Cobalt−Dinitrogen Complexes with Weakened N−N Bonds

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The binding of N_2 to transition metal complexes is a topic of great interest in the chemistry community.[1] While the reactivity of N_2 complexes does not always correlate with their ground-state properties, it has proven useful to estimate "activation" of N_2 using the N−N bond length and stretching frequency, quantities that are readily measurable. One trend that has emerged is that the "early" transition metals in groups 4−6 often give N_2 complexes with weaker, longer N−N bonds, whereas N_2 complexes of the "late" transition metals in groups 8−10 have shorter, stronger N−N bonds ($d_{NN} < 1.15$ Å, $\nu_{NN} > 1900$ cm^{-1}).[2] For example, all N−N distances in satisfactory ($R < 10\%$) structures of metal−N_2 compounds of group 9 metals are less than 1.18 Å, suggesting relatively little activation.[3] This trend is consistent with the importance of π-backbonding, where the low-energy d electrons of the electronegative "late" metals are not transferred effectively to the π^* orbitals of N_2. Paradoxically, biological (nitrogenase) and industrial (Haber−Bosch) catalysts for N_2 reduction use iron, a late metal whose isolated N_2 complexes typically have little N−N weakening. The α form of N_2 on elemental Fe surfaces has an N−N stretching frequency of 1415 cm^{-1}, indicating significant weakening that has never been achieved in a synthetic complex.[4] It is not clear which properties of the catalysts enable them to achieve N−N weakening and cleavage.

Recently, we described a series of low-coordinate Fe−N_2−Fe complexes that have unprecedented weakening of the N−N bond (1.18−1.23 Å; 1583−1810 cm^{-1}) and explored their electronic structure in detail.[5] Experimental and theoretical studies showed that the N_2 weakening in these complexes arises from the unusual low-coordinate geometry at iron, which gives high-energy, singly occupied d orbitals that transfer electron density into the π^* orbitals of N_2.[6] Tetrahedral Fe−N_2−Fe complexes can also give long N−N bonds.[3g,7] Therefore, it is of interest to learn whether low-coordinate geometries would also enable cobalt, which has lower-energy d orbitals than Fe, to weaken the N−N bond of N_2 as well. Here, we report that a dicobalt(I) complex has little N−N weakening ability but that a formally dicobalt(0) complex has significant weakening of the N−N bond from backbonding.

Treatment of LCoCl (L = 2,2,6,6-tetramethyl-3,5-bis(2,6-triisopropylphenylimido)hept-4-yl)[8] with 1 equiv of KC$_8$ gives the bimetallic dinitrogen complex LCoNNCoL[9] and, with 2 equiv of reductant, gives K$_2$LCoNNCoL (Scheme 1). Reduction with metallic Na gives the analogous sodium salt Na$_2$LCoNNCoL. Each deep purple dinitrogen complex is obtained in a yield of 60−70%, and each has a 7-line ^{1}H NMR spectrum in C$_6$D$_6$ solution at room temperature that is consistent with averaged D_{2h} or D_{2d} symmetry on the NMR time scale. Solid-state magnetic susceptibility mea-

Scheme 1. Binding of Nitrogen by Low-Coordinate Cobalt
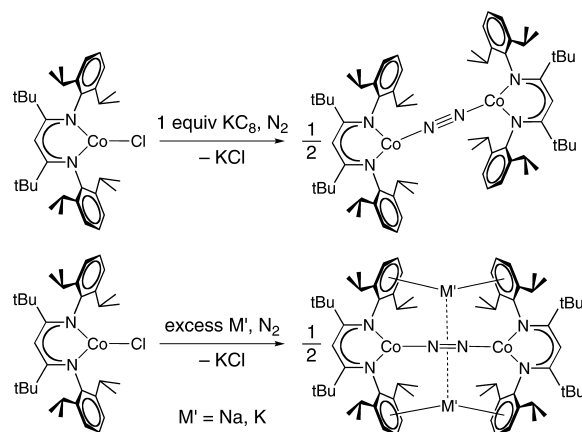
surements show that LCoNNCoL has a quintet ($S = 2$) ground state and K$_2$LCoNNCoL is a triplet ($S = 1$). Interestingly, in each case the CoNNCo group behaves as a single spin system (see Supporting Information for details).[10]

