Synthesis and crystal structure of $Li_4BH_4(NH_2)_3$†

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The solid solution, $(LiNH_2)_x(LiBH_4)_{(1-x)}$, formed through the reaction of the two potential hydrogen storage materials, $LiNH_2$ and $LiBH_4$, is dominated by a compound that has an ideal stoichiometry of $Li_4BN_3H_{10}$ and forms a body-centred cubic structure with a lattice constant of *ca.* 10.66 Å.

The issue of storage is one of the major technical obstacles to the implementation of hydrogen as a fuel for mobile transport and much research effort has been devoted to developing new hydrogen storage methods and materials.[1] It has been shown that vast improvements in the hydrogen storage properties of known materials can be achieved by catalytic or chemical modification, such as in $NaAlH_4$ and MgH_2.[2,3] Although these developments are encouraging, it has also been recognized that an answer to the hydrogen storage challenge is likely to involve new, more complex materials systems.

$LiNH_2$ and $LiBH_4$ have both been extensively studied with regard to their potential hydrogen storage properties.[4,5] Recently, it was shown that, in the presence of lithium hydride, lithium amide reversibly desorbs hydrogen.[4,6,7] It has also been reported[8–10] that lithium amide and lithium borohydride, heated or ball milled in a 2 : 1 mole ratio, form a new body centred cubic phase of composition $Li_3BN_2H_8$,[8] but no further structural information was provided. This new quaternary hydride was shown to have much improved hydrogen desorption properties compared to the separate reactants. It is clear that the mixing of hydrides can provide alternative decomposition pathways promoting the release of hydrogen,[10,11] which may result in new, improved hydrogen storage systems. Here we report the synthesis and structure of the new quaternary hydride, whose stoichiometric composition is in fact $Li_4BN_3H_{10}$, but which tolerates a wide variation in stoichiometry.

$LiNH_2$ and $LiBH_4$ (Sigma-Aldrich) were ground together by hand in the desired mole ratio in an argon atmosphere glovebox (O_2 content < 10 ppm) and placed in a quartz tube. The tube was sealed with a Young's tap *via* an Ultra-Torr fitting and removed from the glovebox, and the reactants were then heated in a tube furnace under a mixture of H_2 and N_2 gas (1 : 9) at 1 bar.

In a series of experiments, we heated different mixtures of $LiNH_2$ and $LiBH_4$ over the entire composition range and identified that a body centred cubic phase with a unit cell of around 10.66 Å was always present across the full compositional range. Synchrotron X-ray powder diffraction experiments showed that the lattice parameters varied between 10.6664 and 10.7080 Å, and that the 80 : 20 composition contained an amide impurity while $LiBH_4$ was detected in the 70 : 30 composition. We concluded that the most likely stoichiometric composition for this structure was 75 : 25, giving the empirical formula $Li_4BN_3H_{10}$. Subsequently we observed that a mixture in a 3 : 1 mole ratio heated at around 100 °C (near the orthorhombic–tetragonal structural transition temperature of $LiBH_4$)[5] gave a pure[12] phase after annealing at 180 °C.[13]

The FTIR spectrum[14] of $Li_4BN_3H_{10}$ suggests that NH_2^- and BH_4^- anions remain intact within the structure and that the compound should be regarded as $Li_4BH_4(NH_2)_3$. There were no absorptions observed in positions expected for bridging B–H–B vibrations, again consistent with the BH_4^- anion remaining intact.[15] B–H stretching modes were shifted relative to $LiBH_4$ by around 8 cm^{-1} to the higher frequencies of 2387, 2293, 2237 (shoulder) and 2225 cm^{-1}. BH_2 deformation bands at 1120 and 1092 cm^{-1} in $LiBH_4$ were observed at 1126 and 1082 cm^{-1} in $Li_4BH_4(NH_2)_3$. In contrast, the observed symmetric and asymmetric stretches of the amide anion[16] were reduced from 3312 and 3259 cm^{-1} in $LiNH_2$ to 3303 and 3243 cm^{-1} in $Li_4BH_4(NH_2)_3$.

