Inorg. Chem. **2006**, *45*, 10786–10789

Inorganic Chemistry
Article

$Li_{80}Ba_{39}N_9$: The First Li/Ba Subnitride

Volodymyr Smetana, Volodymyr Babizhetskyy, Grigori V. Vajenine, and Arndt Simon*

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

Received July 25, 2006

The crystal structure of $Li_{80}Ba_{39}N_9$, a new representative of alkali–alkaline-earth metal subnitrides prepared from the metals and barium azide, was investigated based on single-crystal X-ray diffraction data. The compound has a novel crystal structure with a tetragonal unit cell, space group $I\bar{4}2m$, $a = 16.0763(8)$ Å, $c = 32.267(2)$ Å, $Z = 2$, and $V = 8330.0(8)$ Å^3. The structure can be described in terms of subnitride clusters with internal ionic bonding and metallic bonding in the rest of the space. The compound contains a new cluster $Li_{12}Ba_5N_6$ and polytetrahedral Li clusters based on centered Li_{13} icosahedra, which are typical for Li-rich intermetallic compounds.

Introduction

The chemistry of the most electropositive elements in the periodic table, alkali (A) and alkaline-earth (AE) metals, is dominated by saltlike valence compounds. The wealth of hypermetalated compounds, suboxides of A, and subnitrides of AE (together with A) comes as a surprise.[1] With subnitrides, barium plays a dominant role. Besides the binary phases Ba_2N[2] and Ba_3N[3], numerous metal-rich nitrides form in the presence of sodium: $NaBa_3N$,[4] Na_5Ba_3N,[5] $Na_{16}Ba_6N$,[6] and $Na_nBa_{14}CaN_6$ ($n = 7, 8, 14, 17, 21$, and 22).[7−10] All these compounds feature either isolated or condensed Ba_6N octahedra or larger $Ba_{14}CaN_6$ clusters in $Na_nBa_{14}CaN_6$, centered by CaN_6 octahedra. The main structural features of these compounds are the spatial separation of the rather ionic EA−N bonding within the subnitride clusters and the metallic bonding between these involving sodium atoms as well. The existence of the stable binary phases NaBa and Na_2Ba should be emphasized to point out the importance of metallic bonding for the stability of the Na/Ba subnitrides. The fact that no barium subnitrides with heavier alkali metals could be prepared so far has been correlated with the poor miscibility of barium and K, Rb, and Cs in the solid state. Lithium, on the other hand, forms a stable binary $BaLi_4$ and is, thus, a good candidate to stabilize Li/Ba subnitrides. In this Article, we report the synthesis and structural characterization of the first such metal-rich nitride, $Li_{80}Ba_{39}N_9$.

Experimental Section

Reagents. Ba metal (Merck, 99%, distilled twice with intermediate heating in a closed tantalum container at 1200 K in a vacuum to remove hydrogen), Li metal (Merck, 99%), and $Ba(N_3)_2$ (Schuchardt, 98.5%, recrystallized and dried under vacuum) were used for synthesis.

Synthesis. Due to the extreme sensitivity of the reagents and products to air, all handling was performed under purified argon using the Schlenk technique or a glovebox (99.996% Ar, molecular sieve, BTS catalyst (BTS is a registered trademark of the BASF Company.), <0.1 ppm H_2O, <0.05 ppm O_2). Reactions were run in closed tantalum containers, which were also sealed under argon in Duran (Pyrex-type) glass ampules. Two samples were prepared with the following overall stoichiometries: $Li_{16}Ba_6N$ (sample A: 486 mg of Ba, 22.6 mg of $Ba(N_3)_2$, and 68 mg of Li) and Li_5Ba_3N (sample B: 472.3 mg of Ba, 45.2 mg of $Ba(N_3)_2$, and 42.4 mg of Li). These were heated to 400 °C and annealed at this temperature for 25 h, followed by cooling to 120 °C at a rate of 1 $°C \cdot h^{-1}$, further annealing for one month, and cooling to room temperature by switching off the furnace. Single crystals of $Li_{80}Ba_{39}N_9$ were obtained in both samples, which were contaminated by a second phase. The latter features a powder diffraction pattern similar to that of $NaBa_3N$[11] and is likely to be another Li-containing subnitride (Figure 1). A further sample containing approximately 90 wt % of

---

* To whom correspondence should be addressed. E-mail: A.Simon@fkf.mpg.de.

