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N₂ Reduction and Hydrogenation to Ammonia by a Molecular Iron-Potassium Complex

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Abstract

The most common catalyst in the Haber-Bosch process for the hydrogenation of dinitrogen (N₂) to ammonia is an iron surface promoted with K⁺, but soluble iron complexes have neither reduced the N-N bond of N₂ to nitride nor produced large amounts of NH₃ from N₂. We report a molecular iron complex that reacts with N₂ and a potassium reductant to give a complex with two nitrides, which are bound to iron and potassium cations. The product has a Fe₃N₂ core, implying that three iron atoms cooperate to break the N-N triple bond through a six-electron reduction. The nitride complex reacts with acid and with H₂ to give substantial yields of N₂-derived ammonia. These reactions, though not yet catalytic, give structural and spectroscopic insight into N₂ cleavage and N-H bond-forming reactions of iron.

The Haber-Bosch process is a large-scale method for catalytic reduction of dinitrogen (N₂) with dihydrogen (H₂) to give ammonia (NH₃). This process is vital for production of synthetic fertilizer, which is needed to produce food for the world's expanding population (1). Several metals catalyze the Haber-Bosch process (iron, ruthenium, osmium, uranium and cobalt-molybdenum), but iron has received the most industrial and theoretical attention due to its hardness and low cost (2–4). The most common iron catalyst is promoted by K⁺ additives, and was developed by Mittasch in 1909–1910 (2). In the century since then, chemists have studied the nature of active iron and iron/potassium surfaces, as well as the kinetics of N₂ reduction (3). These studies have shown that iron is predominantly in the zero oxidation state in the catalyst. Importantly, the rate-limiting step of the catalytic process is N₂ chemisorption and N-N bond cleavage to give surface-bound nitrides (N³⁻), which react with H₂ to form the N-H bonds in NH₃ (Fig. 1). However, many details of the bond-breaking and bond-forming steps are difficult to discern using surface science techniques: for example, how many iron atoms are involved in the N-N dissociation step, and whether the K⁺ promoter interacts with N₂ during the N-N dissociation step (4). Similar uncertainties surround postulated mechanisms for N₂ reduction by nitrogenase enzymes, which have iron (in the +2 and +3 oxidation states) at their active sites (5, 6).

Reactions of iron coordination compounds with N₂ are of interest because the products can shed light on iron-N₂ interactions in atomic detail. Though the behavior of iron atoms in a coordination compound (where they have a positive formal charge) is inevitably different than the zerovalent iron atoms on a metallic surface, coordination compounds are more

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amenable to detailed structural characterization. Unfortunately, iron coordination complexes are poor at reducing N₂ (7, 8). Known iron-N₂ complexes have not been observed to give iron-nitride products, and produce little (if any) ammonia upon exposure to acids or H₂ (9–13). Here, we report an iron/potassium system that completely cleaves the N-N triple bond of N₂ to give a product with two nitride (N³⁻) ligands derived from N₂. The N₂-derived nitride complex reacts with H₂ to give a substantial yield of ammonia. This work displays the structural characteristics of an iron-based N₂-cleaving system, and suggests that cooperation between metal atoms helps to achieve N-N bond cleavage and N-H bond formation on iron.

