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Stepwise Reduction of Dinitrogen Bond Order by a Low-Coordinate Iron Complex

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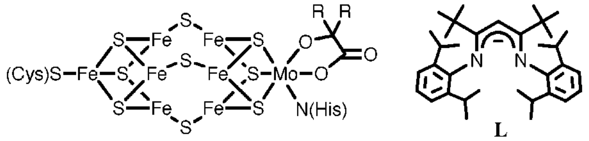
Conversion of atmospheric N_2 into NH_3 is one of the most important chemical processes, because ammonia is the industrial and biological precursor to many nitrogen-containing compounds. Large-scale transformation of N_2 and H_2 into ammonia is performed in industry by the Haber−Bosch process, using "potassium-promoted" porous iron.[1] A view of the N_2-reducing active site of iron−molybdenum nitrogenase, which contains unusual iron atoms with only three sulfur donors, is shown in Chart 1.[2] The presence of iron in the active sites of this and other nitrogenases[3] suggests that iron is again important for activating dinitrogen. Thus iron plays a major role in both natural and industrial N_2 reduction catalysis.

Paradoxically, synthetic iron/N_2 complexes are viewed as "unactivated" despite the importance of iron in the catalytic processes described above.[4] Examples of stepwise metal-promoted N_2 cleavage reactions use metals in groups 5 and 6 of the periodic table.[5] The driving force for these N−N cleavage reactions is the formation of extremely strong metal−nitride bonds. The only synthetic Fe/N_2 complex in which the N−N bond is stretched is the unusual complex $Fe[NNMo(N_3N)]_3$.[6,7] Some iron/N_2 complexes produce ammonia on decomposition, but the intermediates in this process are not known.[6,8] In this report we describe three-coordinate iron complexes that bind N_2 and weaken its N−N bond in a stepwise fashion. A combination of synthetic, structural, spectroscopic, and theoretical studies shows that a low coordination number at iron correlates with the ability to weaken N_2.

Chart 1

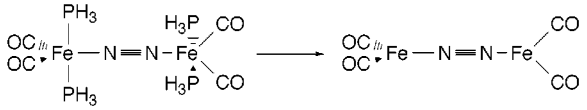


L

In the following discussion, L represents the anion shown at the right of Chart 1.[9] Reduction of the three-coordinate iron(II) complex LFeCl[10] with naphthalenide under a purified N_2 atmosphere gives a highly air-sensitive, dark red, paramagnetic compound, for which the structure LFeNNFeL was revealed by X-ray crystallography (Figure 1a).[11] This is a rare example of a three-coordinate transition-metal dinitrogen complex.[7,12] Consistent with the low coordination number at iron and/or multiple bonding (see below) between iron and N_2, the Fe−N_2 distances are extremely short (1.77−1.78 Å). The most interesting feature of this structure is that the bridging N_2 ligand is stretched substantially (N−N = 1.182(5) Å; N−N in free N_2 = 1.098 Å). The N−N elongation by almost 0.1 Å distinguishes this compound from other crystallographically characterized iron−N_2 complexes, which have N−N distances within about 0.03 Å of that in free N_2.[13,14] An intense band at 1778 cm^{-1} was observed in the resonance Raman spectrum of LFeNNFeL with 514.5 nm excitation. This band shifted to 1718 cm^{-1} in the spectrum of a sample prepared from $^{15}N_2$, consistent with a diatomic N−N oscillator whose force constant is substantially smaller than that of free N_2 (2331 cm^{-1}).[4,15] Thus, structural and spectroscopic evidence shows that iron binding has weakened the N−N bond in LFeNNFeL relative to N_2.

To evaluate the effects of coordination number on the geometry of bound N_2, we performed DFT calculations on five- and three-coordinate iron complexes. Geometry optimization of $\{Fe(CO)_2(PH_3)_2\}_2(\mu\text{-}N_2)$ gave bond lengths of Fe−N = 1.893 Å and N−N = 1.122 Å, in excellent agreement with the experimental structures of $\{Fe(CO)_2(PR_3)_2\}_2(\mu\text{-}N_2)$ (R = C_2H_5, Fe−N = 1.87(1), 1.89(2) Å, N−N = 1.13(2) Å; R = OCH_3, Fe−N = 1.876(9) Å, N−N = 1.13(1) Å).[14] Removal of all PH_3 ligands to give three-coordinate iron (Scheme 1), followed by geometry

Scheme 1. Five-Coordinate and Three-Coordinate Models Evaluated by Density-Functional Theory



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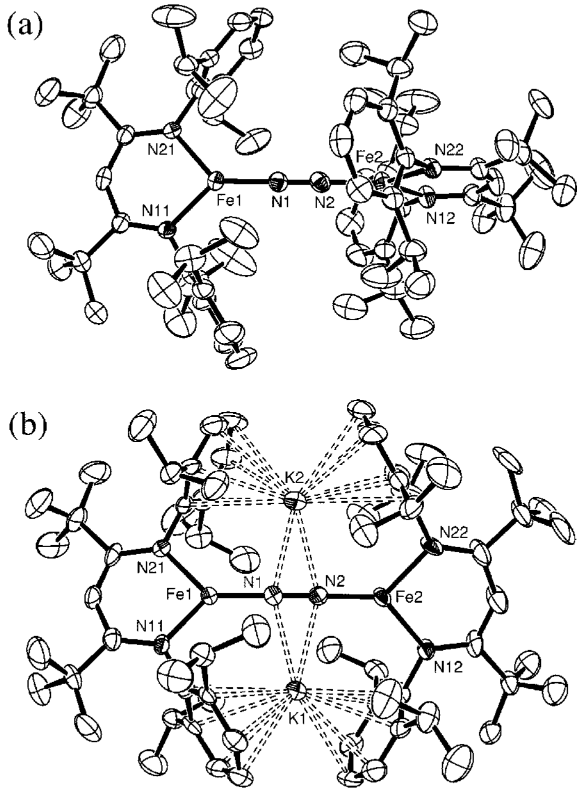