Recrystallization of the compound was attempted from a number of different solvents[17] in order to produce a single crystal for structural determination, but unfortunately $Li_4BH_4(NH_2)_3$ proved to be similar to $LiNH_2$ in its lack of solubility in common solvents. Instead, the crystal structure was solved using a combination of high resolution synchrotron X-ray and neutron powder diffraction measurements.[18] Extremely sharp diffraction peaks were observed in the X-ray data, indicating a high degree of crystallinity (see Fig. 1(a)). The regular spacing of peaks is indicative of a cubic crystal structure, which was verified using the computer program DASH;[19] the refined lattice constant and unit cell volume were 10.66445(1) Å and 1212.875(3) $Å^3$, respectively. Consideration of the volumes of a single formula unit of $LiNH_2$ (V = 32.6 $Å^3$) and $LiBH_4$ (V = 54.2 $Å^3$) from diffraction data collected on ID31 leads to a 3 : 1 ratio and 7.98 formula units in the unit cell. The closeness of this value to 8 is a strong indication that the ideal stoichiometry is indeed $Li_4BN_3H_{10}$. The most probable space groups were also determined using DASH by means of a Bayesian algorithm[20] that evaluates the relative probabilities of different space group extinction symbols; the most probable symbol was found to be *I*- - - which is associated with the space groups $I23$, $I2_13$, $Im3$, $I432$, $I\bar{4}3m$ and $Im3m$. Unless there is substantial disorder in the crystal structure, the only two space groups that are consistent with 8 formula units per unit cell are $I23$ and $I2_13$. Both were assessed in the structure solution process. The contributions of nitrogen and boron together correspond to over half the X-ray scattering in $Li_4BH_4(NH_2)_3$ and thus to simplify

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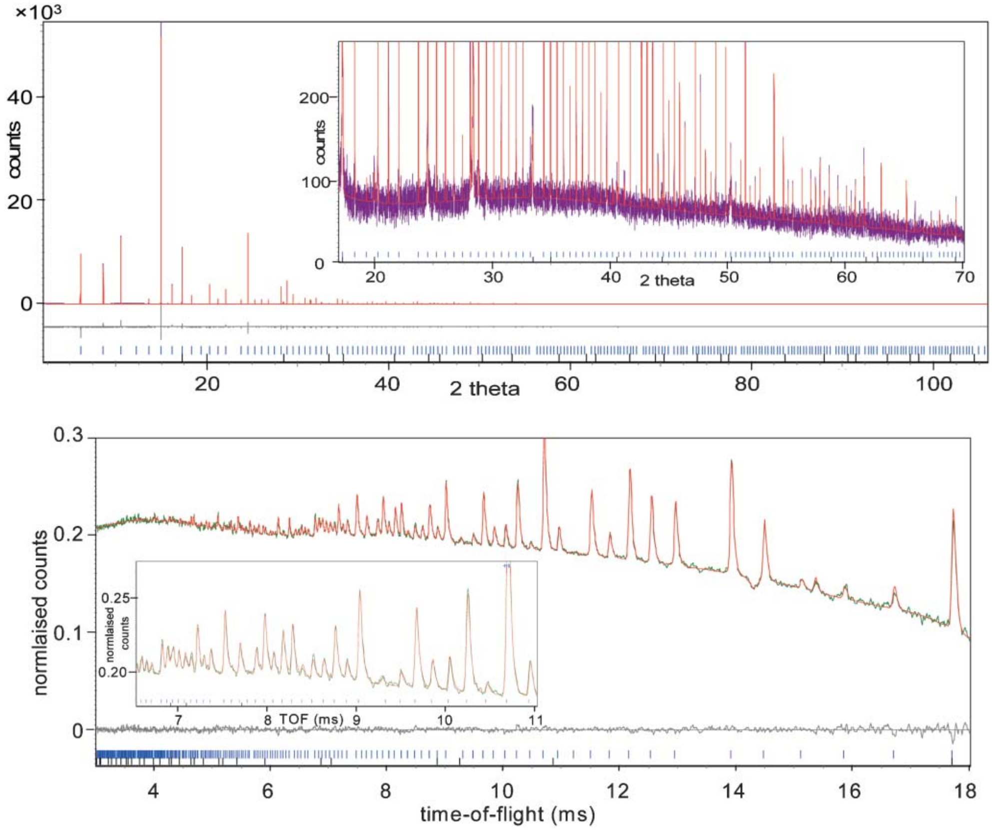

