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Cobalt-Dinitrogen Complexes With Weakened N-N Bonds

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Abstract

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

Reported N₂ complexes of cobalt do not have substantial weakening of the N-N bond. Using diketiminate ligands to enforce three-coordinate geometries, we have synthesized several novel CoNNCo complexes. In formally univalent complexes, cobalt is poorer than iron at weakening the N-N bond, but in formally zerovalent complexes, cobalt and iron give similar N-N weakening. The weakening is due to cobalt-to-N₂ π -backbonding, and cations pull more electron density into N₂. These results show that the low coordination number of a trigonal-planar geometry is impetus enough to make even the electronegative cobalt weaken the N-N bond of N₂.

The binding of N₂ to transition metal complexes is a topic of great interest in the chemistry community.¹ While the reactivity of N₂ complexes does not always correlate with their ground-state properties, it has proven useful to estimate “activation” of the N₂ using the N-N bond length and N-N stretching frequency, which are readily measurable. One trend that has emerged is that the “early” transition metals in groups 4–6 often give N₂ complexes with weaker, longer N-N bonds, whereas N₂ complexes of the “late” transition metals in groups 8–10 have shorter, stronger N-N bonds ($d_{\text{NN}} < 1.15 \text{ \AA}$, $\nu_{\text{NN}} > 1900 \text{ cm}^{-1}$).² For example, all N-N distances in satisfactory ($R < 10\%$) structures of metal-N₂ compounds of group 9 metals are less than 1.18 $\text{\AA}$, 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 N₂. Paradoxically, biological (nitrogenase) and industrial (Haber-Bosch) catalysts for N₂ reduction use iron, a late metal whose isolated N₂ complexes typically have little N-N weakening. The α form of N₂ 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-N₂-Fe complexes that have unprecedented weakening of the N-N bond ($1.18\text{--}1.23 \text{ \AA}$; $1583\text{--}1810 \text{ cm}^{-1}$), and explored their electronic structure in detail.⁵ Experimental and theoretical studies showed that the N₂ 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 N₂.⁶ Tetrahedral Fe-N₂-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 N₂ 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(2,4,6-triisopropylphenylimido)hept-4-yl)⁸ with one equiv of K₂C₈ gives the bimetallic dinitrogen complex LCoNNCoL,⁹ and with 2 equiv of reductant gives K₂LCoNNCoL (Scheme 1). Reduction with metallic Na gives the analogous sodium salt Na₂LCoNNCoL. Each deep purple dinitrogen complex is obtained in a yield of 60–70%, and each has a 7-line ¹H NMR spectrum in C₆D₆ solution at room temperature that is consistent with averaged D_{2h} or D_{2d} symmetry on the NMR time scale. Solid-state magnetic susceptibility measurements show that LCoNNCoL has a quintet ($S = 2$) ground state, and K₂LCoNNCoL 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 FeNNFe⁵ and NiNNNi¹¹ analogues. The Co-N bonds ($1.8401(8) \text{ \AA}$) are longer than the Fe-N bonds ($1.771(5) \text{ \AA}$), and the N-N bond is significantly shorter in the Co complex than in the Fe complex ($1.1390(15) \text{ \AA}$ for Co vs. $1.189(4) \text{ \AA}$ for Fe). In the nickel analogue LNiNNNiL, the N-N bond is even shorter ($1.120(4) \text{ \AA}$). 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 $N_L-Co-N_{N_2}$ angles of $101.01(3)^\circ$ and $162.69(3)^\circ$. 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 1H 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 a $[LCoNNCoL]^{2-}$ core have metrical parameters that are similar to 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 $K_2LNiNNiL$ (1.185(8) Å).¹¹ Resonance Raman spectra ($\lambda_{ex} = 406.7$ nm) of the $[LCoNNCoL]^{2-}$ complexes in toluene solution show bands below 1600 cm^{-1} that shift 50–60 cm^{-1} 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 $\nu_{NN} = 1742\text{ cm}^{-1}$. 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 $\nu_{NN} = 1603\text{ cm}^{-1}$ (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 back-bonding 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 NN bond weakening is similar between the formally zero-valent 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 poorly backbonding metal like cobalt.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

