Lithium Diazenide

DOI: 10.1002/anie.201108252

High-Pressure Synthesis and Characterization of the Alkali Diazenide Li_2N_2**

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In comparison with the versatile chemistry of oxides and their extraordinary impact on mineralogy, materials science, and fundamental research, the chemistry of nitrides appears less varied and their syntheses are usually more elaborate. This observation may be a direct consequence of the high partial pressure of oxygen and the omnipresence of water on our planet. Furthermore, most solid oxides are more stable than nitrides, because chemical bonds to nitrogen are typically weaker than bonds to oxygen.[1–3] And additionally, the electron affinity of nitrogen is significantly lower than that of oxygen, rendering N^{3-} much more endothermic than O^{2-}; both anions require stabilization by counterions in the solid state.[2] Accordingly, a broad systematic investigation of nitrides had not been pursued before the last decades.[4–7]

A similar trend is observed in the variability of homonuclear molecules and ions of oxygen and nitrogen. Besides the allotropes O_2 and O_3, there are peroxides $[O_2]^{2-}$, hyperoxides $[O_2]^-$, ozonides $[O_3]^-$, and the dioxygenyl cation $[O_2]^+$.[2,8–11] In contrast, only the nitrogen allotrope N_2, nitrides N^{3-}, and azides $[N_3]^-$ have been long known.[12] It was not until 2001 that Kniep et al. proved the existence of the homonuclear dinitrogen anion $[N_2]^{2-}$, which is a deprotonated diazene N_2H_2 with a N=N bond.[13–17] These anions were accordingly named diazenides. Unexpectedly, no other binary diazenides except SrN_2 and BaN_2 have been synthesized thus far. Lately, however, the existence of the paramagnetic dinitrogen anions $[N_2]^-$ and $[N_2]^{3-}$, as well as compounds containing the pernitride ion $[N_2]^{4-}$, have been reported.[18–36]

We have been able to extend the range of diazenide composition through a novel synthetic approach employing controlled thermal decomposition of ionic azides in a multianvil device under high-pressure/high-temperature (HP/HT) conditions.[37] We thereby obtained calcium diazenide CaN_2, which is isotypic with SrN_2 and alkaline earth acetylenides crystallizing in a tetragonally distorted NaCl-type structure. To further extend the compositional range of simple metal diazenides, we turned to the investigation of the thermal decomposition of alkali azides under extreme conditions. With respect to the observation that peroxides M_2O_2 and hyperoxides MO_2 are more stable with the heavier alkali metals (M = K, Rb, and Cs),[8–10] we initially targeted synthesis of diazenides in combination with these elements. Surprisingly, we were ultimately successful with the synthesis of a diazenide of the lightest alkali metal, Li_2N_2.

Lithium diazenide was obtained under HP/HT conditions (9 GPa, 750 K) in a Walker-type multianvil assembly by decomposition of LiN_3. It is a black powder with a metallic luster and is extremely sensitive to hydrolysis.

The crystal structure of Li_2N_2 (Table 1) was determined on the basis of powder X-ray diffraction data (Figure 1).[38]

Table 1: Refined atomic coordinates and isotropic displacement factors in 0.01 Å^2 of Li_2N_2.[a]

Atoms	(Wyckoff)	*x*	*y*	*z*	U_{iso}[b]
Li1	(2a)	0	0	0	0.047(13)
Li2	(2c)	1/2	1/2	0	0.057(14)
Li3	(4i)	1/2	1/2	0.2510(6)	0.022(11)
N1	(8l)	1/2	0.1466(5)	0.62321(19)	0.0079(15)

[a] space group *Immm* (no. 71), $a = 3.1181(4)$, $b = 4.4372(4)$, $c = 10.7912(16)$ Å, $Z = 4$; [b] $U_{iso} = B_{eq}/(8\pi^2)$.

