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· Communication

On the Composition and Crystal Structure of the New Quaternary Hydride Phase Li$_4$BN$_3$H$_{10}$

Yaroslav E. Filinchuk,*,† Klaus Yvon,† Gregory P. Meisner,‡ Frederick E. Pinkerton,‡ and Michael P. Balogh§

Laboratory of Crystallography, University of Geneva, 24 quai Ernest Ansermet, CH-1211 Geneva, Switzerland, Materials and Processes Laboratory and Chemical and Environmental Sciences Laboratory, General Motors Research & Development Center, 30500 Mound Road, Warren, Michigan 48090-9055

X-ray data on single crystals of the quaternary metal hydride near the composition LiB$_{0.33}$N$_{0.67}$H$_{2.67}$, previously identified as "Li$_3$BN$_2$H$_8$", reveal that its true composition is Li$_4$BN$_3$H$_{10}$. The structure has body-centered-cubic symmetry [space group $I2_1$3, cell parameter a = 10.679(1)–10.672(1) Å] and contains an ordered arrangement of BH$_4^-$ and NH$_2^-$ anions in the molar ratio 1:3. The borohydride anion has an almost ideal tetrahedral geometry ($\angle$H–B–H ~ 108–114°), while the amide anion has a nearly tetrahedral bond angle ($\angle$H–N–H ~ 106°). Three symmetry-independent Li atom sites are surrounded by BH$_4^-$ and NH$_2^-$ anions in various distorted tetrahedral configurations, one by two B and two N atoms, another by four N atoms, and the third by one B and three N atoms. The Li configuration around B is nearly tetrahedral, while that around N resembles a distorted saddlelike configuration, similar to those in LiBH$_4$ and LiNH$_2$, respectively.

A new quaternary hydride phase having the approximate composition LiB$_{0.33}$N$_{0.67}$H$_{2.67}$, corresponding to the stoichiometry "Li$_3$BN$_2$H$_8$", was reported recently.[1] The compound was prepared by reacting LiNH$_2$ and LiBH$_4$ powders in a 2:1 molar ratio by ball milling or by heating of the mixed powders above 95 °C. It was stable at room temperature, melted at ~190 °C, and released 10 wt % hydrogen above ~250 °C. This composition was found to be optimum for maximum hydrogen and minimum ammonia release,[2] and a new body-centered-cubic phase was identified from powder X-ray diffraction data, but the exact composition and crystal structure of the new quaternary phase were not determined.

* To whom correspondence should be addressed. Present address: SNBL at ESRF, BP-220, 38043 Grenoble, France. E-mail: Yaroslav.Filinchuk@ esrf.fr.
† University of Geneva.
‡ Materials and Processes Laboratory, General Motors.
§ Chemical and Environmental Sciences Laboratory, General Motors.
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Table 1. Crystal Data, Details of Data Collection, and Structure Refinement for Li$_4$BN$_3$H$_{10}$

	empirical formula	
	domain 1	domain 2
fw	90.68	90.68
space group, Pearson code	$I2_1$3, cI144	$I2_1$3, cI144
Wyckoff sequence	c^{4}b^{2}a^3	c^{4}b^{2}a^3
a (Å)	10.6794(10)	10.6723(10)
V (Å^3)	1218.0(2)	1215.6(2)
Z, D_c (g·cm^{-3})	8, 0.989	8, 0.991
$F(000)$	384	384
$2\theta_{max}$ (deg), completeness (%)	53.3, 99.2	53.4, 98.8
R_{int}, R_σ	0.1236, 0.0527	0.1027, 0.0466
reflns collected, unique	3541, 440	3290, 438
data, restraints, parameters	440, 0, 42	438, 0, 42
final R indices [$I > 2\sigma(I)$]	R1 = 0.0322	R1 = 0.0304
	wR2 = 0.0807	wR2 = 0.0701
R indices (all data)	R1 = 0.0331	R1 = 0.0347
	wR2 = 0.0812	wR2 = 0.0714
GOF on F^2	1.123	1.101
$(\Delta/\sigma)_{max}$	0.000	0.000
largest diff. peak and hole/e·Å^{-3}	0.12(2)/−0.07(2)	0.09(2)/−0.08(2)

Here we report X-ray data on single crystals of that phase and show that it crystallizes with body-centered-cubic symmetry and has the composition Li$_4$BN$_3$H$_{10}$.

