Lithium amidoborane hydrazinates: synthesis, structure and hydrogen storage properties†

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The first metal amidoborane hydrazinate with a composition of LiNH₂BH₃-NH₃-NH₃₂ was successfully synthesized and characterized in the present study. LiNH₂BH₃-NH₃-NH₃₂ exhibits a monoclinic P2₁/n space group with lattice parameters of a = 10.065 Å, b = 6.310 Å, c = 7.485 Å, and β = 107.497°. Meanwhile, lithium amidoborane hydrazinates with different molar ratios of LiNH₂BH₃ (LiAB) and NH₃-NH₃₂ were synthesized and characterized. It was found that 4LiAB-NH₃-NH₃₂ can release 1.6 equiv. and 2.5 equiv. of H₂/LiAB at 75 °C and 170 °C, respectively. Therefore, around 71 wt% and 11.1 wt% of hydrogen can be released from 4LiAB-NH₃-NH₃₂ at 75 °C and 170 °C, respectively, which are higher values than those for pristine LiAB. A dehydrogenation mechanism, which may be initiated by the "homogeneous dissociation" of N≡N in hydrazine, is also proposed and discussed in this study.

1. Introduction

The development of efficient hydrogen storage materials is one of the greatest challenges for the realization of a "hydrogen economy". In the past decade, tremendous attention has been given to ammonia borane (AB for short), which has a hydrogen content as high as 19.6 wt%. However, the high kinetic barrier, by-products, and sample foaming during dehydrogenation make AB unsuitable for applications in PEMFC vehicles. To overcome these obstacles, researchers have investigated several approaches and improved the dehydrogenation properties by using nanoscaffolds, transition metal catalysts, acid or base catalysts and ionic liquids. Another important approach is to replace one H atom in NH₃ in AB by alkali (Li, Na, K) or alkaline-earth metals (Mg, Ca), forming metal amidoboranes. Due to the metal ion substitution, the length of the N-H bond is shortened, resulting in the activation of the N-H bond and B-H bond in amidoboranes. As a consequence, the dehydrogenation temperature is reduced to a lower region, which is accompanied by the suppression of the by-product borazine. In the following research, bimetal amidoboranes are obtained as a result of milling LiH-NaH or NaH-MgH₂ mixtures with AB with favorable dehydrogenation properties. Chua et al. synthesized calcium amidoborane diammoniate (CaAB-2NH₃) and found that CaAB-2NH₃ can evolve ammonia at elevated temperatures, forming calcium amidoborane (CaAB) in an open system. However, the ammonia ligands can interact with CaAB and trigger hydrogen release at 70 °C if a closed vessel was employed. Similarly, lithium amidoborane (LiNH₂BH₃; LiAB for short) can also absorb/desorb ammonia reversibly at room temperature and form the corresponding ammoniate (LiAB-NH₃) at low temperatures. The decomposition of LiAB-NH₃ releases 3.0 equiv. of H₂ (11.18 wt%) rapidly under ammonia conditions. In addition, magnesium amidoborane triammoniate (MgAB-3NH₃) can release hydrogen and ammonia in an open system upon heating. However, magnesium amidoborane monoammoniate (MgAB-NH₃) starts to release H₂ rather than NH₃ under dynamic flow, which is quite different from the behavior of CaAB-2NH₃ and MgAB-3NH₃. Therefore, the ligand ammonia plays a very important role not only in the stabilization of amidoboranes, but also in the dehydrogenation of amidoboranes. It has been reported that the dehydrogenation mechanism of metal amidoboranes is likely to include the combination of protonic H⁺ and hydridic H⁻ into hydrogen. However, there are unequal amounts of H⁺ and H⁻ in amidoboranes, which could be balanced by the protonic H⁺ in the ligand NH₃. In the above mentioned ammoniates, the combination of H⁺ in NH₃ and H⁻ in BH₃ is one of the driving forces for dehydrogenation. Thus, it is of great interest to probe other H⁺ containing ligands to balance...
H$$^{+}$$ and H$$^{3–}$$ in amidoboranes and improve the dehydrogenation properties.