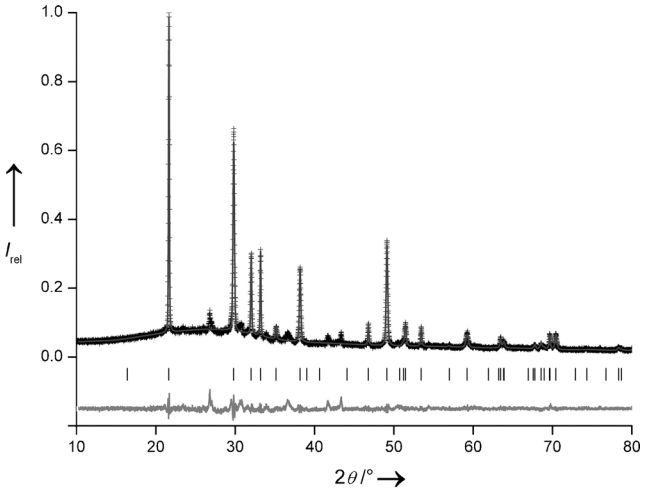

Figure 1. Observed (crosses) and calculated (gray line) powder diffraction pattern (Cu $K_{\alpha1}$ radiation, 1.54056 Å) and difference profile of the Rietveld refinement of Li_2N_2; peak positions are marked by vertical lines.[39]

Extraction of the peak positions, pattern indexing, structure solution, Fourier calculations, and Rietveld refinements were carried out with the TOPAS software package.[40] The reflections of the powder pattern were indexed in the orthorhombic crystal system and the space group *Immm* was derived.

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[**] We thank Thomas Miller (temperature-dependent in situ powder diffractometry) and Franziska Hummel (low-temperature powder diffractometry). The authors gratefully acknowledge financial support from the Fonds der Chemischen Industrie (FCI) and the Deutsche Forschungsgemeinschaft (DFG), project SCHN 377/13-2.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201108252.

Li_2N_2, the first alkali metal diazenide, represents an unprecedented structure type. The diazenide units are oriented along [010] (Figure 2) and have a bond length $d_{NN} = 1.301(3)$ Å, which is between a single- and triple-bonded dinitrogen unit. In contrast to diazene itself and the alkaline earth diazenides CaN_2, SrN_2, and BaN_2, which have N–N distances in the range of 1.20–1.24 Å,[13–17,20,37] the observed bond length in Li_2N_2 is slightly longer. This might be a direct consequence of the metallic character of this compound, as is also predicted for LaN_2 and FeN_2.[33,34]

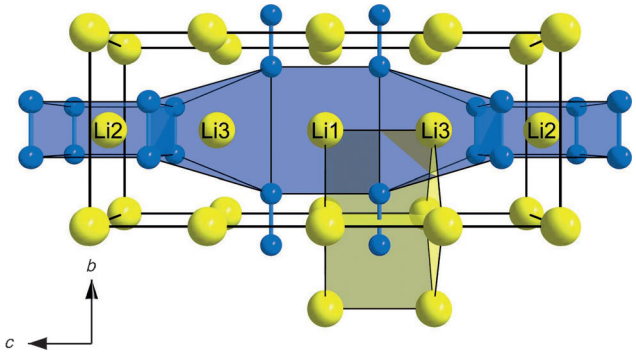

Figure 2. Unit cell of Li_2N_2 viewed along [100]. Polyhedra around Li atoms marked in blue, around diazenide unit marked in yellow; Li yellow, N blue.

The $[N_2]^{2-}$ ions are coordinated in a rhombic prism made up of eight Li atoms. Furthermore, each Li site is coordinated by the diazenide units in a different way: Li1 is coordinated in a square planar shape by four "end-on" diazenide units. Li2 is coordinated by four $[N_2]^{2-}$ ions in a "side-on" manner, resulting in an eightfold coordination, while Li3 is coordinated by two "side-on" and two "end-on" diazenides, resulting in a coordination number of six. The overall Li–Li and Li–N distances match with reported values.[41,42] According to Shannon[43], to compare the obtained Li–N distances with the sum of the ionic radii, the radius of the diazenide ion has to be evaluated first, as the ionic radii of Li^+ depends on its coordination. Starting from the structural data of the alkaline earth diazenides CaN_2, SrN_2, and BaN_2[37] we estimated the average radius of one nitrogen atom in the diazenide ion to be 1.27 Å. Based on this empirical value, the Li–N distances obtained correspond well with the sum of the ionic radii: $r(Li^+_{CN(4)}) = 0.59$, $r(Li^+_{CN(6)}) = 0.76$, and $r(Li^+_{CN(8)}) = 0.92$ Å.

