997**, 387, 370. Abstract:

The coupling of ATP hydrolysis to electron transfer by the enzyme nitrogenase during biological nitrogen fixation is an important example of a nucleotide-dependent transduction mechanism. The crystal structure has been determined for the complex between the Fe-protein and MoFe-protein components of nitrogenase stabilized by ADP AlF₄⁻, previously used as a nucleoside triphosphate analogue in nucleotide-switch proteins. The structure reveals that the dimeric re-protein has undergone substantial conformational changes. The beta-phosphate and AlF₄⁻ groups are stabilized through intersubunit contacts that are critical for catalysis and the redox centre is repositioned to facilitate electron transfer. Interactions in the nitrogenase complex have broad implications for signal and energy transduction mechanisms in multiprotein complexes.

Haber – Bosch Process⁷

1909: Fritz Haber developed a catalytic synthesis of NH₃ from N₂ in collaboration with Carl Bosch (industrial synthetic scale by 1913).⁸ A catalyst, high temperatures, and high pressures are necessary to complete this transformation:



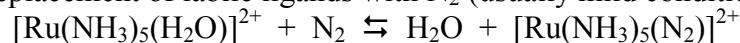
Despite the extreme conditions, the process is quite efficient (engineers *are* good for something). Because of its efficiency, chemists *are not* doing N₂ chemistry to immediately improve upon the Haber – Bosch process. Instead, chemists are interested in the following N₂-related issues:

- Nitrogenase mimics
- N-atom transfer
- Highly controlled (“tuned”) redox processes

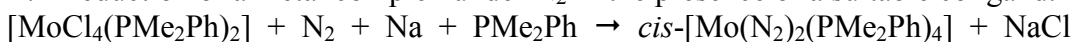
N₂ Complexes of Transition Metals

Today, there are many examples of N₂ complexes of the transition elements. There are, historically, three general methods to prepare this type of compound:¹

1. Direct replacement of labile ligands with N₂ (usually mild conditions, reversible).



2. Reduction of a metal complex under N₂ in the presence of a suitable coligand.



3. Conversion of a ligand with N–N bonds into N₂.



⁷ Read a description of the industrial production of ammonia in *Chemistry of the Elements*, 2nd edn., pp. This book is in the Hayden Reserve Book Room.

⁸ Both Fritz Haber (1918) and Carl Bosch (1931) are Nobel laureates. Read about their accomplishments and these prizes at <http://www.nobel.se/>

⁹ For description of catalysts used in the Haber – Bosch process see the following: K.-I. Aika. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 559.

The method we use in this lab is not any of these! Instead, we are synthesizing a compound that fills its empty coordination site with N₂. Next we'll find out how...

First, some literature references to note:

Allen, Senoff (1965):¹⁰ [Ru(N₂)(NH₃)₅]²⁺, first example of N₂ as a ligand

Taube (1968):¹¹ [(NH₃)₅RuN₂Ru(NH₃)₅]⁴⁺, first example of N₂ as a bridging ligand

Cummins, Laplaza (1995): Mo(N[R]Ar)₃ and NMo(N[R]Ar)₃, first example of nitrido moiety derived from N₂¹²

Hidai (1998): synthesis of ammonia using Ru/W¹³

What is special about Mo(N[R]Ar)₃?

The original motivation for the design and synthesis of Mo(N[R]Ar)₃ was *not* to cleave N₂! But it obviously can. Here are some important points about this compound.

Ligand Design

- Amido ligands with one aliphatic and one aromatic group
- Aromatic groups can π -stack (helps with crystallinity)
- Large enough so that only three fit around the metal center: trigonal planar (see figure below)

Study Questions: Why has this type of ligand (amido with one aliphatic group and one aromatic group) been chosen? Historically, bis(trimethylsilyl)amido ligands saw a lot of use in transition metal and uranium chemistry; why are they avoided here? Malcolm Chisholm, *et al.* have synthesized the compound (Me₂N)₃Mo \equiv Mo(NMe₂)₃,¹⁴ please comment on this compound as compared to Mo(N[R]Ar)₃.