Recently, hydrazine (NH$_2$NH$_2$) with a hydrogen content of 12.5 wt% has received considerable attention. Singh et al. used bimetal catalysts to achieve total conversion of hydrazine into hydrogen and nitrogen at room temperature. 28-29 Meanwhile, He et al. used noble-metal-free catalysts to catalyze the decomposition of hydrazine hydrate and found 100% conversation and more than 93% selectivity for hydrogen. 30 Hydrazine can also coordinate to borane to form NH$_2$NH$_2$-BH$_3$ and NH$_2$NH$_2$-2BH$_3$. 31-33 To optimize the dehydrogenation properties of hydrazine borane, alkali metal hydrides have been introduced to react with hydrazine and NH$_2$NH$_2$-BH$_3$ to synthesize metal hydrazides and metal hydrazinoboranes, respectively. 34-37 Additionally, hydrazine can also be used for regenerating AB or LiAB in liquid ammonia solution, 38-40 where the yield of AB has been claimed to be as high as 95%. It is worth mentioning that, according to the combination of H$$^{+}$$–H$$^{3–}$$ concept, hydrazine has been employed as a ligand and hence complexed with borohydrides to form hydrazinates in our recent results. 41,42 As a ligand, hydrazine showed great improvement in the dehydrogenation of borohydrides. Therefore, it is suggested that hydrazine should be considered as a ligand in amidoboranes. As there are four H$$^+$$ in one hydrazine molecule, the unequal amount of H$$^+$$ and H$$^{3–}$$ in amidoboranes could be modified, which may consequently improve the dehydrogenation performance. In addition, from a chemical point of view, hydrazine can coordinate with metals in amidoboranes and form a series of new compounds, which may exhibit many crystallographically interesting structures. Therefore, the first example of an amidoborane hydrazinate is synthesized, characterized and investigated in the present work. Experimental results show that LiNH$_2$BH$_3$-NH$_2$NH$_2$ exhibits a monoclinic structure with a P2$_1$/n space group and lattice parameters of a = 10.0650 Å, b = 6.3105 Å, c = 7.4850 Å, and β = 107.497°. A composition of 4LiAB-NH$_2$NH$_2$ can release 7.1 wt% and 11.1 wt% of hydrogen at 75 °C and 170 °C, respectively, which are higher values than those for pristine LiAB.

2. Experimental

2.1. Materials synthesis

LiH (Sigma, 97.0%), NaBH$_4$ (Aldrich, 98.0%), and (NH$_4$)$_2$CO$_3$ (Alfa, 99%) were used without further purification. THF solution. LiAB was synthesized from the reaction of NaBH$_4$ and (NH$_4$)$_2$CO$_3$ in THF solution. LiAB was synthesized according to the reaction described in the literature. After the synthesis, the qualities of AB, LiAB and nLiAB-NH$_2$NH$_2$ were examined by X-ray diffraction (XRD) spectroscopy.

Regeneration of the spent fuel of nLiAB-NH$_2$NH$_2$ was carried out in liquid NH$_3$ solution. Around 100 mg of dehydrogenated products of nLiAB-NH$_2$NH$_2$ and 400 mg of hydrazine were suspended in liquid ammonia at 0 °C in a closed vessel. Then, the reactor was heated to 40 °C for 3 days with continuous stirring. Ammonia and hydrazine were removed at room temperature under vacuum for 3 hours. Finally, the solid product was dissolved in THF for $^{11}$B nuclear magnetic resonance (NMR) examination.

2.2. Characterization

A home-made temperature programmed desorption–mass spectroscopy (TPD–MS) combined system was employed to detect the gaseous products during sample decomposition. XRD characterization was conducted on a PANalytical X’pert diffractometer (Cu K$_\alpha$, 40 kV, 40 mA) to avoid air contamination, the samples were sealed in a home-made sample holder covered with a piece of shielding film. The high-resolution XRD data were collected from the diffractometer at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility ($\lambda$ = 1.239800 Å). During the measurements, the sample was sealed in a capillary with a diameter of 0.5 mm. Volumetric release measurements were performed on a home-made Sievert type apparatus to quantify the gas evolution.