X-ray crystal structures were determined for each of the new cobalt−dinitrogen complexes. Table 1 compares the CoNNCo cores to the FeNNFe[5] and NiNNNi[11] analogues. The Co−N bonds (1.8401(8) Å) are longer than the Fe−N bonds (1.771(5) Å), and *the N−N bond is significantly shorter in the Co complex than in the Fe complex* (1.1390(15) Å for Co vs 1.189(4) Å for Fe). In the nickel analogue LNiNNNiL, the N−N bond is even shorter (1.120(4) Å). Because of the exact correspondence of ligands, it is possible to conclude unambiguously that LCo and LNi are less effective at weakening the N−N bond than LFe at this oxidation level. We attribute this difference to the lower d orbital energies of Co and Ni, which give weaker backbonding into the π^* orbital of N_2.

Another difference between the LFeNNFeL and LCoNNCoL is the geometry at the metal. The iron atoms in LFeNNFeL have local C_{2v} symmetry (Y-shaped geometry), with the N_2 ligand on the C_2 axis of the diketiminate−iron unit. However, in the Co complex, the Co atoms have a significant distortion toward a T shape, with N$_L$−Co−N$_{N2}$ angles of 101.01(3)° and 162.69(3)°. An independent crystal structure in a different space group, though poorly refining, showed a similar T distortion with N−Co−N angles of 108° and 156°, suggesting that the T distortion is not from crystal packing effects. There is a low barrier for interconversion of the T shapes in solution, because the two aryl groups of the diketiminate ligand are equivalent on the ^{1}H NMR time scale (apparent D_{2h}/D_{2d} symmetry) at temperatures from 205 to 355 K.

In contrast to these differences between formally cobalt(I) and iron(I) species, the formally cobalt(0) compounds with an [LCoNNCoL]$^{2-}$ core have metrical parameters that are similar to

Table 1. Metrical Parameters and Resonance Raman Frequencies for MNNM Cores

	N_2	$L_2Fe_2N_2{}^a$	$L_2Co_2N_2$	$L_2Ni_2N_2{}^c$	$Na_2L_2Fe_2N_2{}^b$	$Na_2L_2Co_2N_2$	$K_2L_2Fe_2N_2{}^b$	$K_2L_2Co_2N_2$	$K_2L_2Ni_2N_2{}^c$
M−N (Å)	N/A	1.770(4),1.772(4)	1.8401(8)	1.836(3), 1.830(3)	1.749(3), 1.746(3)	1.743(7), 1.735(6)	1.773(7), 1.761(7)	1.750(1)	1.747(4)
N−N (Å)	1.098	1.189(4)	1.139(2)	1.120(4)	1.213(4)	1.211(3)	1.241(7)	1.220(2)	1.185(8)
ν_{N-N} (cm^{-1})^d	2331	1778 (1718)	e	2164 (2093)	1583	1598 (1542)	1589 (1536)	1599 (1545)	1696 (1642)

^{a} Rerefinement of the original data from ref 5a; see Supporting Information. ^{b} Reference 5a. ^{c} Reference 11. ^{d} Stretching frequencies of $^{15}N_2$ isotopomers given in parentheses. ^{e} No isotope-sensitive Raman bands were observed with 514.5, 413.1, or 406.7 nm excitation.

