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Communications

Theoretical Characterization of Nitrogen Fixation: Initial Dinitrogen Activation

Sir:

The fixation of dinitrogen is a reductive process of both biological importances and large-scale industrial interest. Thermodynamically, the conversion of dinitrogen to ammonia is favored and the conversion to hydrazine is feasible for reductants slightly more active than elemental hydrogen.

In known nitrogen-reducing organisms, the catalytic reduction of dinitrogen is carried out by molybdoenzymes known as nitrogenases.[1] These nitrogen-reducing enzymes consist of two protein components: An Fe–Mo protein and an Fe protein. An iron–molybdenum cofactor has been isolated from the Fe–Mo component protein of nitrogenase. Two models of the active site have been proposed that are consistent with Mössbauer and EPR spectroscopic data[2] and an EXAFS analysis[3] of the Fe–Mo cofactor. Operationally, nitrogenase is thought to reduce dinitrogen by binding N_2 at a Mo center followed by a sequence of six one-electron reduction–protonation steps. The electrons are provided from endogenous Fe_4S_4 clusters and the protons from the surrounding medium. Unfortunately the structural models of the active site synthesized to date do not reduce dinitrogen.[4-6]

Industrially, dinitrogen reduction generally occurs over an iron catalyst at high temperatures (500 °C) and pressures (200 atm). The rate-determining step is either the dissociative chemisorption of dinitrogen[7] or the activation of dinitrogen by simple chemisorption. Both of these processes are followed by rapid reaction with hydrogen (either molecular hydrogen or chemisorbed atomic hydrogen).

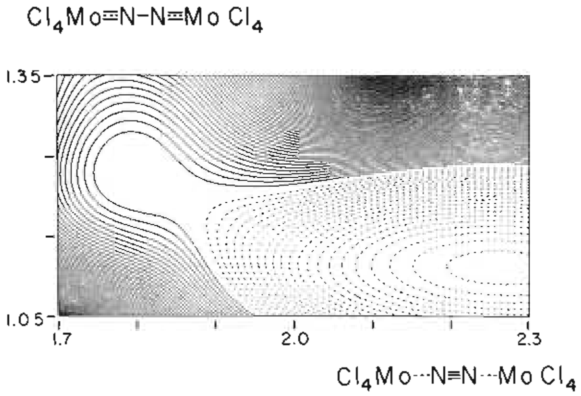


Figure 1. Two-dimensional potential energy surface for the activation of dinitrogen in $[Cl_4MoN]_2$. The energy contours are spaced 1 kcal/mol apart. The dotted contour respresents the energy of the transition state (or zero-energy contour). Dashed contours represent geometric configurations energetically more stable than the transition state. The solid contours represent geometric configurations less stable than the transition state. The abscissa represents nitrogen–nitrogen distances; the ordinate represents molybdenum–nitrogen distances.

Thus, for industrial nitrogen reduction the activation of dinitrogen is a prerequisite for reaction with reductants as mild as hydrogen. Further, for biological nitrogen reduction, activation of the dinitrogen is needed to facilitate the electron reduction steps as elemental nitrogen is not readily reduced.[8]

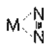
For dinitrogen-containing homogeneous transition-metal complexes, the nitrogen–nitrogen multiple bond is largely intact (nonactivated), with bonding modes **1**–**3** being observed.[8,9] The dinitrogen ligand in these compounds is only reduced by reaction with strong protic acids[8] in nonaqueous media.

$M{\cdots}N{\equiv}N$

1

$M{\cdots}N{\equiv}N{\cdots}M$

2



3

A molecular understanding of the dinitrogen-binding mode recently observed by Schrock and co-workers[10] should provide

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additional insight into biological and industrial nitrogen reduction. Valence-bond structure **4** is expected to be more

$$\mathrm{M{=}N{-}N{=}M}$$

4

reactive than valence-bond structure **2**; metal–nitrogen π bonds should be more reactive than nitrogen–nitrogen π bonds.[11] The reactivity and structural characteristics of this new class of tantalum complexes[10] suggest bonding pattern **4**. The observed Ta–N bond distance for $[\mathrm{TaCl_3(P(bz)_3)THF}]_2(\mu\text{-}\mathrm{N_2})$ of 1.769 (5) Å is only slightly longer than that found in an analogous tantalum imido complex[12] (1.747 (7) Å). In addition, reaction 1 is observed.[10]

$$\mathrm{M{\equiv}NN{\equiv}M + 2R_2C{=}O \rightarrow R_2C{=}NN{=}CR_2 + 2M{\equiv}O} \quad (1)$$

This metathesis reaction is characteristic of imido complexes[12]

$$\mathrm{M{\equiv}NR' + R_2C{=}O \rightarrow R_2C{=}NR' + M{\equiv}O} \quad (2)$$

and of metal–ligand multiple bonds in general[13]

$$\mathrm{M{=}CR'_2 + R_2C{=}O \rightarrow R_2C{=}CR'_2 + M{\equiv}O} \quad (3)$$

Finally, there is an observable lengthening of the nitrogen–nitrogen bond (a N–N bond distance of 1.282 (6) Å compared to free dinitrogen, which has a N–N bond distance of 1.09768 (5) Å[14]).

