A Composite of Complex and Chemical Hydrides Yields the First Al-Based Amidoborane with Improved Hydrogen Storage Properties


Abstract: The first Al-based amidoborane Na[Al(NH$_3$BH$_3$)$_4$] was obtained through a mechanochemical treatment of the NaAlH$_4$–4AB (AB = NH$_4$BH$_4$) composite releasing 4.5 wt% of pure hydrogen. The same amidoborane was also produced upon heating the composite at 70 °C. The crystal structure of Na[Al(NH$_3$BH$_3$)$_4$], elucidated from synchrotron X-ray powder diffraction and confirmed by DFT calculations, contains the previously unknown tetrahedral ion [Al(NH$_3$BH$_3$)$_4$]$^-$, with every NH$_3$BH$_4^-$ ligand coordinated to aluminum through nitrogen atoms. Combination of complex and chemical hydrides in the same compound was possible due to both the lower stability of the Al–H bonds compared to the B–H ones in borohydride, and due to the strong Lewis acidity of Al$^3+$. According to the thermogravimetric analysis–differential scanning calorimetry–mass spectrometry (TGA–DSC–MS) studies, Na[Al(NH$_3$BH$_3$)$_4$] releases in two steps 9 wt% of pure hydrogen. As a result of this decomposition, which was also supported by volumetric studies, the formation of NaBH$_4$ and amorphous product(s) of the surmised composition AlN$_3$B$_4$H$_{10}$–3H$_2$O were observed. Furthermore, volumetric experiments have also shown that the final residue can reversibly absorb about 27% of the released hydrogen at 250 °C and p(H$_2$) = 150 bar. Hydrogen re-absorption does not regenerate neither Na[Al(NH$_3$BH$_3$)$_4$] nor starting materials, NaAlH$_4$ and AB, but rather occurs within amorphous product(s). Detailed studies of the latter one(s) can open an avenue for a new family of reversible hydrogen storage materials. Finally, the NaAlH$_4$–4AB composite might become a starting point towards a new series of aluminum-based tetraamidoboranes with improved hydrogen storage properties such as hydrogen storage density, hydrogen purity, and reversibility.

Introduction

Current concerns over environmental pollution are pushing the development of carbon-neutral energy carriers. Among these carriers, hydrogen has emerged as an ideal candidate. However, there are numerous challenges in its practical application. In order for hydrogen to be used as an environmentally benign energy carrier, efficient storage methods must be developed. This has been a main challenge during the last decades with much research focused on the increasing amount of hydrogen stored per given mass of a support. Recently, the U.S. Department of Energy introduced ultimate targets of 7.5 wt% and 70 g L$^{-1}$ for the gravimetric and volumetric capacities of hydrogen, respectively. These and other technical limitations have reduced the number of potential hydrogen storage systems, giving an advantage to complex metal hydrides with high hydrogen content. Alkali-metal alanates, M(AlH$_4$)$_m$, have shown remarkable hydrogen storage properties. For example, NaAlH$_4$, the most intensively studied member of this class of compounds, has a reversible hydrogen capacity of 5.6 wt%. However, high dendrites and rehydrogenation temperatures for alanates (e.g., 210–220 °C for NaAlH$_4$) as well as a moderate hydrogen content have directed attention to lighter complex hydrides such as borohydrides, M(BH$_4$)$_m$.[2,3] At the same time, reversible systems based on borohydrides were developed only in the form of reactive hydride composites (RHCs), containing complex and binary metal hydrides. In particular, the reversible system, comprising LiBH$_4$ and MgH$_2$ doped with TiCl$_3$ to catalyze rehydrogenation, yields 8–10 wt% of hydrogen according to the following reaction [Eq. (1)].
MgH₂ + 2LiBH₄ ⇒ MgB₂ + 2LiH + 4H₂  

(1)

In the middle of the last decade, an intensive research has been focused on the so-called chemical hydrides, in particular ammonia borane (AB), NH₃BH₃. The high hydrogen content in AB (about 19.6 wt%, 152 g L⁻¹), and its stability under ambient conditions have attracted significant attention to this compound. Ammonia borane undergoes stepwise decomposition (26.3 wt%); NaAlH₄ (18.5 wt%); and from the previously obtained mixture, the mixed-metal (Table 1), obtained after twenty milling/break cycles, exhibits high hydrogen content (∼14.0 wt% 

It was found that the reaction given in Equation (3) is slightly exothermic and non-reversible. However, Na[Al(NH₄)₂] also releases, in two steps, additionally up to eight equivalents of H₂. Remarkably, this desorption is partially reversible. Thus, the decomposition properties of Na[Al(NH₄)₂] were systematically investigated by in situ synchrotron radiation X-ray powder diffraction (SRXRPD), by thermal analysis coupled with mass spectrometry, by temperature-programmed photographic analysis, and by volumetric methods. It was established that the hydrogen re-absorption does not regenerate NaAlH₄ or Na[Al(NH₄)₂], but rather occurs between the amorphous product(s) and intermediate(s) of the dehydrogenation process.