[1] Simon, A. In *Molecular Clusters of the Main Group Elements*; Driess, M., Nöth, H., Eds.; Wiley-VCH: Weinheim, 2004; pp 246−266.

[2] Reckeweg, O.; DiSalvo, J. *Solid State Sci.* **2002**, *4*, 575−584.

[3] Steinbrenner, U.; Simon, A. *Z. Anorg. Allg. Chem.* **1998**, *624*, 228−232.

[4] Rauch, P.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1519−1521.

[5] Snyder, G.; Simon, A. *J. Am. Chem. Soc.* **1995**, *117*, 1996−1999.

[6] Snyder, G.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 689−691.

[7] Simon, A.; Steinbrenner, U. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2117−2123.

[8] Vajenine, G.; Simon, A. *Eur. J. Inorg. Chem.* **2001**, *2001*, 1189−1193.

[9] Vajenine, G.; Steinbrenner, U.; Simon, A. *C. R. Acad. Sci., Ser. IIc* **1999**, *2*, 583−589.

[10] Steinbrenner, U.; Simon, A. *Z. Kristallogr.* **1997**, *212*, 428−438.

[11] Smetana, V. Unpublished work.

10.1021/ic0613816 CCC: $33.50

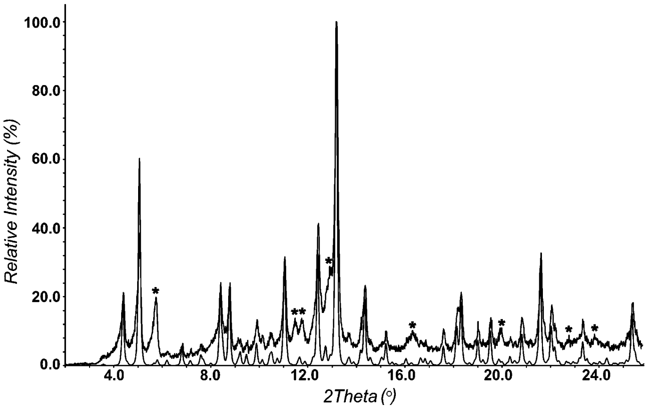

Figure 1. Measured X-ray diffraction pattern of sample A (with the overall composition $Li_{16}Ba_6N$) compared with the simulated diffraction pattern of $Li_{80}Ba_{39}N_9$. Reflections due to an impurity phase (Li-containing subnitride isostructural to $NaBa_3N$[11]) are marked with asterisks.

Table 1. Details of the Crystal Structure Investigation and Refinement for $Li_{80}Ba_{39}N_9$

empirical formula	$Li_{80}Ba_{39}N_9$
formula weight	6037.56
temperature	293 K
wavelength	0.56086 Å
crystal system	tetragonal
space group	$I\bar{4}2m$
a, Å	16.0763(8)
c, Å	32.267(2)
volume, Å^3	8330.0(8)
Z	2
density (calculated), g/cm^3	2.407
μ, mm^{-1}	4.791
F(000)	4974
2θ range	3.8° to 56.3°
index ranges	$-24 \leq h \leq 24$ $-24 \leq k \leq 24$ $-49 \leq l \leq 49$
reflections collected	27544
independent reflections	7996
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5879/0/115
GOF on F^2	1.004
final *R* indices $[I > 2\sigma(I)]^a$	R1 = 0.0395, wR2 = 0.0854
R indices (all data)	R1 = 0.0625, wR2 = 0.0934
largest diff peak and hole, e$^-$/Å^3	2.711 and −1.063