Samples were prepared at the General Motors laboratory from 2:1 mixtures of LiNH$_2$ and LiBH$_4$ by the previously reported procedure.[1,2] The reaction products were enclosed in sealed capillary tubes, remelted, and examined on a powder X-ray diffractometer. The results indicated that the sample consisted mainly of the previously reported phase,[1] except that it also contained some additional Li$_2$O impurity and possibly some unreacted LiNH$_2$ and LiBH$_4$. The grain size was sufficiently large to envision a structure analysis by single-crystal diffraction. The best specimens were selected and examined in Geneva on a single-crystal X-ray diffractometer. All manipulations were done in an argon-filled glovebox because the material was moisture-sensitive and readily decomposed to liquid in air. Diffraction intensities collected on a segment of a capillary were interpreted by five randomly intergrown domains, and the structure was solved by global optimization and refined independently for
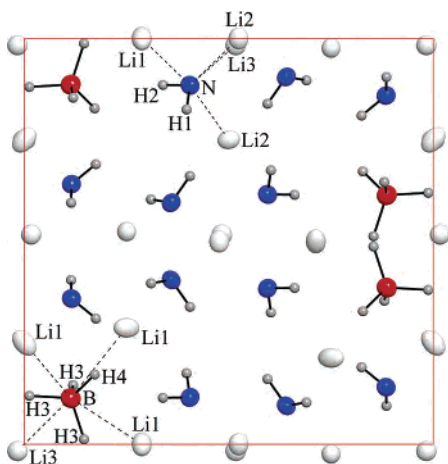
Figure 1. Projection of the $Li_4BN_3H_{10}$ structure on the (001) plane. Only half of the body-centered unit is projected for clarity; arrangement of Li atoms around B and N is highlighted by dashed lines.

Table 2. Atomic Coordinates and Displacement Parameters in $Li_4BN_3H_{10}$

atom	Wyckoff site	x	y	z	$U_{eq/iso}$, Å^2
		Domain 1			
N	24c	0.11536(7)	0.35931(7)	0.40525(9)	0.0264(3)
B	8a	0.11360(10)	x	x	0.0298(4)
Li1	12b	0.2871(2)	0	1/4	0.0402(6)
Li2	12b	0.5237(2)	0	1/4	0.0306(6)
Li3	8a	0.48330(16)	x	x	0.0305(7)
H1	24c	0.1751(17)	0.3100(16)	0.3969(16)	0.059(4)
H2	24c	0.1145(14)	0.4051(14)	0.3391(16)	0.049(4)
H3	24c	0.0123(14)	0.1194(14)	0.1460(12)	0.057(4)
H4	8a	0.1721(14)	x	x	0.049(7)
		Domain 2			
N	24c	0.11531(8)	0.35935(7)	0.40537(9)	0.0260(3)
B	8a	0.11373(10)	x	x	0.0291(4)
Li1	12b	0.2864(3)	0	1/4	0.0403(7)
Li2	12b	0.5234(2)	0	1/4	0.0307(6)
Li3	8a	0.48356(17)	x	x	0.0293(7)
H1	24c	0.1757(17)	0.3099(17)	0.3985(19)	0.057(4)
H2	24c	0.1141(14)	0.4018(15)	0.3378(16)	0.046(4)
H3	24c	0.0147(14)	0.1161(15)	0.1488(13)	0.053(4)
H4	8a	0.1739(17)	x	x	0.052(7)

the two largest domains.[3] Crystal data and details of data collection[3] and structure refinement[3] for the two largest domains are given in Table 1. Atomic positions as standardized by the STRUCTURE TIDY program[4] are listed in Table 2.

Our structural results indicate that the true composition of the quaternary hydride, hitherto known as "$Li_3BN_2H_8$",[1,2] is $Li_4BN_3H_{10}$. The structure contains an ordered arrangement of borohydride (BH_4^-) and amide (NH_2^-) anions in the molar ratio 1:3, as shown in Figure 1.