Liquid $^{11}$B NMR and solid state $^{11}$B magic angle spinning nuclear magnetic resonance (MAS NMR) experiments were carried out at room temperature on a Bruker AVANCE 500 MHz (11.7 T) spectrometer at a frequency of 128.3 MHz. The chemical shifts in the liquid and solid NMR spectra for the $^{11}$B nuclei are referenced to BF$_3$ at 0 ppm and LiBH$_4$ at 41 ppm, respectively.

The ammonia concentration in the gaseous products was determined by using a Thermo conductivity meter, while the accumulated gaseous product was bubbled into a dilute H$_2$SO$_4$ solution and the change in ion conductivity of the solution was monitored.

2.3. First-principles calculations method

First-principles calculations were performed using the plane-wave implementation of density functional theory (DFT) in the PWscf package. The Vanderbilt-type ultrasoft potential and the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof exchange-correlation energy functional were used. A cutoff energy of 408 eV was found to be enough for the total energy and force to converge within 0.5 meV per atom and 0.005 eV Å$^{-1}$. Car–Parrinello molecular dynamics simulations were used to help search for the most likely crystal structures. The conventional unit cell was used with cell dimensions fixed at the experimental values. The initial system temperature was set to 600 K. The system was first allowed to evolve and equilibrate for 20 ps, and then the system temperature was slowly brought to 0 K over a period of 20 ps. Structure optimizations on the resulting candidate structures at 0 K were further performed with respect to the atomic positions with the lattice parameters fixed at the experimental values. Lattice dynamics calculations were then performed on the relaxed structures to rule out unstable candidates. The total energies of the stable candidate
structures at 0 K, including corrections for the zero-point motion, were also evaluated. This information was used in combination with the matching XRD pattern to derive the best crystal structure solutions of the LiAB hydrazinate.

3. Results and discussion

3.1. Formation of nLiNH2BH3–NH2NH2 and the crystal structure of LiNH2BH3–NH2NH2

The reactions of LiAB with hydrazine in molar ratios of 1 : 1 and 2 : 1 yielded two new phases, as identified by the XRD technique (shown in Fig. S1†). However, a slurry state mixture could be obtained by adding more hydrazine to LiAB (for example a 1 : 2 molar ratio). Reducing the hydrazine content to a molar ratio of 4 : 1 (LiAB : hydrazine) resulted in mixed phases of 2LiAB–NH2NH2 and LiAB (Fig. S1†). The XRD pattern of LiAB·NH2NH2 was indexed using a monoclinic P21/n space group with lattice parameters of approximately \(a = 10.0650\) Å, \(b = 6.3105\) Å, \(c = 7.4850\) Å, and \(\beta = 107.497^\circ\). The crystal structure was then partially solved using direct space methods under this space group. Due to the uncertain \(H\) positions, first-principles molecular dynamics simulated annealings were then performed to confirm the LiAB and NH2NH2 configuration with the lowest energy. Rietveld structural refinement on the optimal structural candidate was performed using the GSAS package with the XRD data. LiAB and NH2NH2 were kept as rigid bodies with common refined bond lengths and bond angles constrained as reasonable values due to the inadequate number of observations. One LiAB group and one NH2NH2 group together with the lattice parameters were refined, yielding agreement factors of \(R_{wp} = 0.0222\), \(R_p = 0.0172\) and \(\chi^2 = 1.693\). The Rietveld fit with the XRD pattern is shown in Fig. 1.