Na[Al(NH₄)₂] is the first compound coming from the combination of a complex and chemical hydrides, its formation is favored by the lower stability of the Al–H bonds compared to the B–H ones, and due to the Lewis acidity of the complex-forming aluminium cation. Furthermore, the NaAlH₄–AB system opens a route to design a series of aluminium tetraamidoboranes by using, for example, other alkali and alkali-earth metal alanates instead of NaAlH₄ with improved hydrogen storage properties.

**Results and Discussion**

**Phase analysis and in situ SRXRPD data**

The in situ SRXRPD patterns have been collected from room temperature to 150 °C (5 °C min⁻¹) (Figure 1) for the NaAlH₄–4AB mixture s₁, obtained after 160 milling/break cycles (Table 1). The temperature-dependent composition of s₁, extracted from the sequential Rietveld refinement, is given in Figure 1.

At room temperature s₁ contains Bragg reflections from AB (26wt%), NaAlH₄ (18.5 wt%), and from the previously unknown Na[Al(NH₄)₂] (55 wt%). Peaks from AB disappear at around 90 °C without the appearance of new peaks. At the same time, the intensities of the peaks of Na[Al(NH₄)₂] are continuously increasing and the peaks become narrower. According to the sequential refinement, the weight fraction of Na[Al(NH₄)₂] increases after approximately 80 °C, due to the reaction of AB with NaAlH₄ (Figure 1). Its peaks disappear at about 120 °C with an appearance of peaks for NaBH₄ implying also the formation of amorphous product(s).

Complementary measurements on the NaAlH₄–4AB mixture s₂ (Table 1), obtained after twenty milling/break cycles, exhibited the formation of a negligible amount of Na[Al(NH₄)₂] (Figure S1 in the Supporting Information). Thus, mixture s₂, being a homogenous physical mixture of AB and NaAlH₄, was
the formation of NaBH₄ and amorphous product(s) (Figure S2 in the Supporting Information). The same behavior was described by Ohnuki et al.[26] However, in their work, numerous peaks were not well resolved, probably due to a negligible amount of the then-unknown Na[Al(NH₄)BH₄]₄ and the limitations of the laboratory XRPD. Indeed, the formation of Na[Al(NH₄)BH₄]₄ with high yields requires a long-time milling that was not done earlier. Moreover, the stoichiometry of the starting mixture studied previously was 1:1[26] but not 1:4, hence, significantly decreasing the yield. Thus, Na[Al(NH₄)BH₄]₄ can be readily obtained by gentle heating of the NaAlH₄–4AB composite at about 80 °C. However, the resulting Na[Al(NH₄)BH₄]₄ starts to decompose extensively upon keeping it for longer at this temperature. Therefore, this synthetic approach seems to be less attractive and a more reliable alternative synthesis should be suggested. With this in mind, we have directed our attention to long-time ball milling of the NaAlH₄–4AB composite at room temperature. Indeed, as a result we have obtained the mixture s3, containing about 90 wt% of Na[Al(NH₄)BH₄]₄ (Table 1, Figure S3 in the Supporting Information).

We have also attempted to characterize the corresponding Li-containing system,[23,25,26] by milling the LiAlH₄–4AB composite by using the same experimental conditions as for the Na-containing mixture. However, the reaction has appeared to be extremely violent. In particular, after a few seconds of milling the pressure exceeded twice the calculated value, coming close to the limit of the reaction vial, and as a result, the milling was automatically stopped. Characterization of the resulting sample by PXRD revealed metallic Al and LiBH₄ along with other unidentified phases present as weak peaks (Figure S4 in the Supporting Information). This indicates that the LiAlH₄–4AB mixture reacts highly exothermically, and the ball milling is not an appropriate synthesis route.

The formation of borohydrides upon decomposition of Na[Al(NH₄)BH₄]₄ of the LiAlH₄–4AB composite, also recently found in the reaction products from MHₓ–4AB[23] and MAIHₓ–4AB (M = Li, Na)[26] composites, is remarkable. The origin of the BH₄⁻ ion in the systems with AB was explained[27] by the exchange reaction between its ionic dimer, diammoniate of diborane (DADB) [(NH₄)₂ BH₄]²⁻[29] and the alkali-metal alanate salts. This mechanism is not suitable in our case, because NaBH₄ is one of the decomposition products of Na[Al(NH₄)BH₄]₄. Characteristic peaks of NaBH₄ appear immediately after the decomposition of Na[Al(NH₄)BH₄]₄. It should be noted, that the unreacted AB does not participate in this process, because it still remains in the mixture some time after the decomposition of Na[Al(NH₄)BH₄]₄ and the appearance of the NaBH₄ peaks (Figure S2 in the Supporting Information). Thus, our work shows that the formation of borohydrides is not an intrinsic property of AB but of the amidoboranes.