Electronic Structure

- Mo is in group 6
 - Mo, W stabilize high oxidation states more easily than does Cr
 - *d* orbitals:
 - What does not favor multiple bonding to ligands? “The very early transition metals have higher energy, diffuse *d* orbitals, and therefore form more ionic, less covalent bonds than the later metals. The more polar the bond, it could be argued, the greater the basicity of the ligand and the greater the tendency to bridge. To the right of the iron triad, the metal *d*

¹⁰ A.D. Allen; C.V. Senoff. *Chem. Commun.* **1965**, 621.

¹¹ D.F. Harrison; E. Weissberger; H. Taube. *Science, New Series*, **1968**, 159, 3812, 320-322. Find this online at the JSTOR database: <http://www.jstor.org/>

¹² C.E. Laplaza; C.C. Cummins. *Science* **1995**, 118, 709. This article is available online at <http://www.jstor.org/>

¹³ Y. Nishibayashi; S. Iwai; M. Hidai. *Science* **1998**, 279, 540. See also the following reviews: M. Hidai; Y. Mizobe. *Top. Organomet. Chem.* **1999**, 3, 227. M. Hidai. *Coord. Chem. Rev.* **1999**, 185-186, 99.

¹⁴ M.H. Chisholm; W. Reichert. *J. Am. Chem. Soc.* **1974**, 96, 1249.

orbitals become too contracted for good π -bonding and bridged structures are again favored.”¹⁵

- What is the trend in orbitals down a triad?
- Ground state quartet (see next section)
- Stabilized by π -bonding from amido ligands

Study Questions: Does $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ obey the 18 electron rule? Does $\text{NMo}(\text{N}[\text{R}]\text{Ar})_3$? What are the d electron count and oxidation states of the compounds in this synthesis (starting from MoCl_5 , not counting the intermediates)?

Paramagnetism

Paramagnetism is “the opposite of” diamagnetism: A diamagnetic compound has all of its electrons paired, while a paramagnetic compound has some unpaired electrons.

There are several physical differences between diamagnetic and paramagnetic compounds:

- NMR line broadening, signal shifting (ligand deuteration, Evans’ method)
 - ^2H NMR signals are less broadened than ^1H NMR signals
 - Spin-only magnetic moment, $\mu_s = [n(n + 2)]^{1/2}$
- Paramagnetic compounds are drawn into a magnetic field (Guoy balance)
- Paramagnetic compounds are sometimes more reactive than diamagnetic ones

Isolobal Analogy

Roald Hoffmann: Nobel Prize (1981)

Molecular fragments are isolobal

if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar – not identical, but similar.¹⁶

What this means for the chemistry we’re currently studying:

The HOMO and the LUMO of $\text{Mo}(\text{N}[\text{R}]\text{Ar})_3$ and the HOMO and LUMO of N_2 are similar in energy, symmetry, and electronic population, so they can react with one another.

Reactivity

¹⁵ W.A. Nugent; J.M. Mayer. *Metal-Ligand Multiple Bonds*, pp. 29-32, John Wiley & Sons, New York, 1988.

¹⁶ You can read Hoffmann’s Nobel lecture here: *Angew. Chem. Int. Ed. Engl.* **1982**, 21, 711. You can read his Nobel autobiography here: <http://www.nobel.se/chemistry/laureates/1981/hoffmann-autobio.html>

