DOI: 10.1002/anie.200904968

Nitrogen Radicals

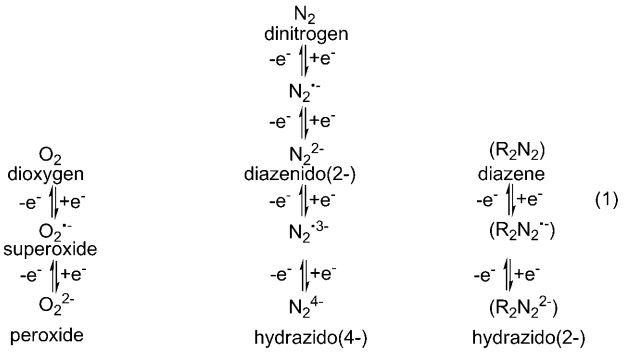
$N_2^{\bullet 3-}$: Filling a Gap in the N_2^{n-} Series

Wolfgang Kaim and Biprajit Sarkar**

coordination chemistry · nitrogen · radical complexes · rare-earth metals · superoxide analogues

Parallel to the elucidation of the heterogeneous catalytic reactions leading from adsorbed N_2 and H_2 to NH_3 under real or idealized conditions[1] and in addition to continued studies of enzymatic nitrogen fixation,[2] the primary products of N_2 reduction have received special attention as surface- or metal-stabilized molecular ions. Thus, the one-electron addition to $N_2^{\bullet -}$ [3] and the stabilization of two-electron reduced diazenido(2−) ions ("pernitride", N_2^{2-}) in solids[4] or metal complexes,[5] or of the conjugated acid H_2N_2 (diazene, "diimine") in coordination compounds[6] have been acknowledged with considerable interest.[7]

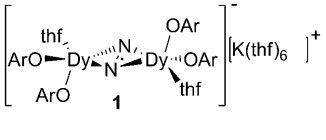
The next step leading to three-electron reduced $N_2^{\bullet 3-}$ (dinitride(3−), see Equation (1)) was not seriously considered until now, possibly because of the high negative charge in addition to the radical character. This lack of interest is surprising, however, in view of the isoelectronic relationship of $N_2^{\bullet 3-}$ with the hyperoxide (superoxide) radical anion $O_2^{\bullet -}$ which has a long-established structural[8] and coordination

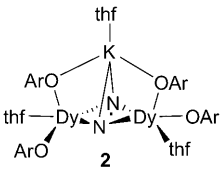


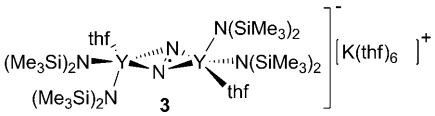
(1)

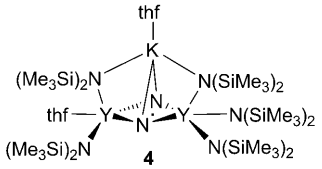
chemistry[9] and which is widely researched because of its biological and industrial relevance.[10]

Using dysprosium and yttrium complex fragments, Evans and co-workers have now observed the three-electron reduced N_2 as a bridging ligand in complexes **1**–**4** (Figure 1).[11] The compounds were obtained from N_2 and DyI_2/KOAr (OAr = 2,6-$(CMe_3)_2C_6H_3O$) or $Y[N(SiMe_3)_2]_3$/K and were









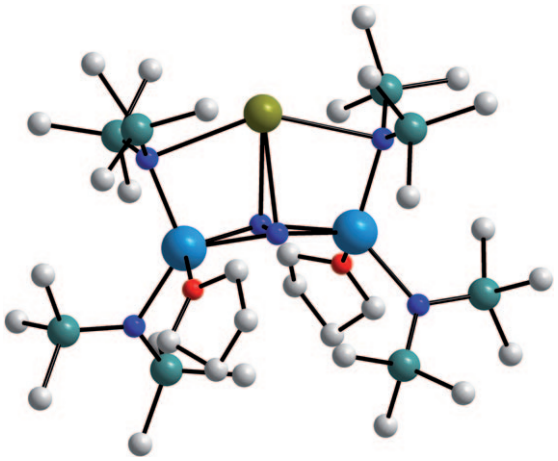
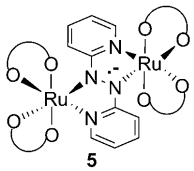


Figure 1. Molecular structure of complex **4** (solvent molecule THF omitted for clarity); gray C, yellow K, dark blue N, red O, turquoise Si, light blue Y.

[*] Prof. Dr. W. Kaim, Dr. B. Sarkar
Institut für Anorganische Chemie, Universität Stuttgart
Pfaffenwaldring 55, 70550 Stuttgart (Germany)
Fax: (+49) 711-685-641-65
E-mail: kaim@iac.uni-stuttgart.de
sarkar@iac.uni-stuttgart.de
Homepage: http://www.iac.uni-stuttgart.de/Arbeitskreise/AKSarkar/default.htm

characterized by elemental analyses, Raman and EPR spectroscopy, and by X-ray crystallography.