Fig. 1 Final Rietveld plots for (a) X-ray and (b) neutron diffraction data showing observed (purple and green respectively), calculated (red) and difference (grey) plots. The inserts show the low d-spacing region at a magnified scale. Peak positions for $Li_4BH_4(NH_2)_3$ and Li_2O are indicated.

structure solution only these atoms were considered initially in the solution process which was undertaken using the computer program TOPAS.[21] Solutions of similar quality were found for both space groups $I23$ and $I2_13$. Examination of the resulting structures indicated that the only difference between the two space groups was the permutation of N and B atoms over the same set of sites in the unit cell[22] which explains the similar qualities of fit.

The B and N sites occupy half of the possible positions at approximately ($[2\ell + 1]/8$, $[2m + 1]/8$, $[2n + 1]/8$) where $\ell,m,n = \{0,1,2,3\}$; this arrangement is reminiscent of the nitrogen positions in $LiNH_2$ (Fig. 2(b)). Building upon the apparent close similarity between $Li_4BH_4(NH_2)_3$ and $LiNH_2$, all sites at ($\ell/4$, $m/4$, $n/4$) (where $\ell,m,n = \{0,1,2,3\}$) were considered to be possible lithium candidate positions. The next stage involved the refinement of the occupancies of each of these sites. At this point, $I2_13$ became a better option than $I23$. The final stage of the structure solution process involved neutron diffraction data.[18] Usually deuteration and ^{11}B enrichment are required for neutron powder diffraction experiments because of problems with high background and absorption. The high count-rate of GEM, however, means that natural $Li_4BH_4(NH_2)_3$ could be used without isotopic enrichment (see Fig. 1(b)). Four hydrogen atoms were placed in tetrahedral coordination around boron initially at 1.25 Å while two hydrogen atoms were located around each nitrogen atom at a distance of 1 Å in a configuration similar to $LiNH_2$. Initial bond length and angle restraints were used for both BH_4^- and NH_2^- anions and all atomic positions were refined. In the final refinement using the neutron diffraction data (Table 1), all restraints were removed and

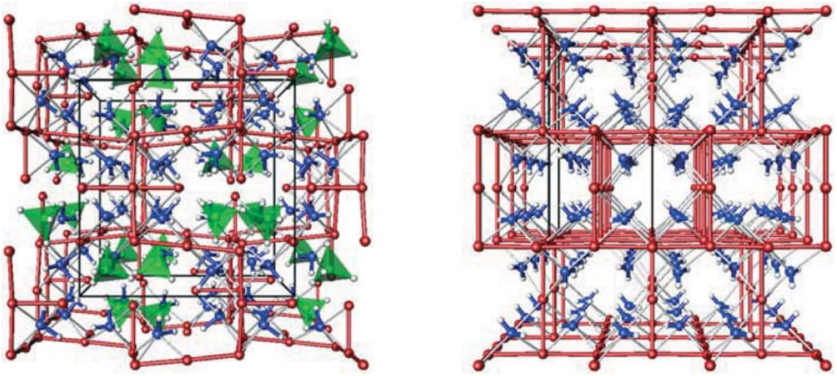

Fig. 2 (a) Crystal structure of $Li_4BH_4(NH_2)_3$; (b) $LiNH_2$ for comparison. Li atoms are depicted in red, N in blue, H in grey and BH_4^- as green tetrahedra.

an excellent fit was obtained over the full d-spacing range down to 0.44 Å. The resulting crystal structure is shown in Fig. 2(a). The corresponding fits to the X-ray and neutron diffraction data are shown in Figs. 1 (a) and (b) respectively.