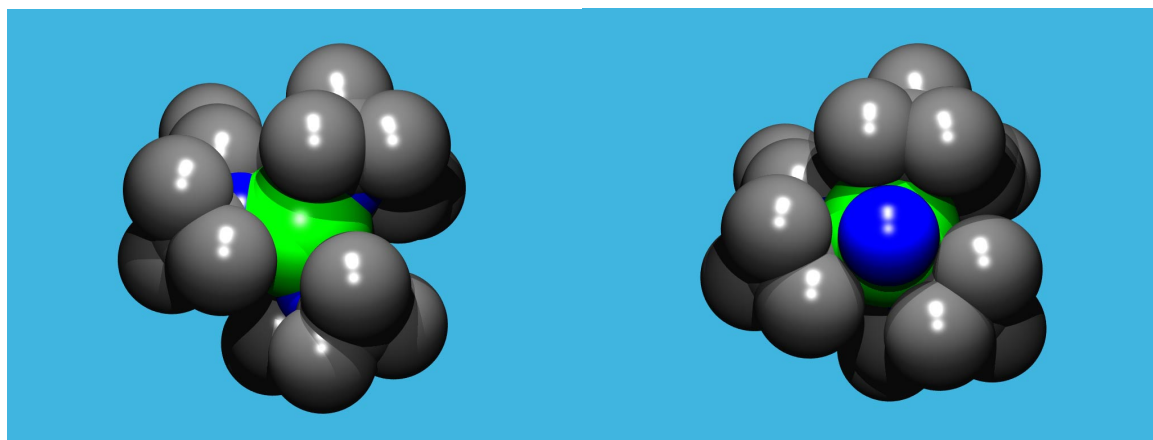
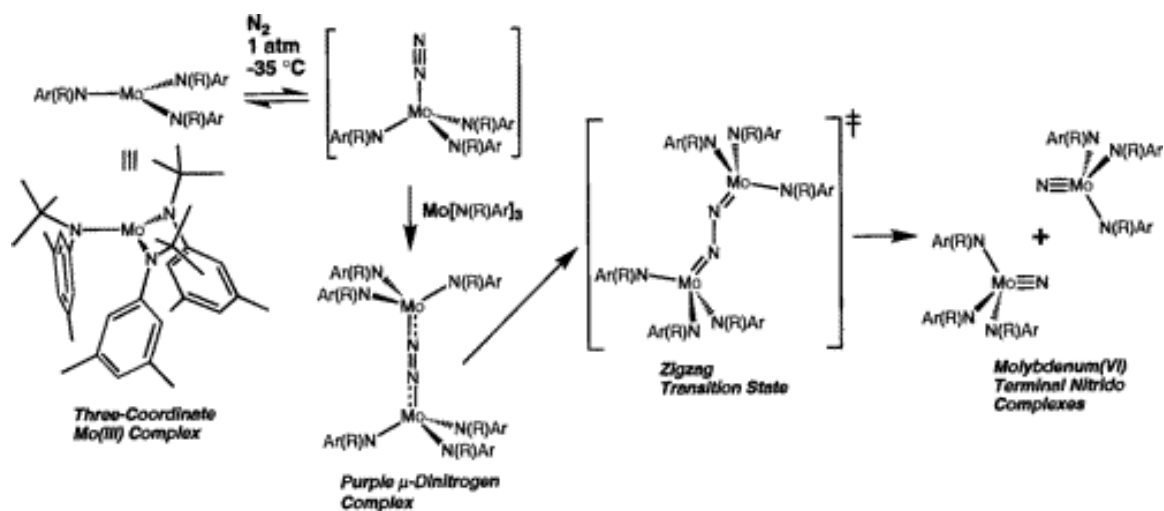


Figure 1. Left: Top view of $Mo(N[t-Bu]Ph)_3$ from X-ray crystallographic coordinates. Right: Top view of $NMo(N[t-Bu]Ph)_3$ from X-ray crystallographic coordinates.¹⁷

¹⁷ Images generated using Platon – Program for the Automated Analysis of Molecular Geometry (A.L. Spek, Utrecht University, The Netherlands, 2001) and POV-Ray for Windows (The Persistence of Vision Development Team, 1999).

Mechanism of cleavage