^{a} $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \sum[w(F_o^2 - F_c^2)]/[\sum(w|F_o|^2)^2]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent/Isotropic Thermal Displacement Parameters for $Li_{80}Ba_{39}N_9$

atom	position	*x*	*y*	*z*	$U_{eq/iso}$, Å^2
Ba1	2b	1/2	1/2	0	0.0347(2)
Ba2	4e	0	0	0.08566(2)	0.0298(1)
Ba3	8f	0	0.17435(3)	0	0.0294(1)
Ba4	8h	1/2	0	0.16286(1)	0.0294(1)
Ba5	8i	0.10502(3)	0.10502(3)	0.19630(1)	0.0338(1)
Ba6	8i	0.35312(3)	0.35312(3)	0.07463(2)	0.0349(1)
Ba7	8i	0.40487(3)	0.40487(3)	0.19882(2)	0.0321(1)
Ba8	16j	0.00351(3)	0.32699(2)	0.25034(1)	0.0298(1)
Ba9	16j	0.40390(3)	0.10675(3)	0.04809(1)	0.0312(1)
N1	2a	0	0	0	0.014(2)
N2	4d	0	1/2	1/4	0.013(1)
N3	4e	1/2	1/2	0.0869(2)	0.012(1)
N4	8g	0.3271(3)	1/2	0	0.011(1)
Li1	8i	0.148(1)	0.148(1)	0.3083(8)	0.064(6)
Li2	8i	0.1481(7)	0.1481(7)	0.0728(4)	0.025(3)
Li3	8i	0.255(1)	0.255(1)	0.2510(8)	0.048(4)
Li4	8i	0.298(1)	0.702(1)	0.1011(7)	0.045(4)
Li5	8i	0.377(1)	0.377(1)	0.3128(8)	0.058(6)
Li6	8i	0.4291(9)	0.5709(9)	0.1080(6)	0.043(4)
Li7	8i	0.763(1)	0.237(1)	0.0123(6)	0.045(4)
Li8	8i	0.8312(8)	0.1688(8)	0.0934(5)	0.036(3)
Li9	16j	0.002(1)	0.7489(9)	0.1244(4)	0.049(3)
Li10	16j	0.1879(9)	0.3308(9)	0.3353(4)	0.039(3)
Li11	16j	0.3511(7)	0.1475(6)	0.1781(3)	0.023(2)
Li12	16j	0.526(1)	0.238(1)	0.1311(5)	0.052(3)
Li13	16j	0.5709(9)	0.2862(9)	0.0352(4)	0.041(3)
Li14	16j	0.645(1)	0.116(1)	0.0719(6)	0.064(4)

$Li_{80}Ba_{39}N_9$ was obtained in an attempt to prepare a single-phase product according to the nominal composition.

Elemental Analysis. The chemical composition of the products was determined by energy-dispersive X-ray analysis (EDX) performed on a Tescan 5130MM scanning electron microscope (SEM) equipped with an Oxford EDX detector. Selected crystals were fixed on the SEM sample holder using carbon tape. Data was collected by applying a 20 kV accelerating voltage with an accumulation time of 60 s. The atomic ratio Ba/N in the sample ranged from 4.5:1 to 3.2:1, which corresponds to $Li_{80}Ba_{39}N_9$ or a mixture of two phases in the sample, $Li_{80}Ba_{39}N_9$ and $LiBa_3N$,[11] in good agreement with the results from X-ray diffraction analysis. A more accurate determination of the Ba/N ratio by EDX was not possible due to partial hydrolysis of the sample during transfer in air.

Crystal Structure Investigations. Single-crystal diffraction data was collected at room temperature using a STOE IPDS I diffractometer on a crystal from sample A. The crystal structure of the new subnitride was solved by direct methods and refined (SHELXS-97 and SHELXL-97[12,13]) in the space group $I\bar{4}2m$. All barium and nitrogen atoms could be refined anisotropically. The positions of the lithium atoms were found in difference Fourier maps according to reasonable interatomic distances between found and new, proposed atoms. The highest peak in the final ΔF map (2.7 e/Å^3) lies approximately 0.8 Å apart from the positions of the lithium atoms (Li(2), Li(11)). Inversion twin refinement was carried out with the resulting fraction of 53% for one of the enantiomers. Details of the crystal structure investigation are summarized in Tables 1 and 2 and in the Supporting Information.