The crystal structure of LiAB·NH2NH2 and the local coordination of the Li\(^+\) cation are shown in Fig. 2, and the interatomic distances in LiAB·NH2NH2 compared with pristine LiAB and pristine hydrazine can be found in Table 1. In LiAB·NH2NH2, each Li\(^+\) cation is surrounded by two NH2BH3\(^–\) ions and two NH2NH2 molecules, leading to a distorted tetrahedral coordination. The distances between Li\(^+\) and N in the adjacent NH2NH2 are 2.151 Å and 2.153 Å, similar to the Li–N distances in other coordinate bonds, such as in LiBH4·NH2NH2 (2.131–2.427 Å). At the same time, the Li\(^+\) cation directly bonds to a NH2BH3\(^–\) ion with a closest Li–N distance of 2.084 Å, similar to the Li–N distances in ionic bonds, such as in LiAB (2.063 Å) and LiNH2 (2.06–2.21 Å). In addition, each Li\(^+\) cation also coordinates to the other NH2BH3\(^–\) group with a Li–B distance of 2.487 Å. Therefore, the coordination of Li\(^+\) is consistent with the Li(nv) tetrahedral coordination preferred in commonly observed complex hydrides, e.g. LiNH2, LiBH4 and LiAB. Unfortunately, the crystal structure of 2LiAB·NH2NH2 is still unresolved due to the poor quality of the XRD pattern.

Since the coordination of NH2NH2 to LiAB is through the donation of a lone pair of electrons, Li\(^+\) will bear a higher electron density than Li\(^+\) in pristine LiAB, resulting in an elongated Li–N distance (Li–NH4BH4) in LiAB·NH2NH2, as shown in Table 1. Similarly, due to the lower electron density of N, the N–H (in the NH2NH2 ligand) distances in LiAB·NH2NH2 are longer than in the pristine hydrazine. In addition, two N atoms in hydrazine are coordinated to two Li\(^+\) ions, and the N–N distance is elongated consequently, showing the higher activation of the hydrazine ligand compared with the pristine one. Moreover, the B–H and N–H (in LiAB) distances in LiAB·NH2NH2 are longer than in the pristine LiAB, indicating the activation of the N–H and B–H bonds after coordinating with hydrazine. From the crystal structure, it was found that H\(^6\) (in NH2NH2 or NH4BH4) has a short distance with its neighboring H\(^5\) in BH3 ranging from 1.888 to 2.139 Å, which indicates the establishment of a dihydrogen bonding network. Such an interaction between the oppositely charged H\(^5\) (in NH2NH2 and NH4) and H\(^6\) (in BH3) may consequently also contribute to the elongated N–H and B–H bonds in LiAB·NH2NH2. It has been reported that the dihydrogen bonding network in ammonia borane\(^{43}\) is primarily responsible for the stability of the molecular crystal at room temperature. The dihydrogen bonding network and the ionic/electrostatic interactions between Li and NH2BH3/NH4H ligands in LiAB·NH2NH2 are thus responsible for the structural stabilization and is expected to have a profound impact on the thermal decomposition.

![Fig. 2 Crystal structure of LiAB·NH2NH2 (left) and local coordination of the Li\(^+\) cation (right).](Image 310x637 to 546x729)
3.2. Decomposition and dehydrogenation of \( n \text{LiNH}_2\text{BH}_3 \text{–NH}_2\text{BH}_3 \)