Table 1 Refined crystallographic data: space group $I2_13$ a = 10.66445(1) Å

Atom	x/a	y/a	z/a	B_{iso}/Å^2
Li1	0.25	−0.0428(14)	0.0	1.5(1)
Li2	−0.2622(16)	0.0	0.25	1.5(1)
Li3	0.2722(12)	0.2722(12)	0.2722(12)	1.5(1)
B	0.1354(5)	0.1354(5)	0.1354(5)	1.4(2)
H1	0.0721(15)	0.0721(15)	0.0721(15)	4.1(2)
H2	0.0969(10)	0.1361(9)	0.2480(8)	4.1(2)
N	−0.1559(3)	0.1101(2)	0.3668(3)	1.8(1)
H3	−0.1533(12)	0.0533(15)	0.4394(12)	5.6(2)
H4	−0.0773(12)	0.1672(12)	0.3768(14)	5.6(2)

[a] X-ray data[18] – R_{wp} = 13.8, R_{exp} = 10.6, χ^2 = 1.7. Neutron data[23] – R_{wp} = 0.821 (11.9%), R_{exp} = 0.726 (10.5%), χ^2 = 1.3.

Interestingly, the B–H bonds in $Li_4BH_4(NH_2)_3$ are shorter than in $LiBH_4$; however, as with $LiBH_4$, one B–H bond is significantly (1.17 Å) shorter than the other three (1.27 Å).[23] N–H bond lengths are close to the N–D bond lengths observed in $LiND_2$.[24] These observations agree with the FTIR data, which showed a strengthening and weakening of the B–H and N–H bonds relative to $LiBH_4$ and $LiNH_2$, respectively.

The $Li_4BH_4(NH_2)_3$ structure accommodates a wide range of stoichiometries. Direct substitution of NH_2^- ions by the larger BH_4^- ions (anion volumes of 0.43 and 0.66 nm^3, respectively) results in an increase in observed lattice parameter.[25] Annealing experiments are currently in progress to determine the exact limits of this non-stoichiometry; preliminary results indicate that the composition range for $(LiNH_2)_x(LiBH_4)_{(1-x)}$ may extend from $x = 0.5$ to $x = 0.8$. It is worth noting that the replacement of an NH_2^- anion in the unit cell of $LiBH_4(NH_2)_3$ by an additional BH_4^- necessarily results in shorter distances between BH_4^- ions than in the stoichiometric compound and that non-stoichiometric compositions may be less stable as a result. In samples containing less than 40 mol% $LiNH_2$, we also observed a second body centred cubic phase with a larger unit cell size of ~ 11.1 Å, which co-exists with the $Li_4BH_4(NH_2)_3$ structure and an excess of $LiBH_4$. Early indications suggest that this phase may represent a second preferred composition within the $(LiNH_2)_x(LiBH_4)_{(1-x)}$ solid solution range. Further studies to determine the stoichiometry of this second phase are ongoing, but this work is complicated by its lack of stability over time with respect to $LiBH_4(NH_2)_3$ and $LiBH_4$.

When Chen *et al.* observed that the intimate mixing of LiH with $LiNH_2$ suppresses the usual release of ammonia in favour of hydrogen evolution at a much reduced decomposition temperature, it was suggested that this could be due to an interaction between partly positively charged hydrogen atoms in $LiNH_2$ and the negatively charged hydride anions in LiH,[26] and a mechanism for hydrogen desorption has recently been discussed.[27] We hypothesize that a similar interaction may occur in $Li_4BH_4(NH_2)_3$, as H atoms in BH_4^- are also partially negative.[28] Significantly, in $Li_4BH_4(NH_2)_3$ the BH_4^- ions are close to the NH_2^- on a molecular level, obviating the need for mechanical mixing. Initial findings confirm that the major gaseous decomposition product of $Li_4BH_4(NH_2)_3$ above 260 °C is indeed H_2 with ammonia present only in trace amounts. Similar findings have been reported for the decomposition of the 2 : 1 $LiNH_2/LiBH_4$ mixture.[8,10] Remarkably, this new quaternary complex hydride, constituted mainly of—and with striking structural similarities to—$LiNH_2$, has a completely different decomposition pathway from the pure amide, favouring H_2 evolution over that of ammonia.

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