Consistent with their low reactivity toward N-N bond cleavage, the N-N bonds in most mononuclear and dinuclear iron-N₂ complexes are within 0.04 Å of the N-N distance in free N₂ (1.10 Å) (7, 8). A few research groups have reported significant N-N bond weakening in iron-N₂ complexes by using bulky, electron-rich ligands with N or P donors (15–17). Our research has revealed that iron-N₂ complexes with low-coordinate iron weaken the N-N bond to between 1.17 and 1.23 Å (14, 15). The greatest weakening (N-N = 1.23 Å; $\nu_{\text{N-N}} = 1589 \text{ cm}^{-1}$) is in β -diketiminato complex K₂[L¹FeNNFeL¹] (L¹ = HC[C(^tBu)N(2,6-*i*Pr₂C₆H₃)]₂⁻; Fig. 2A), which comes from treating L¹FeCl with potassium graphite (KC₈) under N₂ (15). Similar N-N weakening is observed in analogues containing the slightly less hindering L² (L² = HC[C(Me)N(2,6-*i*Pr₂C₆H₃)]₂⁻; Fig. 2B). The research reported here uses L³ (L³ = MeC[C(Me)N(2,6-Me₂C₆H₃)]₂⁻; Fig. 2C), which is less sterically hindering by virtue of having methyl rather than isopropyl groups on the aryl rings. The new iron(II) chloride complex [L³Fe(μ -Cl)]₂ (**1**) can be prepared like earlier β -diketiminato-supported iron(II) chloride complexes (18, 19).

Mixing **1** with two molar equivalents of KC₈ in tetrahydrofuran (THF) under an atmosphere of N₂ gives a red-brown tetrairon bis-nitride complex (**2**) (Fig. 2C). This product can be isolated as analytically pure crystals in 43% yield. The use of THF as reaction solvent is critical: formation of **2** is not observed by proton nuclear magnetic resonance (NMR) spectroscopy when the reaction is performed in other solvents such as pentane and toluene. No formation of **2** is observed when **1** is treated with KC₈ under an atmosphere of argon rather than N₂; instead, a mixture of unidentified products is evident. Use of ¹⁵N₂ gives an isotopically labeled product (see below), demonstrating that the nitrides originate from N₂. Solutions of purified **2** decompose to unidentified products with a half-life of 8 hours at 25 °C in benzene-*d*₆, though crystalline samples of **2** suffer no apparent decomposition when stored for up to one month at -40 °C.

X-ray crystallography shows the molecular structure of **2** (Fig. 3), which has a core of three iron centers (Fe1, Fe2, Fe3) surrounding two bridging nitrogens. The N-N distance of 2.799(2) Å indicates that there is no N-N bond; thus six-electron reduction of N₂ has given two bridging nitrides (N³⁻). One of the nitrides (N2) is attached to three irons, and the other (N1) bonds to two irons as well as two potassiums. Each potassium interacts with two chlorides and with a diketiminato aryl group through a π -cation interaction. A fourth iron center (Fe4) is bound to the chlorides, and displays a pseudotetrahedral geometry. The Fe-N distances to the potassium-bound N1 are shorter than the Fe-N distances to the triply-bridging N2, most likely from steric clashes between the three β -diketiminato ligands bound to Fe1, Fe2, and Fe3.

NMR spectroscopy suggests that the solution structure of **2** is similar to the solid-state structure. Fifteen paramagnetically shifted resonances are observed in the ¹H NMR spectrum of **2**, and the number and integrations of the resonances are consistent with C_{2v} symmetry in solution, with equivalent β -diketiminato ligands on Fe1 and Fe2. The solubility

of **2** in nonpolar solvents like hexane and diethyl ether also suggests that the potassium cations are held tightly within the structure in solution.

The zero-field Mössbauer spectrum of a crystalline sample of **2** at 80 K (Fig. 4A) indicates three different iron environments, and the isomer shifts (δ) can be used to gauge their oxidation states by comparison to literature values (Table S2). The isomer shift for subspectrum (I) ($\delta = 0.29$ mm/s) is similar to those for high-spin Fe³⁺ sites in nitride and sulfide clusters (20–22). Subspectrum (I) has twice the intensity of the other subspectra, indicating that the equivalent Fe1 and Fe2 sites are high-spin Fe³⁺. Subspectra (II) and (III) of **2** exhibit higher isomer shifts that are typical of high-spin Fe²⁺ sites. The Mössbauer parameters of subspectrum (II) ($\delta = 0.68$ mm/s, $\Delta E_Q = 1.54$ mm/s) resemble those for the planar three-coordinate Fe²⁺ complexes L¹FeNHR (R = *p*-tolyl and *tert*-butyl), which have a similar environment as Fe3 (23). Subspectrum (III) shows parameters ($\delta = 0.96$ mm/s, $\Delta E_Q = 1.80$ mm/s) that are typical of quasi-tetrahedral high-spin Fe²⁺ compounds such as L²Fe(μ -Cl)₂Li(ether)₂ (24). Comparison of the Fe-N(diketiminato) bond lengths in Fe4 to Fe²⁺ and Fe³⁺ compounds of L³ also suggests a Fe²⁺ assignment for Fe4 (Table S1). Thus signal (II) can be confidently assigned to Fe3, and signal (III) to Fe4.