their Fe analogues, with N−N distances of 1.21−1.22 Å (Table 1). These N−N distances are similar to the N−N double bond in azobenzene of 1.24(2) Å.[12] *These are the longest N−N distances in any cobalt dinitrogen complex*, including tetrahedral examples.[3] They are also significantly longer than the N−N bond in the nickel analogue K_2LNiNNNiL (1.185(8) Å).[11] Resonance Raman spectra (λ_{ex} = 406.7 nm) of the [LCoNNCoL]$^{2-}$ complexes in toluene solution show *bands below 1600 cm^{-1}* that shift 50−60 cm^{-1} lower in the $^{15}N_2$ isotopomer. The very low N−N stretching frequency confirms the crystallographically observed weakening of the N−N bond. Thus, even though Co is less activating than Fe in LMNNML species, it is as effective as Fe at weakening N_2 in [LMNNML]$^{2-}$ compounds. The short Co−N bonds of 1.73−1.75 Å suggest some multiple bond character from π-backbonding.[13]

Is the N−N weakening in the Co_2 dianions due to the additional electron density at cobalt or from the influence of the alkali metal cations? Because the alkali-metal-free dianions have not been isolable, DFT calculations are used to elucidate the reasons for the exceptional N−N bond weakening. Calculations use a simplified β-diketiminate ligand (L' = $C_3N_2H_5{}^-$) with a pure functional and an extended all-electron basis set, BPW91/6-311+G(d). The triplet dianion [L'CoNNCoL']$^{2-}$ optimizes to a Y-shape minimum with Co−N = 1.76 Å, N−N = 1.19 Å, and ν_{NN} = 1742 cm^{-1}. This shows that reduction alone gives significant N−N stretching, but not as much as the observed compounds. Interestingly, geometry optimization of triplet K_2L'CoNNCoL' gives a model that has excellent agreement with the experimental metrical data, with Co−*N* = 1.74 Å (expt 1.75), N−*N* = 1.22 Å (expt 1.22), and ν_{NN} = 1603 cm^{-1} (expt 1599). The presence of the potassium ions heightens the electron transfer from Co to N_2; Natural Bond Order (NBO) analyses show that the N−N bond order changes from 2.05 to 1.82 upon incorporation of the K^+ ions. Clearly, both reduction and alkali metal binding work in concert to weaken N_2, whereby the positively charged alkali metal pulls electrons into N_2.

Thus, iron and cobalt have different abilities to weaken N_2 in formally monovalent compounds and similar abilities in formally
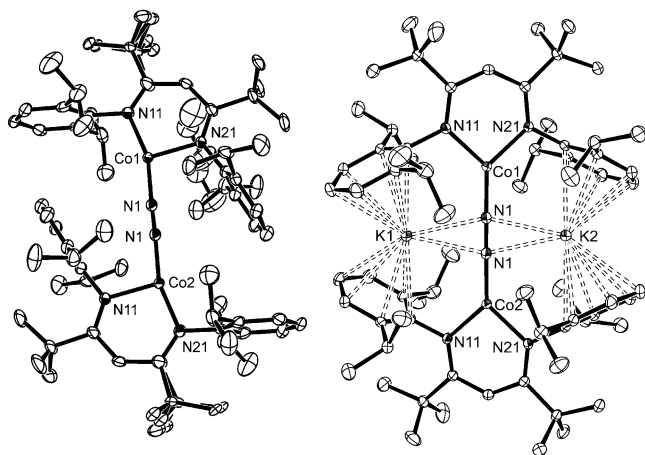
zerovalent compounds. In neutral LMNNML, Fe is significantly better than Co at backbonding into the π^* orbitals of N_2. Reduction of LCoNNCoL by two more electrons gives the first Co complex with a significantly weakened N_2 ligand, and this N−N bond weakening is similar between the formally zerovalent complexes (alkali)$_2$[LMNNML] with Fe and Co. These results demonstrate that the coordination geometry and presence of alkali metals can have a major impact on the reduction level of bound N_2, even with a more poorly backbonding metal like cobalt.

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

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Figure 1. Solid state structures of (a) LCoNNCoL and (b) K_2LCoNNCoL (right), using 50% thermal ellipsoids. Metrical parameters are in Table 1.