Like the better known $(O_2)^k$ ($k = 0,-,2-$) or $(NO)^m$ ($m = +,0,-$) redox systems,[12] N_2 is a potentially non-innocent[13a] (or "suspect"[13b]) ligand, capable of acting in different oxidation states (N_2, N_2^{2-}, N_2^{4-}) in coordination compounds.[14] The assignment of the dinitrogen ligand as the radical trianion $N_2^{\bullet 3-}$ in the compounds **1**–**4** is foremost based on the N–N bond length, although such popular[15] correlations between bond length and bond order have to be used with great care.[16] The N–N distances of about 1.40 Å[11] for **1**–**4** are in agreement with a bond order of 1.5 as observed for slightly shorter bonds in diorganodiazene (azo) radical anion complexes, such as **5**.[16]

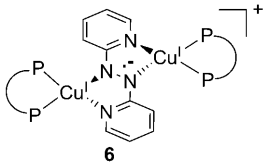


5
d(N-N) = 1.37 Å

Superoxide[8] and its metal complexes[9] exhibit still shorter element–element distances of about 1.33 Å in agreement with the lower negative charge. Metal complexes of larger radical trianion ligands are known, for instance the chlorophyll anions $[(Chl^{\bullet 3-})(Mg^{2+})]^-$ (Chl = chlorin) formed as primary electron-transfer products in photosynthesis,[17] or the dinuclear complexes of doubly deprotonated 2,5-dihydroxy-*p*-benzosemiquinones.[18]

The identification of a radical ligand like $N_2^{\bullet 3-}$ in complexes with potentially redox-active metals is not without possible pitfalls. Claims for the "stabilization of unusual molecules" such as radicals (e.g. $R_2N^{\bullet}$)[19] or radical ions (e.g. $CO_2^{\bullet -}$)[20] by metal complexation require hard evidence for the individual oxidation states of metal and ligands. For instance, the formation of metal-complex-stabilized aminyl radicals[19] has had a controversial history with respect to the alternatives $[L_nM^k(R_2N^{\bullet})]$ and $[L_nM^{k+1}(R_2N^-)]$.[19a]

In addition to the N–N bond length and further bond parameters, such as the M–N and K–N distances,[21] the assignment is supported by the Raman spectra ($\tilde{\nu}(^{14}N\text{-}^{14}N) = 1425\ cm^{-1}$ for compound **4**), MO considerations, and DFT calculations.[11] However, most indicative of an anion radical complex[22] formulation $Y^{III}(\mu\text{-}N_2^{\bullet 3-})Y^{III}$ are the EPR spectra of the paramagnetic species **3** and **4**. These show high EPR resolution, little deviation of $g = 2.0038$ from g(free electron) = 2.0023, small metal hyperfine coupling for ^{89}Y(I=1/2) of only 3.1 G but a rather large $^{14}N/^{15}N$ hyperfine splitting of 5.8/8.2 Gauss, similar to that observed for the radical complex **6**.[23] These results confirm predominantly ligand-based spin density, an assignment which is also supported by DFT calculations.[11] The dysprosium complexes **1** and **2** could not be studied in this way because of the $4f^9$ configuration of Dy^{3+} (in contrast to the $4f^0$ configuration of Y^{3+}).



6
$a(^{14}N_{azo})$ = 5.73 G

It remains remarkable that the redox and coordination chemistry of simple N_2 still offers surprises, producing unexpected, and as yet unnamed but fundamentally relevant species.[7,14] In complexes **1**–**4**, the special coordination environment, the highly ionic bonding, and the symmetry of the π-orbital on N_2 offer both steric protection and prevention of unwanted electron transfer (disproportionation). As in the $(O_2)^{k-}$ series, more extensive reduction of N_2 eventually leads to element–element bond cleavage, as was demonstrated most recently through a dissociative, five-electron reduction of dinitrogen to produce nitride species.[24] In a wider perspective, the successful identification of the missing link $N_2^{\bullet 3-}$ as the isoelectronic analogue of $O_2^{\bullet -}$ (superoxide) prompts a renewed search for $NO^{\bullet 2-}$ which is also isoelectronic with $O_2^{\bullet -}$ and is a member of the NO^m redox series of which only the $m = +$, 0, and − states are known.