TPD-MS measurements were employed to investigate the dehydrogenation properties of \( n \text{LiAB–NH}_2\text{NH}_2 \) compared with pristine \( \text{LiAB} \), as shown in Fig. 3. Pristine \( \text{LiAB} \) releases hydrogen in two steps, giving a sharp peak centered at 92 °C and a broad peak centered around 120 °C in the first and second step, respectively, which is identical to that in the literature.\(^\text{12}\) For the \( \text{LiAB} \text{–NH}_2\text{NH}_2 \) sample (Fig. 3b), the release of hydrogen starts around 70 °C and three successive steps are exhibited. However, a large amount of ammonia, which is a poison to fuel cells, can also be observed during dehydrogenation. The evolution of \( \text{NH}_3 \) should be attributed to the excess \( \text{N} \) in the system. Therefore, to suppress the ammonia evolution, the content of hydrazine was reduced to a 2 : 1 (\( \text{LiAB} : \text{NH}_2\text{NH}_2 \)) molar ratio (Fig. 3c). It can be seen that the dehydrogenation of 2\( \text{LiAB–NH}_2\text{NH}_2 \) is a two-step reaction with peak temperatures centered at 74 °C and 130 °C. As expected, only a small amount of ammonia can be detected. If we further decrease the ratio of \( \text{NH}_2\text{NH}_2/\text{LiAB} \) to 4 : 1 (\( i.e. \ 4 \text{LiAB–NH}_2\text{NH}_2 \) in Fig. 3d), which possesses equal amounts of \( \text{H}^0 \text{ and } \text{H}^+ \)), no ammonia can be detected from the MS. At the same time, the dehydrogenation profile of 4\( \text{LiAB–NH}_2\text{NH}_2 \) is similar to that of 2\( \text{LiAB–NH}_2\text{NH}_2 \) with dehydrogenation peak temperatures at 76 °C and 130 °C. It is noticeable that the dehydrogenation temperature of the first step for 2\( \text{LiAB–NH}_2\text{NH}_2 \) and 4\( \text{LiAB–NH}_2\text{NH}_2 \) is about 17 °C lower than that of pristine \( \text{LiAB} \), whereas the second dehydrogenation temperatures are about 10 °C higher than that of pristine \( \text{LiAB} \). It has been reported that the decomposition of hydrazine follows two competitive routes, giving rise to \( \text{H}_2 \) and \( \text{N}_2 \) or \( \text{N}_2 \) and \( \text{NH}_3 \) under mild conditions, even in the presence of noble metal or noble metal-like catalysts.\(^\text{16–48}\) However, no \( \text{N}_2 \) can be observed during the dehydrogenation/decomposition of \( n \text{LiAB–NH}_2\text{NH}_2 \). Therefore, the evolution of \( \text{NH}_3 \) during the decomposition of \( \text{LiAB} \text{–NH}_2\text{NH}_2 \) is not from the self-decomposition of hydrazine, which means the hydrogen is derived from the interaction between \( \text{LiAB} \) and hydrazine.

To quantify the evolution of hydrogen from the \( n \text{LiAB–NH}_2\text{NH}_2 \) systems, volumetric release measurements were employed at 75 °C and 170 °C (Fig. 4). At 75 °C, around 1.2 equiv. of \( \text{H}_2/\text{LiAB} \) can be released from the pristine \( \text{LiAB} \) in 3 hours. However, the \( \text{LiAB–NH}_2\text{NH}_2 \) system can release around 1.5 equiv. of gas/\( \text{LiAB} \), which is composed of \( \text{NH}_3 \) and \( \text{H}_2 \), as determined by MS. For the 2\( \text{LiAB–NH}_2\text{NH}_2 \) and 4\( \text{LiAB–NH}_2\text{NH}_2 \) systems, around 1.6 equiv. of \( \text{H}_2/\text{LiAB} \) are generated from both samples under the same conditions. At the same time, we can see that the onset dehydrogenation temperatures of 2\( \text{LiAB–NH}_2\text{NH}_2 \) and 4\( \text{LiAB–NH}_2\text{NH}_2 \) are lower than that of pristine \( \text{LiAB} \), which is consistent with the TPD results. It is worth mentioning that, calculated from the volumetric release measurements, around 7.1 wt% of hydrogen can be evolved from the 4\( \text{LiAB–NH}_2\text{NH}_2 \) component at 75 °C, which is a higher value than that for pristine \( \text{LiAB} \) (6.5 wt%). At 75 °C, around 14.1 mol% of ammonia is found in the gaseous products of \( \text{LiAB–NH}_2\text{NH}_2 \), agreeing with the TPD results. However, the concentration of by-product ammonia is even lower than 0.2 mol% in the 2\( \text{LiAB–NH}_2\text{NH}_2 \) and 4\( \text{LiAB–NH}_2\text{NH}_2 \) samples, as shown in Table S1.\(^\dagger\)

For the pristine \( \text{LiAB} \), around 2 equiv. of \( \text{H}_2 \) can be released at 170 °C, which is identical to the literature.\(^\text{12,13}\) Under the same conditions, \( \text{LiAB–NH}_2\text{NH}_2 \) can release more than 3.6 equiv. of gas, which is composed of hydrogen and ammonia, as detected