Results and Discussion

The crystal structure of $Li_{80}Ba_{39}N_9$ is best described as a packing of four different fragments. Typical for lithium-rich phases, centered Li_{13} icosahedra (Li(4) in the center and Li(1, 6−8, 10, 12−14) in the outer shell) with additional lithium atoms present the backbone of the structure, forming an fcc-type arrangement (A sites, Figures 2A, 3, and 4). The tetragonal unit cell is the result of doubling the pseudocubic unit cell along the *c* axis, which explains the nearly $c/a \approx 2$ ratio in $Li_{80}Ba_{39}N_9$. Half of the tetrahedral voids in the A packing are filled by Ba_4 tetrahedra (Ba(5, 7, 9); B sites, Figure 2B), so that the AB packing corresponds to the zinc blende (sphalerit) structure type. The remaining tetrahedral voids in the A packing are filled in an ordered way by subnitride clusters Ba_6N (Ba(2−4, 8), N(1, 2); C sites, Figure 2C) and Ba_5N_6 (Ba(1, 6), N(3, 4); D sites, Figure 2D). Thus, the packing of the four fragments can also be regarded as an ordered variant of the fluorite structure type.

Li_{13} icosahedral fragments, also known from the interme-

---

(12) Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1997.

(13) Sheldrick, G. M. *SHELXL-97: Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.

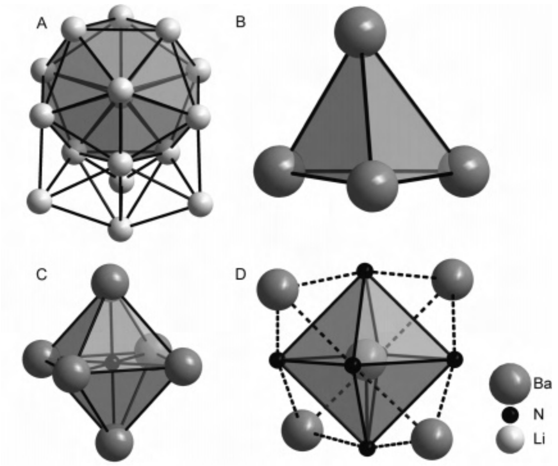

Figure 2. Structural fragments in $Li_{80}Ba_{39}N_9$: Li_{17} cluster (A), Ba_4 tetrahedron (B), Ba_6N octahedron (C), and Ba_5N_6 cluster (D).

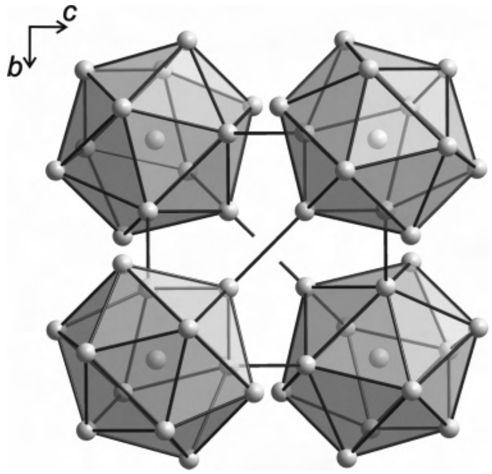

Figure 3. Tetrahedral arrangement of icosahedral Li_{13} clusters. The position in the center is taken by the Ba_5N_6 cluster (D site).