Figure 1. Thermal ellipsoid diagrams (50% probability). In each compound, the Fe−N−N−Fe core is virtually linear. (a) Key bond distances for LFeNNFeL: Fe−N(N_2) = 1.770(5), 1.779(5) Å; N−N = 1.182(5) Å. (b) Key bond distances for K_2[LFeNNFeL]: Fe−N(N_2) = 1.763(6), 1.765(6) Å; N−N = 1.233(6) Å; K−N = 2.697(6), 2.697(5), 2.701(5), 2.706(6) Å. Key bond distances for Na_2[LFeNNFeL] (not shown here; see Figure S-3): Fe−N(N_2) = 1.750(3), 1.744(3) Å; N−N = 1.239(4) Å; Na−N = 2.483(3), 2.488(3), 2.495(3), 2.484(3) Å.

optimization of the resulting $\{Fe(CO)_2\}_2(\mu\text{-}N_2)$ complex, gave Fe−N = 1.773 Å and N−N = 1.173 Å. It is apparent from the significant shortening of the Fe−N bonds (ΔFeN = −0.12 Å) and lengthening of the N−N bond (ΔNN = +0.05 Å) that the lower coordination number correlates with N_2 stretching.

The specific reasons for N−N bond weakening in LFeNNFeL were elucidated by using MCSCF calculations to determine its electronic structure. For simplicity, calculations were done on L′FeNNFeL′ (L′ = $C_3N_2H_3$), a model of LFeNNFeL in the crystallographically determined geometry stripped of alkyl and aryl groups and symmetrized to D_{2d} symmetry. The lowest energy spin state of L′FeNNFeL′ has six unpaired electrons ($^7B_3$ in the point group D_2), consistent with the solution magnetic moment for LFeNNFeL (8.4 μ_B). The nature of the orbitals in which these six electrons lie is informative (Figure 2). Each of the b_1/b_2 pairs has π-bonding character between the iron atoms and the N_2 ligand, and π-antibonding character between the nitrogen atoms of N_2. Population of these back-bonding orbitals is expected to give stronger Fe−N bonds and a weakened N−N bond, as observed experimentally.

Further reaction of LFeNNFeL with sodium or potassium metal in diethyl ether gave blue (Na) or green (K) products M_2[LFeNNFeL] (M = Na; M = K, Figure 1b) that were characterized by X-ray crystallography. In these compounds, the $[FeNNFe]^{2+}$ core of LFeNNFeL is reduced by two electrons to $[FeNNFe]^0$, and the alkali metal cations coordinate to the N_2 fragment and the aryl rings of the ligand.[16] In each compound, the combination of reduction and alkali metal coordination has lengthened the N−N bond to 1.23−1.24 Å. Vibrations at 1589 and 1123 cm^{-1} with substantial N−N stretching character were observed in K_2[LFeNNFeL] by resonance Raman spectroscopy (λ_{ex} = 406.7 nm).[17] These bond lengths and stretching frequencies are consistent with N−N double bonds.[4,15] Examination of the molecular orbital diagram in Figure 2 shows that N_2 is weakened because two additional electrons fall into the $11b_{1,2}$ orbitals with N−N antibonding character. The complex K_2[LFeNNFeL] (Figure 1b), which has two iron and two potassium atoms each coordinated to N_2, reminds one that the Haber−Bosch catalyst typically contains potassium "promoter" that is known to contribute to N_2 binding.[18]

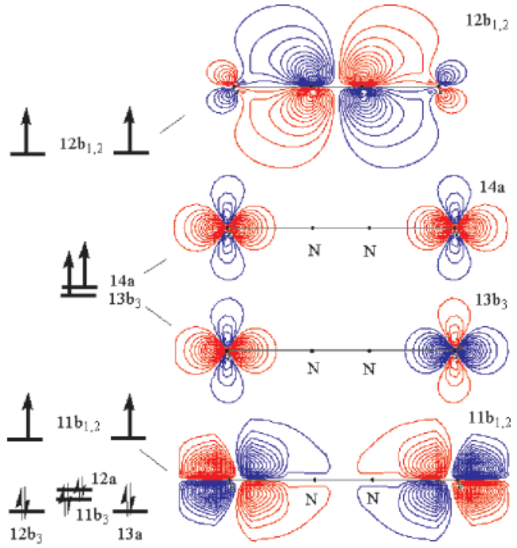

Figure 2. The frontier orbitals of **L′**FeNNFe**L′**, from MCSCF calculations under D_2 symmetry. The left side shows the relative energies of the orbitals and their occupancies; the right has contour plots of the singly occupied MO's, viewed along a 2-fold rotation axis. Both $11b_{1,2}$ and $12b_{1,2}$ are pairs of corresponding, orthogonal partners with Fe−N π-bonding and N−N π-antibonding character.

This work shows that low-coordinate iron is adept at the binding and weakening of N_2, and provides the first well-characterized example of stepwise reduction of N−N bond order by reduction of an iron complex. We are currently attempting to evaluate the N_2 reactivity brought about by the structural and electronic effects of low-coordinate metal atoms.

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Supporting Information Available: Experimental, spectroscopic, computational, and crystallographic details (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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