Recently, Zhang et al. attempted to predict the ground-state structure of Li_2N_2, but the reported data do not match with our experimental results.[44]

Infrared spectroscopy revealed a significant feature at 1326.8 cm^{-1}, which was assigned to the N–N stretching vibration of the diazenide ion, in accordance with previous vibrational spectroscopic measurements on CaN_2, SrN (a nitride-diazenide), SrN_2, and BaN_2.[37,45]

To better understand the electronic character of Li_2N_2 and its bonding situation, first-principles calculations on the electronic structure were performed using the LMTO method.[46] As expected, the electronic band structure calculations suggest that the compound is metallic, which is in good agreement with the black color of the sample. The crystal orbital Hamilton population (COHP) plot of the N–N combination clearly shows the expected situation for the $[N_2]^{2-}$ ion: it is not surprising that, on the one hand, the states near the Fermi level are antibonding and that, on the other hand, the Fermi level crosses these states at about half of their antibonding character. These observations match well with the 50% occupation of the antibonding π states in the isolated diazenide ion.

In summary, the structural, spectroscopic, and electronic characterization of Li_2N_2 confirm it to be the first alkali diazenide and show that it crystallizes in an unprecedented structure type. Furthermore, the experimental approach that is used to generate this class of diazenides is very promising for the synthesis of even more binary compounds in the alkali–nitrogen system.

Received: November 23, 2011
Published online: January 13, 2012

Keywords: electronic structure · high-pressure chemistry · high-temperature chemistry · lithium · nitrides

[1] W. Schnick, *Angew. Chem.* **1993**, *105*, 846–858; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 806–818.
[2] A. F. Holleman, E. Wiberg in *Lehrbuch der Anorganischen Chemie*, *Vol. 102*, de Gruyter, Berlin, **2007**.
[3] G. H. Aylward, T. J. Findlay in *Datensammlung Chemie*, Verlag Chemie, Weinheim, **1975**.
[4] R. Niewa, F. J. DiSalvo, *Chem. Mater.* **1998**, *10*, 2733–2752.
[5] D. H. Gregory, *J. Chem. Soc. Dalton Trans.* **1999**, 259–270.
[6] D. H. Gregory, *Coord. Chem. Rev.* **2001**, *215*, 301–345.
[7] M. Zeuner, S. Pagano, W. Schnick, *Angew. Chem.* **2011**, *123*, 7898–7920; *Angew. Chem. Int. Ed.* **2011**, *50*, 7754–7775.
[8] N. G. Vannerberg, *Prog. Inorg. Chem.* **1962**, *4*, 125–297.
[9] I. I. Vol'nov in *Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals*, *Vol. II*, Plenum, New York, **1966**.
[10] W. Hesse, M. Jansen, W. Schnick, *Prog. Solid State Chem.* **1989**, *19*, 47–110.
[11] D. H. Lohmann, N. Bartlett, *Proc. Chem. Soc.* **1962**, *115*, 5253–5261.
[12] Recently, the pentazenium cation $(N_5)^+$ has been characterized in detail; see: K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112–2118; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004–2009.
[13] G. Auffermann, Y. Prots, R. Kniep, *Angew. Chem.* **2001**, *113*, 565–567; *Angew. Chem. Int. Ed.* **2001**, *40*, 547–549.
[14] G. V. Vajenine, G. Auffermann, Y. Prots, W. Schelle, R. K. Kremer, A. Simon, R. Kniep, *Inorg. Chem.* **2001**, *40*, 4866–4870.
[15] G. Auffermann, U. Schmidt, B. Bayer, Y. Prots, R. Kniep, *Anal. Bioanal. Chem.* **2002**, *373*, 880–882.
[16] G. Auffermann, R. Kniep, W. Bronger, *Z. Anorg. Allg. Chem.* **2006**, *632*, 565–571.
[17] Y. Prots, G. Auffermann, M. Tovar, R. Kniep, *Angew. Chem.* **2002**, *114*, 2392–2394; *Angew. Chem. Int. Ed.* **2002**, *41*, 2288–2290.
[18] S. Pfirrmann, C. Herwig, R. Stößer, B. Ziemer, C. Limberg, *Angew. Chem.* **2009**, *121*, 3407–3411; *Angew. Chem. Int. Ed.* **2009**, *48*, 3357–3361.
[19] P. J. Chirik, *Nat. Chem.* **2009**, *1*, 520–522.
[20] W. J. Evans, M. Fang, G. Zucchi, F. Furche, J. W. Ziller, R. M. Hoekstra, J. I. Zink, *J. Am. Chem. Soc.* **2009**, *131*, 11195–11202.