The assignments of high-spin Fe³⁺ for Fe1 and Fe2, and of high-spin Fe²⁺ for Fe3 and Fe4, are corroborated by the magnetic properties of solid **2**. The temperature dependence of the magnetic moment (Fig. 4B) can be simulated using the spin topology indicated in the inset of Fig. 4B. The triad made up of Fe1, Fe2, and Fe3 has ground state $S_{123} = 3$ because of dominant antiferromagnetic coupling of S_3 to both S_1 and S_2 , which is stronger than the antiferromagnetic coupling between S_1 and S_2 . The effective magnetic moment of **2** fits the superposition of the moments from S_{123} and from the uncoupled ferrous Fe4 site, with $\mu_{\text{eff}}^2 = \mu_{\text{eff},123}^2 + \mu_{\text{eff},4}^2$ (25).

The yield of ammonia derived from N₂ upon addition of acid is a measure of N₂ activation. Some carefully designed molybdenum compounds can produce ammonia catalytically with acids (26, 27), but previous Fe-N₂ complexes have not given more than 10% yield of ammonia, indicating weak activation of coordinated N₂ (7–13, 28). In contrast, treatment of a THF solution of **2** with 100 molar equivalents of ethereal HCl gives ammonia (present as its conjugate acid, NH₄⁺) in 82 ± 4% yield. Control experiments with other complexes of L³, or N₂ complexes of other diketiminato ligands, give no detectable amount of ammonia. Reaction of **2** with acid to give a high yield of ammonia demonstrates that the N-N bond is completely cleaved and that the nitrides are nucleophilic.

The reaction of **1** with KC₈ may be carried out under an atmosphere of ¹⁵N₂ to generate isotopically labeled samples of **2**-¹⁵N. Purified **2**-¹⁵N reacts with acid to form ¹⁵NH₄⁺, which may be identified from its characteristic 1:1 doublet in the ¹H NMR spectrum. An analogous reaction with unlabeled **2** and excess acid shows a 1:1:1 triplet for ¹⁴NH₄Cl. These labeling studies verify that the nitrides in **2** come from N₂, and that the ammonia comes from these nitrides.

Iron-nitride complexes typically have terminal and bridging nitrides that are derived from reactive N sources such as N₃[−] (22). Recently reported iron clusters with triply bridging nitrides use N(SnMe₃)₃ as the nitride source (20, 21). The iron system reported here generates nitrides instead from the six-electron reduction of N₂, and we suggest two possible explanations for its N₂-reducing ability. First is the influence of the K⁺ generated from reduction of the Fe²⁺ ions in **1** by potassium graphite. On metallic iron-potassium catalysts, it is thought that surface K⁺ promotes N₂ dissociation by pulling more electron density toward the surface iron atoms (3). The interaction of K⁺ with the nitrides in our synthetic compound suggests that direct K⁺-N₂ interactions could also be considered as contributors

to the potassium promotion effect. Second, since more hindered L^1Fe and L^2Fe gave bimetallic Fe_2N_2 species without N-N cleavage (14, 15), and the less protected L^3Fe gives N-N cleavage in **2**, it is likely that the ability of more metal atoms to simultaneously access the N_2 molecule is important for N_2 cleavage. From a thermodynamic perspective, it is reasonable that the formation of more iron-nitrogen bonds can better balance the energetic cost of breaking the N-N triple bond. On iron metal, the surfaces that are most active for N_2 reduction are those with sites that expose subsurface atoms (29). N_2 bound at such a site may interact in a cooperative fashion with several iron atoms to facilitate N-N cleavage, as suggested by computational studies (30).