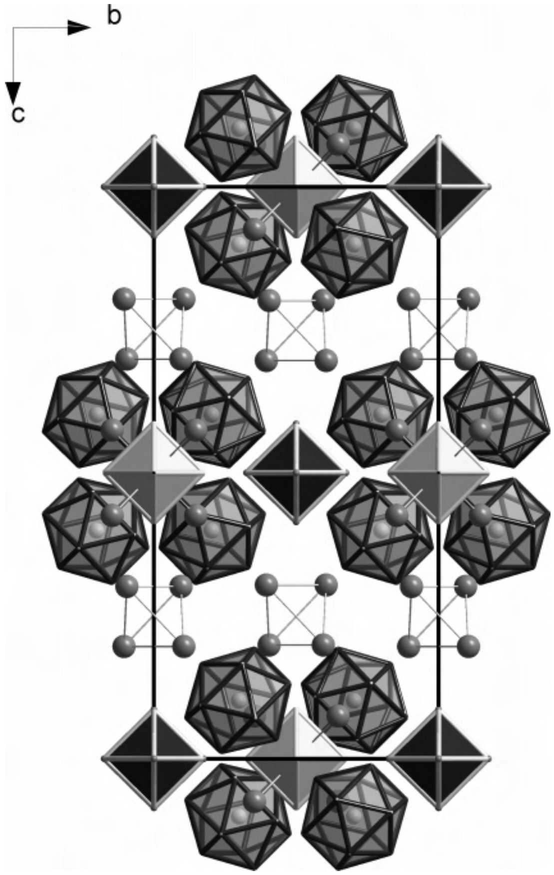

Figure 4. Location of Ba_4 (A), Ba_6N (C), and Ba_5N_6 (D) fragments in the crystal structure of $Li_{80}Ba_{39}N_9$. The tetragonal unit cell is outlined.

tallic phases $BaLi_4$[14] and $Li_{13}Na_{29}Ba_{19}$,[15] comprise the basis of the lithium framework in $Li_{80}Ba_{39}N_9$. Four additional lithium atoms (Li(3, 5, 9)) lie above four neighboring faces of the icosahedral cluster, as shown in Figure 2A. The resulting Li_{17} clusters are further interconnected by direct Li−Li bonds (Figure 3) or by monatomic lithium bridges (Li(2, 11)) into a 3D network. Eight such lithium clusters and 24 bridging atoms account for all 160 lithium atoms in the unit cell. Interatomic distances within the lithium clusters are in the range 2.92(1)−3.34(2) Å, comparable to the other lithium intermetallic compounds. Interatomic distances between these clusters lie in the range from 3.20(1) to 3.50(1) Å.

As mentioned above, the fcc-type packing of the lithium clusters leaves tetrahedral voids of various sizes. Half of these are filled by Ba_4 tetrahedra, and the other half contain Ba_6N and Ba_5N_6 subnitride clusters. So, the overall composition can be written as $A_8B_8C_6D_2 \cong Li_{160}(Ba_4)_8(Ba_6N)_6(Ba_5N_6)_2 \cong Li_{160}Ba_{78}N_{18} \cong Li_{80}Ba_{39}N_9$. This separation is instructive, but somewhat artificial, since the Ba−Ba distances between the Ba_4 tetrahedra and the subnitride clusters of 4.165(1)−4.366(1) Å are even slightly shorter than the Ba−Ba interatomic separations within the Ba_4 tetrahedra (4.323(1)−4.664(1) Å). All of these Ba−Ba distances lie in the range typical for metallic bonding unbridged by nitride anions.