[21] W. Kaim, B. Sarkar, *Angew. Chem.* **2009**, *121*, 9573 – 9575; *Angew. Chem. Int. Ed.* **2009**, *48*, 9409 – 9411.
[22] W. Uhl, B. Rezaeirad, M. Layh, E. Hagemeier, E.-U. Würthwein, N. Ghavtadze, I. Kuzu, *Chem. Eur. J.* **2010**, *16*, 12195 – 12198.
[23] J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nat. Chem.* **2011**, *3*, 538 – 542.
[24] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H.-K. Mao, R. J. Hemely, *Nat. Mater.* **2004**, *3*, 294 – 297.
[25] J. von Appen, M.-W. Lumey, R. Dronskowski, *Angew. Chem.* **2006**, *118*, 4472 – 4476; *Angew. Chem. Int. Ed.* **2006**, *45*, 4365 – 4368.
[26] J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morrall, J. L. Ferreira, A. J. Nelson, *Science* **2006**, *311*, 1275 – 1278.
[27] A. F. Young, J. A. Montoya, C. Sanloup, M. Lazzeri, E. Gregoryanz, S. Scandolo, *Phys. Rev. B* **2006**, *73*, 153102.
[28] J. A. Montoya, A. D. Hernandez, C. Sanloup, E. Gregoryanz, S. Scandolo, *Appl. Phys. Lett.* **2007**, *90*, 011909.
[29] J. C. Crowhurst, A. F. Goncharov, B. Sadigh, J. M. Zaug, D. Aberg, Y. Meng, V. B. Prakapenka, *J. Mater. Res.* **2008**, *23*, 1 – 5.
[30] Z. W. Chen, X. J. Guo, Z. Y. Liu, M. Z. Ma, Q. Jing, G. Li, X. Y. Zhang, L. X. Li, Q. Wang, Y. J. Tian, R. P. Liu, *Phys. Rev. B* **2007**, *75*, 054103.
[31] R. Yu, Q. Zhan, L. C. De Jonghe, *Angew. Chem.* **2007**, *119*, 1154 – 1158; *Angew. Chem. Int. Ed.* **2007**, *46*, 1136 – 1140.
[32] W. Chen, J. S. Tse, J. Z. Jiang, *J. Phys. Condens. Matter* **2010**, *22*, 015404.
[33] M. Wessel, R. Dronskowski, *J. Am. Chem. Soc.* **2010**, *132*, 2421 – 2429.
[34] M. Wessel, R. Dronskowski, *Chem. Eur. J.* **2011**, *17*, 2598 – 2603.
[35] M. Wessel, R. Dronskowski, *J. Comput. Chem.* **2010**, *31*, 1613 – 1617.
[36] M. Wessel, PhD thesis, RWTH Aachen University, Aachen, **2010**.
[37] S. B. Schneider, R. Frankovsky, W. Schnick, *Inorg. Chem.* **2012**, DOI: 10.1021/ic2023677.
[38] Further details on the crystal structure may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de), depository number: CSD-423831.
[39] Non-indexed reflections definitively do not belong to Li_2N_2, which is confirmed by a slight variation of synthesis conditions (only a few K and about 0.5 GPa) and by temperature-dependent in situ X-ray diffractometry (see Supporting Information).
[40] A. A. Coelho, TOPAS-Academic Version 4.1, Coelho Software, Brisbane, **2007**.
[41] O. Reckeweg, A. Simon, *Z. Naturforsch. B* **2003**, *85*, 1097 – 1104.
[42] a) E. Zintl, G. Z. Brauer, *Elektrochem.* **1935**, *41*, 102; b) A. Rabenau, H. Schultz, *J. Less-Common Met.* **1976**, *50*, 155 – 159; c) N. E. Brese, M. O'Keeffe in *Structural Bonding*, *Vol. 79*, Springer, Berlin, **1992**.
[43] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751 – 767.
[44] X. Zhang, A. Zunger, G. Trimarchi, *J. Chem. Phys.* **2010**, *133*, 194504.
[45] G. Auffermann, Y. Prots, R. Kniep, S. F. Parker, S. M. Bennington, *ChemPhysChem* **2002**, *3*, 815 – 817.
[46] O. K. Andersen, O. Jepsen, Tight-Binding LMTO Version 4.7, Max-Planck-Institut für Festkörperforschung, Stuttgart, **1994**.

