A Fixation with Fixation

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Just over 100 years ago, it was finally established that biological systems are capable of fixing nitrogen (*1*). Chemists were a little further behind, but by 1913, Haber and Bosch had set up the first commercial nitrogen-fixing plant and coincidentally founded the modern chemical industry (*2*). However, the mechanisms by which these two related processes actually occur have still not been completely determined. On page 861 of this issue, Laplaza and Cummins report on a reaction that represents the culmination of 30 years of work by the chemical community and bears intimately on both of these processes. This discovery is that of a simple inorganic complex that can split the triple bond of N_2 to yield a known nitrido complex without the need for any other reagent (*3*).

Detailed work on the biological mechanism of nitrogen fixation only started with the isolation of cell-free extracts of nitrogenase in 1960 (*4*). Chemists became interested in the problem when Vol'pin described the reaction of highly reduced metal salts with N_2 in 1964 (*5*). These Vol'pin systems have been described as "nitriding systems," thereby implying that the metal ions break the very strong N≡N triple bond (*6*), but in truth, there is little evidence to support this. Notwithstanding, chemists jumped onto the nitrogen bandwagon with great glee, promising lots of cheap ammonia and consequently lots of cheap food. These promises were all hollow. Cheap ammonia is not mentioned any more, and no more it should because ammonia is cheap anyhow. The mechanism of the formation of ammonia on the Haber catalyst has still not been completely clarified, although it is evident that the rate-determining step involves the breaking of the N≡N triple bond to release nitrogen atoms. The products may be regarded as nitride ions, although whether they are formally present in the form Fe≡N is not clear (*6*). The focus of much chemical work since the discoveries of Vol'pin has been to understand how one or two metal ions could supply the six electrons required to convert N_2 to two N^{3-} ions and also supply a suitable environment to stabilize the nitrides. This dilemma is presumably less of a problem for nitrogenase, which can use a flux of protons and electrons to operate a cycle.

Until lately it had been thought that molybdenum was absolutely necessary for biological nitrogen fixation, although iron was also recognized to be required. Only recently has it become clear that vanadium may replace molybdenum in some systems and that there are nitrogenases that can function using iron alone (*7*). The necessity of a metal ion in biological nitrogen fixation suggested that complexes of dinitrogen analogous to the well-known carbonyl complexes (CO is isoelectronic with N_2) should exist, and sure enough, in 1965, the first dinitrogen complex, $[Ru(NH_3)_5(N_2)]^{2+}$, was described (*8*). It had no obvious nitrogen-fixing activity. However, it is ironic that Taube recognized the possibility of splitting the N≡N triple bond to form nitrido-complexes quite early in the game and tried to achieve this in a related osmium system (*9*). In fact, he achieved the converse, the formation of complexed N_2 from formal complexed nitride.

Many dinitrogen complexes were announced in the next few years, and they seemed to fall into three classes (*10*). The major class contained dinitrogen bonded to a metal end-on, at one end only. In this class of complex, the N-N bond length is not much greater than that in free N_2 itself, and there is little evidence of "activation." The second class contains N_2 bound end-on but bridging two metal atoms, with N-N separations that have little difference from that in free N_2. The two metal atoms are normally of the same kind. The third major class of dinitrogen complex also contains N_2 bridging two metal atoms, but in this case, the N-N separation is considerably longer than that in N_2 (see table).

What is happening is that a system M←N≡N→M in the second class is moving toward M=N–N=M. The final stage would then be M≡N N≡M, and it is this step that has finally been achieved in the simplest possible way by Laplaza and Cummins.

Once the possibility of synthesizing dinitrogen complexes had been clearly demonstrated, research was concentrated on opening up dinitrogen chemistry. It became evident that certain complexes of coordinated dinitrogen could be protonated. The foremost examples are complexes of molybdenum and of tungsten, containing N_2 bound at one end only (*11*). A sequence of protonations has been established, taking the following form: M←N_2, M–N=N–H, M=N–NH_2, M≡N–NH_3. However, it has proven impossible to break the N-N bond completely in this way without degrading the complexes entirely. The metal can provide up to four electrons, but six are necessary to reduce N_2 completely. This problem was solved by adding extra electrons from an external source, either chemically or electrochemically (*12*). This resulted in the controlled breaking of the N-N bond to generate ammonia or an amine, together with a nitrido complex, and electrochemical reduction has given rise to a cyclic system for converting dinitrogen to ammonia (*13*). This is a magnificent achievement but hardly a source of cheap ammonia.