Published online: November 7, 2009

[1] G. Ertl, *Angew. Chem.* **2008**, *120*, 3578; *Angew. Chem. Int. Ed.* **2008**, *47*, 3524.
[2] B. M. Hoffman, D. R. Dean, L. C. Seefeldt, *Acc. Chem. Res.* **2009**, *42*, 609.
[3] M. Chiesa, E. Giamello, D. M. Murphy, G. Pacchioni, M. C. Paganini, R. Soave, Z. Sojka, *J. Phys. Chem. B* **2001**, *105*, 497.
[4] G. V. Vajenine, G. Auffermann, Y. Prots, W. Schnelle, R. K. Kremer, A. Simon, R. Kniep, *Inorg. Chem.* **2001**, *40*, 4866.
[5] I. Vidyaratne, J. Scott, S. Gambarotta, P. H. M. Budzelaar, *Inorg. Chem.* **2007**, *46*, 7040.
[6] D. Sellmann, W. Soglowek, F. Knoch, M. Moll, *Angew. Chem.* **1989**, *101*, 1244; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1271.
[7] a) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, Chichester, **1999**, pp. 340–342; b) F. Tuczek, *Nachr. Chem. Tech.* **2006**, *54*, 1190; c) F. Studt, F. Tuczek, *Angew. Chem.* **2005**, *117*, 5783; *Angew. Chem. Int. Ed.* **2005**, *44*, 5639.
[8] H. Seyeda, M. Jansen, *J. Chem. Soc. Dalton Trans.* **1998**, 875.
[9] a) S. Schmidt, F. W. Heinemann, A. Grohmann, *Eur. J. Inorg. Chem.* **2000**, 1657; b) C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer, S. Schindler, *Angew. Chem.* **2006**, *118*, 3951; *Angew. Chem. Int. Ed.* **2006**, *45*, 3867.
[10] a) I. Ivanovic-Burmazovic, R. van Eldik, *Dalton Trans.* **2008**, 5259; b) J. Huber in *Handbook of Heterogeneous Catalysis*, *Vol. 7* (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, pp. 3359–3384.
[11] W. J. Evans, M. Fang, G. Zucchi, F. Furche, J. W. Ziller. R. M. Hoekstra, J. I. Zink, *J. Am. Chem. Soc.* **2009**, *131*, 11195.
[12] J. A. McCleverty, *Chem. Rev.* **2004**, *104*, 403.
[13] a) M. D. Ward, J. A. McCleverty, *J. Chem. Soc. Dalton Trans.* **2002**, 275; b) C. K. Jørgensen, *Coord. Chem. Rev.* **1966**, *1*, 164.
[14] B. A. Mackay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385.
[15] S. Bhattacharya, P. Gupta, F. Basuli, C. G. Pierpont, *Inorg. Chem.* **2002**, *41*, 5810.
[16] a) B. Sarkar, S. Patra, J. Fiedler, R. B. Sunoj, D. Janardanan, G. K. Lahiri, W. Kaim, *J. Am. Chem. Soc.* **2008**, *130*, 3532; b) B. Sarkar, S. Patra, J. Fiedler, R. B. Sunoj, D. Janardanan, S. M. Mobin, M. Niemeyer, G. K. Lahiri, W. Kaim, *Angew. Chem.* **2005**, *117*, 5800; *Angew. Chem. Int. Ed.* **2005**, *44*, 5655.
[17] S. E. J. Rigby, I. P. Muhiuddin, S. Santabarbara, M. C. W. Evans, P. Heathcote, *Chem. Phys.* **2003**, *294*, 319.
[18] S. Ghumaan, B. Sarkar, S. Maji, V. G. Puranik, J. Fiedler, F. A. Urbanos, R. J. -Aparicio, W. Kaim, G. K. Lahiri, *Chem. Eur. J.* **2008**, *14*, 10816.

[19] a) R. Gross, W, Kaim, *Angew. Chem.* **1985**, *97*, 869; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 856; b) T. Büttner, J. Geier, G. Frison, J. Harmer, C. Calle, A. Schweiger, H. Schönberg, H. Grützmacher, *Science* **2005**, *307*, 235; c) W. Kaim, *Science* **2005**, *307*, 216; d) R. G. Hicks, *Angew. Chem.* **2008**, *120*, 7503; *Angew. Chem. Int. Ed.* **2008**, *47*, 7393.
[20] I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A. L. Rheingold, K. Meyer, *Science* **2004**, *305*, 1757.
[21] For side-on coordination of K^+ with unreduced N_2 see S. Pfirrmann, C. Limberg, C. Herwig, R. Stößer, B. Ziemer, *Angew. Chem.* **2009**, *121*, 3407; *Angew. Chem. Int. Ed.* **2009**, *48*, 3357.
[22] a) W. Kaim, *Coord. Chem. Rev.* **1987**, *76*, 187; b) W. Kaim, *Coord. Chem. Rev.* **2001**, *219–221*, 463.
[23] S. Roy, M. Sieger, P. Singh, M. Niemeyer, J. Fiedler, C. Duboc, W. Kaim, *Inorg. Chim. Acta* **2008**, *361*, 1699.
[24] G. B. Nikiforov, I. Vidyaratne, S. Gambarotta, I. Korobkov, *Angew. Chem.* **2009**, *121*, 7551; *Angew. Chem. Int. Ed.* **2009**, *48*, 7415.