It is most relevant to the Haber-Bosch process to show that formation of ammonia from an iron-nitride is possible through reaction with dihydrogen (H_2). When electropositive early transition metal complexes cleave N_2 to metal-nitride complexes, the products rarely react with H_2 to give ammonia. In the best previous example, reaction of free H_2 with a well-characterized N_2 -derived zirconium nitride complex formed ammonia in 10 to 15% yield (31). Shaking a solution of **2** in toluene with 1 atm of H_2 at room temperature for 6 hours produces NH_3 in $42 \pm 2\%$ yield (Eq. 1). The main iron-containing product of the reaction of **2** with H_2 is $[L^3Fe(\mu-H)]_2$, which is generated in $85 \pm 8\%$ yield as shown by ^1H NMR spectroscopy. Thus, the soluble molecular iron system described here is capable of performing both N_2 cleavage and hydrogenation.

(1)

How do these results relate to the Mittasch iron catalyst that is used for the Haber-Bosch process? It is likely that potassium reduction of the Fe^{2+} precursor **1** leads to a high-spin Fe^{1+} intermediate, by analogy to related complexes (15). The metal in a low oxidation state can donate charge to N_2 that weakens the N-N bond, and this effect is heightened by a low coordination number at the metal (15). Surface irons on the Mittasch catalyst also have a low oxidation state and low coordination number (3), suggesting a potential parallel. In a second commonality, a molecule of N_2 may react simultaneously with multiple unsaturated iron atoms during the formation of **2** and on an iron surface. Nitrogenase uses a cluster of iron atoms to reduce N_2 (5,6), suggesting that cooperativity may be important in biological N_2 reduction as well. Thirdly, potassium has a beneficial effect on N-N bond cleavage by the Mittasch catalyst, perhaps through a direct interaction between potassium and nitrogen like that observed in **2**. Finally, we suggest that the presence of a three-coordinate iron atom near the nitrides may enable iron to split H_2 at the unsaturated site and form N-H bonds without extensive reorganization. Further studies will test these hypotheses derived from the structure and behavior of **2**.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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on Science Online. Crystallographic data for **2** (two independent structures with different solvents of crystallization), L^3FeCl_2 , $L^3FeCl_2K(18\text{-crown-}6)$, and $[L^3FeH]_2$ have been deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 836870-836874.

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Fig. 1.
Simplified scheme of the ammonia formation pathway in the Haber-Bosch process.

Fig. 2. Iron complexes with varying steric bulk give different N_2 products upon reduction by potassium (introduced as KC_8 , potassium graphite). A) Bulky ligand L^1 (14); B) Bulky ligand L^2 (15); C) Less bulky ligand L^3 (this work). tBu = *tert*-butyl.

Fig. 3.

Molecular structure of **2** using 50% probability ellipsoids. Hydrogen atoms and cocrystallized solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe1-N1, 1.812(2); Fe1-N2, 1.906(2); Fe2-N1, 1.809(2); Fe2-N2, 1.918(2); Fe3-N2, 1.832(2); Fe1-Fe2, 2.4531(4); N1-N2, 2.799(2); Fe1-N1-Fe2, 85.27(7); Fe1-N2-Fe2, 79.79(7); Fe3-N2-Fe1, 135.9(1); Fe3-N2-Fe2, 143.6(1).

Fig. 4.

A) Zero-field Mössbauer spectrum of solid **2** at 80 K. The red line is a superposition of the three Lorentzian doublets (I), (II), and (III) with intensity ratio 2:1:1. B) Temperature dependence of the effective magnetic moment of **2** measured at B = 1 T. The solid line represents a spin Hamiltonian simulation with four spins and two exchange coupling constants as indicated in the inset.