Isolated octahedral Ba_6N clusters in $Li_{80}Ba_{39}N_9$ are very similar to those in $Na_{16}Ba_6N$:[6] the Ba−N distances lie in the range from 2.755(1) to 2.801(1) Å (2.825 Å in $Na_{16}Ba_6N$[6]), and the Ba−N−Ba angles deviate little from 90°, which is indicative of nearly ideal octahedral geometry. In contrast, the Ba_5N_6 clusters are observed for the first time. Here, the central barium atom is surrounded by an octahedron of nitrogen atoms, which is, in turn, capped on every second face by four additional barium atoms in a tetrahedral fashion (Figure 2D). Since each of the six nitrogen atoms has close contact with two lithium atoms of the neighboring lithium clusters, the overall composition of this novel subnitride cluster may be written as $Li_{12}Ba_5N_6$ (Figure 5d). The central part of the cluster with the BaN_6 octahedron is similar to the CaN_6 octahedron in the center of the $Ba_{14}CaN_6$ cluster found in the subnitrides $Na_nBa_{14}CaN_6$. The latter cluster can also be regarded as a six-face-sharing nitrogen-centered Ba_5-Ca octahedron with the common calcium vertex. A different description is needed for the $Li_{12}Ba_5N_6$ cluster. Here, each nitrogen atom is surrounded by a trigonal bipyramid of equatorial Ba(8), two Li(6), and two axial Ba(9) atoms. Six such polyhedra share Ba−Ba edges and one Ba vertex (equatorial to all six trigonal bipyramids), yielding the Li_{12}-

---

(14) Wang, F. E.; Kanda, F. A.; Miskell, C. F.; King, A. J. *Acta Crystallogr.* **1965**, *18*, 24−31.

(15) Smetana, V.; Babizhetskyy, V.; Vajenine, G.; Simon, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 6051−6053.

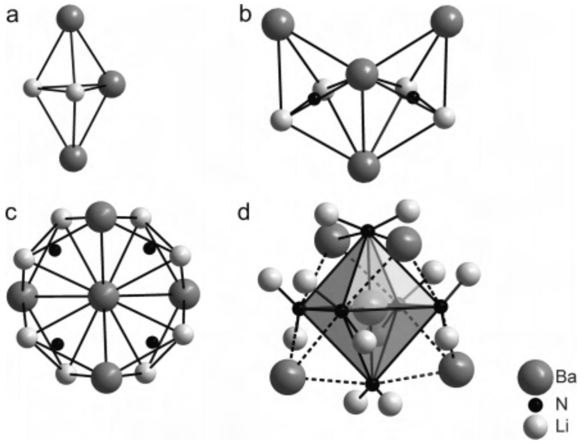

Figure 5. The $Li_{12}Ba_5N_6$ cluster in $Li_{80}Ba_{39}N_9$: pentagonal bipyramid Li_2Ba_3N (a), edge-sharing between two (b) and four (c) such fragments, and full $Li_{12}Ba_5N_6$ cluster (d).

Table 3. Interatomic Distances for the $Li_{12}Ba_5N_6$ Cluster in the $Li_{80}Ba_{39}N_9$ Compound

distance	multiplicity	length, Å
Ba(1)−N(3)	2×	2.797(6)
Ba(1)−N(4)	4×	2.780(1)
Ba(6)−N(3)	4×	3.361(1)
Ba(6)−N(4)	8×	3.392(1)
Li(6)−N(3)	4×	1.75(2)
Li(13)−N(4)	8×	1.73(1)
Ba(1)−Ba(6)	4×	4.1111(5)
Li(6)−Li(6)	2×	3.22(2)
Li(6)−Li(13)	8×	3.28(2)
Li(13)−Li(13)	4×	3.21(2)
Li(13)−Li(13)	4×	3.25(2)
Ba(1)−Li(6)	4×	3.83(2)
Ba(1)−Li(13)	8×	3.79(1)
Ba(6)−Li(6)	8×	3.86(1)
Ba(6)−Li(13)	8×	3.87(1)
Ba(6)−Li(13)	8×	3.89(1)