The borohydride anion has an ideal tetrahedral geometry with average B−H bond lengths of ∼1.12 Å (see Table 3), which are consistent with those observed in $LiBH_4$[5] and Be-$(BH_4)_2$.[6] On the other hand, the very short N−H bonds in the amide anion (∼0.84 Å) are clearly biased by the strong polarization of the electron cloud along the H−N bond direction. A similar bias occurs in lithium amide $LiNH_2$,[7] for which anomalously short N−H bond distances of 0.70−0.76 Å were found by X-ray diffraction as compared to the theoretically predicted value of 1.03 Å.[8] The H−N−H angle in the present compound is close to tetrahedral. The shortest

Table 3. Interatomic Distances (Å) and Angles (deg) in $Li_4BN_3H_{10}$

	domain 1	domain 2
	Intramolecular Values	
N−H1	0.83(2)	0.84(2)
N−H2	0.859(17)	0.852(18)
H1−N−H2	106.2(15)	105.9(17)
B−3×H3	1.137(15)	1.121(15)
B−H4	1.08(3)	1.11(3)
H3−B−H3	108.9(10)	109.2(11)
H3−B−H4	110.0(7)	109.8(8)
	Intermolecular Values	
N−Li3	2.0689(13)	2.0678(14)
N−Li1	2.1147(16)	2.1127(16)
N−Li2	2.1166(15)	2.1189(18)
N−Li2	2.1571(16)	2.1568(16)
B−Li3	2.410(3)	2.406(3)
B−3×Li1	2.651(2)	2.642(2)

H⋯H contact occurs within the amide anion (1.35 Å), which, however, increases to a value greater than 1.6 Å if the H atoms are placed at the theoretically expected N−H bond lengths. The shortest intramolecular H⋯H contacts in the borohydride anion are 1.82−1.85 Å, while the intermolecular H⋯H contacts are all longer than 2.4 Å.

(3) The capillary was mounted on a Stoe IPDS II diffractometer equipped with an image-plate detector and a Mo X-ray tube. The segment giving the best individual diffracting spots and practically no Debye rings was selected for measurement. 180° ω oscillation images with an increment of 1° were collected at 20 °C with 1 min of exposure and a crystal-to-detector distance of 120 mm. All diffraction intensities could be indexed[3a] by assuming five randomly intergrown domains, each possessing a body-centered-cubic lattice with $a \sim 10.7$ Å. The four largest domains were accounted for during the intensity integration. Although overlapping intensities were omitted, highly redundant data sets (∼99% completeness; on average 13 equivalents per unique reflection) were obtained for two domains. The data were corrected for Lorentz factor and polarization effects. Absorption correction was not applied. Cell parameters were obtained by a least-squares refinement based on reflection angles in the range of $4 < 2\theta < 54°$. No significant variation of the average intensity during the measurement was observed. The merging R factor suggested Laue symmetry $m\bar{3}$, and the systematic absences indicated the possible space groups $I23$, $I2_13$, and $Im\bar{3}$. Structure solution by direct methods[3b] at the nominal composition $Li_3BN_2H_8$, $Z = 10$, failed for all three space groups. However, a satisfactory model was obtained by FOX[3c] in space group $I2_13$, by allowing an excess of N, B, and Li atoms. The latter were partially merged during global optimization, yielding one N, one B, and three symmetry-independent Li atom sites. Subsequent difference Fourier maps[3b] revealed four H atom positions. At this stage, the true composition of the domains turned out to be $Li_4BN_3H_{10}$ with eight formula units per cell ($Z = 8$), yielding a calculated density of 0.99 g·cm^{-3}, which was close to the experimental value of 0.96 g·cm^{-3}.[1] A full-matrix least-squares refinement on F^2 was performed on positional and thermal parameters for all atoms (anisotropic for N, B, and Li) by using SHELXL-97.[3b] Neutral atom scattering factors were used, yielding refined occupancies that were very close to 100%. Reduced cell calculations and a noncrystallographic symmetry check (PLATON, 2003)[3d] did not indicate higher lattice symmetry or missed symmetry elements. A small twin component (<1%) related to the main domain by a 2-fold axis at 1/2, 1/2, 0 (supergroup $I4_132$) was modeled with an extra parameter. No warnings for twinning or superstructure were observed thereafter. Because of the absence of anomalous scatterers for Mo Kα radiation, an absolute structure could not be determined. (a) Stoe & Cie, X-RED and X-Area Software; Stoe & Cie: Darmstadt, Germany, 2003. (b) Sheldrick, G. M. SHELXS97 and SHELXL97. Programs for the solution and refinement of crystal structures; University of Göttingen: Göttingen, Germany, 1997. (c) Favre-Nicolin, V.; Cerny, R. J. Appl. Crystallogr. 2002, 35, 734. (d) Spek, A. L. PLATON. A Multipurpose Crystallographic Tool; University of Utrecht: Utrecht, The Netherlands, 2003.
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Three symmetry-independent Li atom sites are surrounded by BH_4^- and NH_2^- anions in various distorted tetrahedral configurations. Li1 is surrounded by two B and two N atoms, Li2 by four N atoms, and Li3 by one B and three N atoms. The shortest Li−H distance slightly exceeds 2 Å; the shortest Li···Li contact is 2.499(2) Å.