Herein we report energetic support for the kinetic and thermodynamic accessibility of **4** for $[\mathrm{Cl_4MoN}]_2$, experimentally observed but structurally uncharacterized.[15] We have determined[16] the "reaction path"[17] connecting the two resonance structures **2** and **4** (complexes **5** and **6**, respectively) within the singlet manifold. As shown in Figure 1, we find local minima characteristic of each resonance structure. This indicates that the "resonance" interaction between these two forms is not strong enough to result in a single averaged structure.[18] However, the resonance interaction is of sufficient strength to provide a very low barrier interconnecting them (less than 1 kcal/mol). Thermodynamically we find **5** to be 21 kcal/mol more stable than **6**.

In general, stablization of **4** relative to **2** can be achieved by changing the ligand backbone or metal to form stronger metal–ligand covalent bonds. For example, addition of σ-donor ligands such as phosphines, amines, or ethers such as tetrahydrofuran will expand the metal d orbitals, enhancing the overlap with the nitrogen π orbitals and thus increasing the metal–nitrogen bond strengths. Alternately, moving to tungsten, niobium, or tantalum will increase the size of the d orbitals and thus also stengthen the metal–nitrogen π bonds.[19] Finally, substitution of hard π-donor ligands such as alkoxides for the soft chloride ligands present in **5** and **6** will also expand the d orbitals and stabilize higher oxidation states[20] (increase Mo–N bond strengths).

Geometrically, the Mo–N distance for **5** was calculated to be 2.26 Å and the N–N distance 1.11 Å. These distances are consistent with resonance structure **2**. Mo–N σ-donor lengths are typically 2.1 Å,[8] suggesting that **5** contains little Mo–N multiple bonding. Further, the N–N distance for **5** is similar to that of free dinitrogen. For **6** the Mo–N distance is 1.80 Å and the N–N distance 1.23 Å. These bond distances suggest that the tetrachloride backbone is not capable of fully activating dinitrogen to resonance structure **4**. A fully activated N–N distance should be on the order of 1.30 Å,[10] and imido Mo–N distances range from 1.73 to 1.77 Å.[12] As would be expected from the energetics described above the transition state connecting **5** and **6** is only slightly distorted from **6**, the Mo–N distance is 1.86 Å, and the N–N distance is 1.20 Å.

In conclusion, we have demonstrated that high-valent Mo complexes should support the activated bonding mode of dinitrogen **4** (with a proper ligand backbone). Further, our results suggest a low kinetic barrier for its formation. Finally, we suggest that a systematic study of M–N bond strengths in $\mathrm{L_nM{=}NR}$ complexes will aid in the design of nitrification catalysts and provide insight into biological nitrogen reduction.[21]

Registry No. $\mathrm{N_2}$, 7727-37-9; $[\mathrm{MoCl_4N}]_2$, 69492-89-3.

Supplementary Material Available: Details of the wave function, basis set utilized, and total energies calculated (2 pages). Ordering information is given on any current masthead page.

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(15) (a) The complex $[\mathrm{MoNCl_4}]_2$ has been observed and characterized by IR, magnetic susceptibility, and mass spectroscopy. The molecule appears to have a Mo–N multiple bond (ν (MoN) of 1005 and 1022 $\mathrm{cm^{-1}}$). Further, the mass spectrum fragmentation pattern is consistent with a metal dimer. However, the observed effective magnetic moment of 1.63 μ_B at 297 K is consistent with one unpaired electron. (b) Liebelt, W.; Dehnicke, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *B34*, 7–9.

(16) See paragraph regarding supplementary material.

(17) For all calculations the Mo–Cl bond distance was held fixed at 2.35 Å, the N–Mo–Cl bond angle was fixed at 103°, and D_{4h} geometry was retained throughout. For a grid of 16 points the energy was calculated for **5** and **6**; the lower of the two CI energies was used in determining the potential surface plotted in Figure 1. The Mo–N distance ranged from 1.70 to 2.30 Å in steps of 0.1 Å, and the N–N distance ranged from 1.05 to 1.35 Å in steps of 0.1 Å.

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