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<th>Interatomic distances (Å) in LiAB–NH₂NH₂ compared with pristine LiAB and hydrazine at room temperature</th>
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![Fig. 3 TPD–MS results of nLiAB–NH₂NH₂ compared with pristine LiAB. (a): LiAB, (b): LiAB–NH₂NH₂, (c): 2LiAB–NH₂NH₂, (d): 4LiAB–NH₂NH₂.](image)
NH$_2$NH$_2$ from DTA (Fig. S2 and S3) released from 2LiAB. Gaseous impurity (NH$_3$) release during the TG experiments. The wt% from the volumetric release measurements, indicating the evolved from these two samples at 170 °C, words, around 10.9 wt% and 11.1 wt% of hydrogen can be products. XRD spectroscopy was also employed to characterize the solid due to the low ammonia concentration in the gaseous products. According to the quantity of hydrogen evolution, the dehydrogenation reactions can be expressed as follows:

$$2\text{LiNH}_2\text{BH}_3 - \text{NH}_2\text{NH}_2 \xrightarrow{170 ^\circ \text{C}} 2[\text{Li}_2\text{N}_2\text{BH}] + 6\text{H}_2$$  \hspace{1cm} (R1)

$$4\text{LiNH}_2\text{BH}_3 - \text{NH}_2\text{NH}_2 \xrightarrow{170 ^\circ \text{C}} 2[\text{Li}_2\text{N}_3\text{B}_2\text{H}_2] + 10\text{H}_2$$  \hspace{1cm} (R2)

Since the dehydrogenated products were in amorphous states, $^{11}$B MAS NMR technique was carried out to investigate the chemical environment of the post-dehydrogenated products. As shown in Fig. 5, the pristine LiAB exhibits a peak around –21.6 ppm, which belongs to the BH$_3$ signal. Both synthesized 2LiAB–NH$_2$NH$_2$ and 4LiAB–NH$_2$NH$_2$ samples show BH$_3$ signals around –22.3 ppm, indicating the formation of new phases. From the XRD results (Fig. S1†), the 4LiAB–NH$_2$NH$_2$ sample is composed of LiAB and 2LiAB–NH$_2$NH$_2$ phases. However, there is only one peak for the 4LiAB–NH$_2$NH$_2$ sample around –22.3 ppm. No signal or shoulder peak around –21.6 ppm for the pristine LiAB can be observed. This may be attributed to the overlap of the LiAB and 2LiAB–NH$_2$NH$_2$ signals in the solid NMR measurements. It is worth noting that the chemical shift of $^{11}$B in the 2LiAB–NH$_2$NH$_2$ sample has a 0.7 ppm up-shift compared to the pristine LiAB, which is consistent with that of CaAB–2NH$_2$ in the literature. The post decomposed LiAB sample at 170 °C gives a broad peak ranging from 33 ppm to 15 ppm, which is consistent with the amorphous [LiNHBH] reported in the literature. For the 2LiAB–NH$_2$NH$_2$ and 4LiAB–NH$_2$NH$_2$ samples, there is still a small amount of BH$_3$ residue after dehydrogenation at 170 °C, as shown in Fig. 5. Most of the $^{11}$B signals in the products are sp$^2$ hybridized B species, maybe in the form of Li$_3$BN$_2$, [BN$_2$H] or [BN$_3$], which is similar to the decomposition of the ammonia borane family.

Due to the exothermic nature of the dehydrogenation (Fig. S2 & S3†), the system is unlikely to achieve direct hydrogenation from the spent fuel of nLiAB–NH$_2$NH$_2$. However, it has been reported that AB or LiAB can be regenerated by the interaction.
of the spent fuel with hydrazine in NH₃ solution.38-40 Therefore, we investigated the regeneration of the spent fuel of 4LiAB-NH₂NH₃ by using hydrazine in NH₃ solution at 40 °C. From liquid NMR spectroscopy (Fig. S4†), two BH₃ species can be observed after regeneration, which can be assigned to BH₃-NH₂NH₃ and NH₂BH₃. Therefore, the regeneration of BH₃ species can be realized. However, LiAB and nLiAB-NH₂NH₂ compounds are not observed. It is worth mentioning that the yield of regenerated BH₃ species is less than 10% and there is a possibility for further optimization.