The Li atoms are distributed unequally around the BH_4^- and NH_2^- anions. The Li configuration around B is nearly tetrahedral [Li−B−Li bond angle = 100.79(5)−117.17(4)°], while that around N resembles a distorted saddlelike configuration, similar to those in $LiBH_4$[5] and $LiNH_2$,[7] respectively (see Figure 1 and Table 3). The structures of tetragonal $LiNH_2$ and cubic $Li_4BN_3H_{10}$ are actually closely related to each other. The former can be described in terms of a cubic-face-centered (Cu-type) sublattice made of NH_2 groups, in which the N atoms are centering cubes of four Li atoms and four Li vacancies and have a saddlelike Li_4 environment. In the $Li_4BN_3H_{10}$ structure, one-quarter of the NH_2 groups are replaced by BH_4^- anions in an ordered manner. This substitution induces a rearrangement of the Li atoms and Li vacancies within the B-centered cubes, so that the Li_4 environment for the B atoms becomes tetrahedral. The fact that in the quaternary hydride $Li_4BN_3H_{10}$ the BH_4 and NH_2 environments are closely similar to those in the corresponding ternary hydrides $LiBH_4$ and $LiNH_2$, while the Li sublattice is strongly influenced by the nature of the surrounding anions, suggests that the $Li···NH_2^-$ and $Li···BH_4^-$ interactions are structure-determining. Extra evidence for the Li···anion interactions was obtained from a residual electron density map as calculated from the experimental diffraction data and the final structure. The five highest peaks in that map were

Table 4. Difference Electron Density Peaks in $Li_4BN_3H_{10}$ (Domain 1)

no.	e·Å^{-3}	x	y	z	nearest neighbors, Å
1	0.12	0.0585	0.3101	0.4696	N, 1.06; Li2, 1.07
2	0.12	0.3472	−0.0538	0.1945	N, 1.07; Li1, 1.05
3	0.11	0.5810	0.0376	0.1812	N, 1.13; Li2, 1.04
4	0.08	0.0770	0.4177	0.4646	N, 0.98; Li3, 1.10
5	0.08	0.5434	0.5434	0.5434	B, 1.30; Li3, 1.11

located on the middle of four N−Li bonds and along the shortest B···Li contact (Table 3). Peak positions as calculated from the data for the first domain are listed in Table 4, and identical features were observed for the second domain. We attribute these peaks to polarization effects of the anions' electron shells along the bond directions to the Li cations.

Neutron diffraction is able to provide data not hampered by such effects and therefore would be useful for the determination of, and a comparison between, the real N−H and B−H bond distances in $Li_4BN_3H_{10}$. Finally, we want to point out that the small variation of cell parameters as observed for different crystals of the new compound precludes the presence of a significant defect concentration on either anion or cation sites, thus suggesting $Li_4BN_3H_{10}$ to be a nearly stoichiometric compound.

Supporting Information Available: Structural data as CIF files. This material is available free of charge via Internet at http://pubs.acs.org.

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