A metal ion capable of splitting the N≡N bond should function both as a Lewis acid (electron acceptor), accepting electrons from the N_2, and should also supply electrons to weaken further, and eventually break, the N-N bond. Protons can only be electron acceptors. The class of dinitrogen complex with the long N-N bonds and the intermediates in the protonation of coordinated N_2 represent systems in which the N-N bond-breaking process has commenced but in which it cannot be finished without the intervention of further reagents. An alternative would be to use two metal ions and require them each to provide three electrons, and that is what Laplaza and Cummins have managed to do with the Lewis acid $[Mo\{NBu^t(C_6H_3Me_2\text{-}3,5)\}_3]$ (Bu, butyl).

Stretching the N-N Bond

	Compound N-N	Bond length (Å)
	N≡N	1.098(1)
Class 1	$[(NH_3)_3Os\leftarrow N\equiv N]^{2+}$	1.12(2)
Class 2	$[(NH_3)_5Ru\leftarrow N\equiv N\rightarrow Ru(NH_3)_5]^{4+}$	1.12(2)
Class 3	$[(N_2)\ (C_3Me_5)_2Zr\Leftarrow N{=}N\Rightarrow Zr(C_5Me_5)_2\ (N_2)]$	1.182(5)
Class 3	$[(Et_2)NCS_2)_3Nb\Leftarrow N{=}N\Rightarrow Nb(S_2CNEt_2)_3]$	1.252(16)
	Me–N=N–Me	1.25(2)
	H_2N–NH_2	1.454(20)
Laplaza/Cummins	$[\{(C_6H_3Me_2)\ Bu^tN\}_3Mo\equiv N]\ [N\equiv Mo\{NBu^t\ (C_6H_3Me_2)\}_3]$	No bond

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The work of Laplaza and Cummins has revealed many interesting prospects, most of which have been only aspirations, or paper chemistry, until present. One can envisage several other systems that may achieve what has been achieved here. For example, will alkoxides or thioalkoxides support this kind of chemistry? Can one cleave suitable acetylenes? Could the correct choice of ligands make the N≡N bond splitting reversible? Is it possible to form organonitriles, for example $CH_3C{\equiv}N$ from N_2 and $CH_3C{\equiv}CCH_3$? The related cleavage of dinitrogen monoxide also reported by Laplaza *et al.* (*14*) to generate a nitrido complex and a nitrosyl complex is in some ways even more surprising than the splitting of N_2.

Given that Laplaza and Cummins's N_2 reaction duplicates the major step in the Haber process but at single metal atom sites rather than on a metal surface, the question arises of the application of reactions of this kind to industrially useful transformations. The ligand framework seems to be reasonably robust and can clearly support the change of oxidation state necessary for the reduction of N_2. It is unlikely that ammonia will be an industrially attractive product from this system, although it should be easily attainable. Whatever might arise in this context, the problem of regenerating the molybdenum(III) starting material to make a cyclic system would still have to be solved. An electrochemical approach would appear to be best at this stage.

Finally, is this the way that nature fixes nitrogen, end-on between two metal atoms? I doubt it. The recent crystal structures of the larger, molybdenum-iron protein of two different nitrogenases, supposed to contain the active site at which dinitrogen is reduced, show that the molybdenum atoms could not take part simultaneously in a nitrogen reduction process such as that discovered by Laplaza and Cummins because the atoms are too far apart. It is equally unlikely that a heterometal system Mo-N_2-Fe is involved. Currently it seems most likely that nitrogenases bind N_2 at one end, presumably at molybdenum, that electrons reach the N_2 from the iron-sulfur part of the cluster, and that protons reach it from solution. This is chemistry that is 20 years old. If this is so, it means that chemists, who have for so long tried to mimic nature, have, in the persons of Laplaza and Cummins, really for the first time in this context produced something that is radically different. The next few years will be interesting indeed.

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