3.3. Discussion on the dehydrogenation pathway

Due to the unbalanced H⁺ and H⁻ in LiAB, hydrazine with four H⁻ in one molecule was selected and complexed with LiAB. It is known that the decomposition of hydrazine follows two competitive ways (R3 and R4):[46-48]

\[
\begin{align*}
\text{NH}_2\text{NH}_2 & \rightarrow \text{N}_2 + 2\text{H}_2 \quad \text{(R3)} \\
3\text{NH}_2\text{NH}_2 & \rightarrow \text{N}_2 + 4\text{NH}_3 \quad \text{(R4)}
\end{align*}
\]

Since nitrogen was not observed during the decomposition of nLiAB-NH₂NH₂, the hydrogen is not from the self-decomposition of hydrazine. As mentioned above, the elongated B–H and N–H bonds in LiAB-NH₂NH₂ showed the activation of both hydrazine and LiAB. Consequently, we propose that the hydrogen release is more likely to be via the interaction of LiAB and NH₂NH₂. Here, two dehydrogenation pathways of 2LiAB-NH₂NH₂ are proposed, as illustrated in Scheme 1. Since the dissociation energy of the N–N bond (60 kJ mol⁻¹) is lower than that of the N–H bond (84 kJ mol⁻¹) in hydrazine,[53,54] “homogeneous dissociation” of the N–N bond forming [NH₂] radicals may occur, which is observed on the surface of metal catalysts.[46] The [NH₂] radical is an active species and can react with LiAB readily. Therefore, [NH₂] may attack the NH₂ group in LiNH₂BH₃, forming lithium hydrazinoborane (LiNH₂BH₃)₃[34,36] and H₂. It has been reported that lithium hydrazinoborane can be dehydrogenated readily under mild conditions. For the second dehydrogenation pathway, it has been reported that a bridged H between Li and B (Li⋯H⋯B) can be formed during the activation of LiAB,[35-37] which is called the “hydride transfer mechanism”. The [NH₂] radical may attack the bridged H in the BH₃ group forming [LiNH₂BH₂NH₃] and H₂, which may further decompose and release hydrogen in the following steps. For the LiAB-NH₂NH₂ sample, since more [NH₂] radicals could be generated, the H atom generated from the interaction between [NH₂] and LiAB may have more chance to combine with the excessive [NH₂] radicals forming NH₃, which may in turn explain the formation of the large amount of NH₃ in the TPD results for LiAB-NH₂NH₂. For the 4LiAB-NH₂NH₂ sample, two phases (LiAB and 2LiAB-NH₂NH₂) can be observed from the XRD pattern. The decomposition of 2LiAB-NH₂NH₂ is prior to that of pristine LiAB, as shown in Fig. 3. Therefore, LiAB may interact with the intermediate species of the decomposition of 2LiAB-NH₂NH₂, forming [Li₂N₂B₂H₆] and H₂, as shown in R2.

4. Conclusions

The coordination of hydrazine to the Li⁺ cation in lithium amidoborane results in the formation of hydrazinates, among which LiNH₂BH₃-NH₂NH₂ crystallizes in the monoclinic P2₁/n space group. Around 7.1 wt% of hydrogen can be evolved from the 4LiAB-NH₂NH₂ component at 75 °C, which is a larger amount compared to that from pristine LiAB. Two possible dehydrogenation pathways for the hydrazinates are proposed. However, more investigations and characterization are needed to obtain various metal amidoborane hydrazinates with appropriate dehydrogenation properties. Research shall also be devoted to the regeneration of amidoborane hydrazinates to realise the “reversibility” of these materials.

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Notes and references