Ba_5N_6 cluster (Figure 5). Thus, $Li_{80}Ba_{39}N_9$ is the first example of a subnitride with nitrogen atoms bonded to both alkali and alkaline-earth metal atoms. None of the previously known subnitrides contain a Na−N bonding contact; the only examples of bonding between the nonmetal atoms and two different metal atom types in subnitrides or suboxides are $Na_nBa_{14}CaN_6$, $(Sr_{0.48}Ba_{0.52})_2N$,[16] and $Rb_{2.59}Cs_{8.37}O_3$,[17] in which the metal atoms in question are of the same valence. The Ba−Ba and Ba−N bond lengths in $Li_{12}Ba_5N_6$ (Table 3) are comparable with the bond lengths in the $Ba_{14}CaN_6$ cluster. The Ba−N and Ba−Ba distances here are in the ranges 2.42−2.85 and 3.62−4.26 Å, respectively. The Li−N distances (1.73(1)−1.75(2) Å) are shorter than those found in Li_3N[18] ($d_{Li-N} = 1.93$ Å, $CN_N = 8$); however, the nitrogen atoms in $Li_{12}Ba_5N_6$ have only three near neighbors, one of them barium, general for all, and only two barium atoms lying farther away. The Li−N distances in Li_3N under pressure[19] are $d_{Li-N} = 2.05-2.31$ Å ($CN_N = 11$).

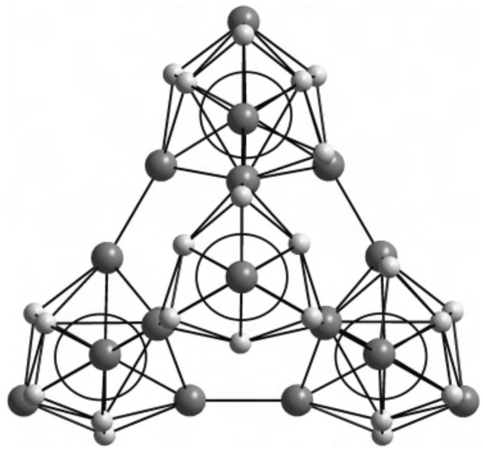

Figure 6. A fragment of the $Li_{80}Ba_{39}N_9$ structure with the voids (marked with circles).

In the structure of $Li_{80}Ba_{39}N_9$, there are also two types of voids. Some are situated in the Ba_4 tetrahedra (B site), with the distance from the center of the void to the four Ba atoms being 2 × 2.717(1) and 2 × 2.946(1) Å. The voids of the other kind are situated in the space near the tetramers of lithium icosahedral clusters. These voids are also arranged tetrahedrally (Figure 6). The distances from the center of this kind of void to the nearest three lithium atoms and two barium atoms that form a distorted trigonal bipyramid are 2.70(1), 2.72(1), 2.77(1), 3.403(1), and 3.472(1) Å, respectively. Both kinds of voids are too small to be occupied by lithium but too large for nitrogen. Such voids are quite characteristic for the compounds in the $Na_nBa_{14}CaN_6$[1] series. In $Na_7Ba_{14}CaN_6$,[8] the distances from the center of the void to the surrounding barium atoms range from 3.162 to 3.663 Å. It has been demonstrated[7] that these voids do not contain undetected light atoms, particularly hydrogen. They are rather a consequence of the packing of rigid clusters with soft contacts between them, and hence, they become particularly obvious for small values of *n*.

In conclusion, the first Li/Ba subnitride $Li_{80}Ba_{39}N_9$ has been synthesized from the metals and barium azide. The compound has a complex crystal structure with ionically bonded subnitride clusters in a metallic environment. Its structure can be regarded as an fcc packing of polytetrahedral lithium clusters with Ba_4, Ba_6N, and Ba_5N_6 fragments in the tetrahedral voids of the packing. The last mentioned fragment belongs to the novel $Li_{12}Ba_5N_6$ subnitride cluster. $Li_{80}Ba_{39}N_9$ is the first example of a metal-rich nitride in which both the mono- and divalent metal atoms are bonded to the nitrogen atoms.

Supporting Information Available: Details of the crystal structure investigation. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0613816

---

(16) Reckeweg, O.; DiSalvo, F. J. *Solid State Sci.* **2002**, *4*, 575−584.

(17) Deiseroth, H.-J.; Simon, A. *Rev. Chim. Miner.* **1983**, *20*, 475−487.

(18) Schulz, H.; Schwarz, K. *Acta Crystallogr., Sect. A* **1978**, *34*, 999−1005.

(19) Beister, H. J.; Haag, S.; Kniep, R.; Stroessner, K.; Syassen, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1101−1103.