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References and Notes

- MacKay BA, Fryzuk MD. *Chem. Rev* 2004;104:385–401. [PubMed: 14871129]
- Tuczek F, Lehnert N. *Angew. Chem., Int. Ed* 1998;37:2636–2638. Note that geometric “activation” and reactivity do not necessarily correlate. We emphasize ground-state weakening here because it is more readily quantified. See also: Leigh GJ. *Acc. Chem. Res* 1992;25:177.
- Selected cobalt complexes: a Davis BR, Payne NC, Ibers JA. *Inorg. Chem* 1969;8:2719–2728. b Hammer R, Klein HF, Schubert U, Frank A, Huttner G. *Angew. Chem* 1976;88:648–9. c Yamamoto A, Miura Y, Ito T, Chen HL, Iri K, Ozawa F, Miki K, Sei T, Tanaka N, Kasai N. *Organometallics* 1983;2:1429–1436. d Jones RA, Stuart AL, Atwood JL, Hunter WE. *Organometallics* 1983;2:1437–1441. e Bianchini C, Peruzzini M, Zanobini F. *Organometallics* 1991;10:3415–3417. f Detrich JL, Konecny R, Vetter WM, Doren D, Rheingold AL, Theopold KH. *J. Am. Chem. Soc* 1996;118:1703–1712. g Betley TA, Peters JC. *J. Am. Chem. Soc* 2003;125:10782–10783. h Scott J, Gambarotta S, Korobkov I. *Can. J. Chem* 2005;83:279–285. i Fout AR, Basuli F, Fan H, Tomaszewski J, Huffman JC, Baik M-H, Mindiola DJ. *Angew. Chem., Int. Ed* 2006;45:3291–3295. 3295
- Freund HJ, Bartos B, Messmer RP, Grunze M, Kühlenbeck H, Neumann M. *Surf. Sci* 1987;185:187–202.
- a Smith JM, Lachicotte RJ, Pittard KA, Cundari TR, Lukat-Rodgers G, Rodgers KR, Holland PL. *J. Am. Chem. Soc* 2001;123:9222–9223. [PubMed: 11552855] b Smith JM, Sadique AR, Cundari TR, Rodgers KR, Lukat-Rodgers G, Lachicotte RJ, Flaschenriem CJ, Vela J, Holland PL. *J. Am. Chem. Soc* 2006;128:756–769. [PubMed: 16417365] c Stoian SA, Vela J, Smith JM, Sadique AR, Holland PL, Münck E, Bominaar EL. *J. Am. Chem. Soc* 2006;128:10181–10192. [PubMed: 16881648]
- Holland PL. *Acc. Chem. Res* 2008;41:905–914. [PubMed: 18646779]
- Chomitz WA, Arnold J. *Chem. Commun* 2007:4797–4799.
- Holland PL, Cundari TR, Perez LL, Eckert NA, Lachicotte RJ. *J. Am. Chem. Soc* 2002;124:14416–14424. [PubMed: 12452717]
- An iron-cobalt heterobimetallic dinitrogen complex LFeNNCoL is also accessible, though it has not been crystallographically characterized. Its ^1H NMR spectrum is consistent with two inequivalent diketiminate environments. An N–N stretching vibration is present in the IR spectrum at 1806 cm^{-1} (1743 cm^{-1} with $^{15}\text{N}_2$). The N–N stretching mode is not observed in infrared spectra of LFeNNFeL or LCoNNCoL , and the observation of an infrared-active N–N band is strong evidence for the heterobimetallic complex LFeNNCoL . See the Supporting Information for characterization of this and other compounds.
- Related magnetism of an MNNM core: Curley JJ, Cook TR, Reece SY, Muller P, Cummins CC. *J. Am. Chem. Soc* 2008;130:9394–9405. 9405 [PubMed: 18576632]
- Pfaffmann S, Limberg C, Herwig C, Stösser Ziemer, B. *Angew. Chem. Int. Ed. Engl* 2009;48:3357–3361. [PubMed: 19322853]
- Harada J, Ogawa K. *J. Am. Chem. Soc* 2004;126:3539–3544. [PubMed: 15025482]
- The Co–N single bonds in LCoNNCoL are 1.83 Å , and a Co–N triple bond in a three-coordinate diketiminate complex is 1.62 Å . See: Dai X, Kapoor P, Warren TH. *J. Am. Chem. Soc* 2004;126:4798–4799. 4799 [PubMed: 15080682]

Scheme 1.
Binding of Nitrogen by Low-Coordinate Cobalt

Figure 1. Solid state structures of (a) LCoNNCoL and (b) K₂LCoNNCoL (right), using 50% thermal ellipsoids. Metrical parameters are in Table 1.

Table 1
Metrical parameters and resonance Raman frequencies for MNM 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)	1.743(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)	1.211(3)	1.241(7)	1.220(2)	1.185(8)
ν_{N-N} (cm ⁻¹) ^d	2331	1778(1718)	<i>e</i>	2164(2093)	1598 (1542)	1589 (1536)	1599 (1545)	1696(1642)

^a Re-refinement of the original data from ref ^{5a}, see Supporting Information.

^b Reference 5a.

^c Reference 11.

^d Stretching frequencies of ¹⁵N₂ isotopomers given in parentheses.

^e No isotope-sensitive Raman bands were observed with 514.5, 413.1 or 406.7-nm excitation.