**Crystal structure**

The crystal structure of Na[Al(NH₄)BH₄]₄ was solved in the clinic space group P1. The experimental coordinates and those optimized by DFT methods are listed in Table S1 in the Sup-

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**Table 1. Samples studied in this work.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Synthetic approach</th>
<th>Phase composition from XRPD (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>NaAlH₄–4AB</td>
<td>≈ 55 of Na[Al(NH₄)BH₄]₄</td>
</tr>
<tr>
<td></td>
<td>160 milling/break</td>
<td>≈ 26 of NH₃BH₄</td>
</tr>
<tr>
<td></td>
<td>cycles of 3/5 min</td>
<td>≈ 19 of NaAlH₄</td>
</tr>
<tr>
<td>s2</td>
<td>NaAlH₄–4AB</td>
<td>≈ 83 of NH₃BH₄</td>
</tr>
<tr>
<td></td>
<td>20 milling/break</td>
<td>≈ 17 of NaAlH₄</td>
</tr>
<tr>
<td></td>
<td>cycles of 3/3 min</td>
<td></td>
</tr>
<tr>
<td>s3</td>
<td>NaAlH₄–4AB</td>
<td>≈ 90 of Na[Al(NH₄)BH₄]₄</td>
</tr>
<tr>
<td></td>
<td>240 milling/break</td>
<td>≈ 4 of NH₃BH₄</td>
</tr>
<tr>
<td></td>
<td>cycles of 3/5 min</td>
<td>≈ 6 of NaAlH₄</td>
</tr>
<tr>
<td>s4</td>
<td>NaAlH₄–4AB doped</td>
<td>≈ 88 of Na[Al(NH₄)BH₄]₄</td>
</tr>
<tr>
<td></td>
<td>with 2 mol% of TiCl₃</td>
<td>≈ 11 of NH₃BH₄</td>
</tr>
<tr>
<td></td>
<td>240 milling/break</td>
<td>≈ 1 of NaAlH₄</td>
</tr>
</tbody>
</table>

used to examine the temperature as a stimulus of the formation of Na[Al(NH₄)BH₄]₄ in the reaction given in Equation (3). Variable-temperature XRPD studies made on s2 from room temperature to 76 °C at a rate of 1 °C min⁻¹ have revealed the formation of Na[Al(NH₄)BH₄]₄, accompanied by the disappearance of the crystalline precursors (Figure S2 in the Supporting Information). The XRPD patterns collected on s2 at 76 °C show that Na[Al(NH₄)BH₄]₄ gradually decomposes during 1 h with

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**Figure 1.** Top) Variable-temperature plot of the SIRXRD patterns of s1 (SNBL/ESRF synchrotron, λ = 0.823065 Å), and bottom) fractional content of compounds extracted from the Rietveld refinement of the powder patterns.
porting Information. Solution of triclinic structures from powder diffraction data is generally difficult, and this is the second amidoborane with a triclinic crystal system, after the mixed-metal complex Na[Li(NH$_2$BH$_3$)$_3$]. The central Al$^{3+}$ atom has a tetrahedral environment formed by four nitrogen atoms from four NH$_2$BH$_3$ ions (Figure 2). Thus, the tetrahedrally configured [Al(NH$_2$BH$_3$)$_4$]$^-$ ion is a new member of Al$^{3+}$ complex hydrides with a tetrahedral coordination, after alanates [AlH$_4$]$^-$, complex amides [Al(NH$_2$)$_4$]$^-$, and complex borohydrides [Al(BH$_4$)$_4$]$^-$.[19] The Na$^+$ atoms are octahedrally coordinated by six BH$_3$ groups arising from six NH$_2$BH$_3$ ions (Figure 2), similar to Na$^+$ in Na$_2$[Mg(NH$_2$BH$_3$)$_4$].[20] Thus, all NH$_2$BH$_3$ ions exhibit a bridging coordination mode linking Al$^{3+}$ and Na$^+$ ions with the formation of a 3D polymer structure (Figure 3).

The Al–N bond lengths range from 1.840(9) to 1.929(8) Å and are close to 1.90 Å found in the DFT-optimized experimental model of Na[Al(NH$_2$BH$_3$)$_4$], which, in turn, is slightly longer than 1.85 Å, as observed in Na[Al(NH$_2$)$_4$].[30] The Na–B distances are 2.92(1)–3.55(2) and 2.90–3.64 Å, as evidenced from the PXRD experiments and DFT calculations, respectively. These values are in line with Na–B distances of 2.90–3.63 Å found in Na$_2$[Mg(NH$_2$BH$_3$)$_4$].[20] Remarkably, the dihydrogen N–H$^+$–H$^+$–B bonds in Na[Al(NH$_2$BH$_3$)$_4$] (1.96(1)–2.28(1) Å from PXRD and 1.92–2.34 Å from DFT calculations) are close to the shortest dihydrogen bonds (1.91(5) Å in pristine AB,[31] and significantly shorter compared to all known MABs (Table S2 in the Supporting Information).[11–19]

**Fourier transform infrared (FTIR) spectroscopy**

In order to characterize changes induced by ball milling, FTIR measurements on the mixtures s2 and s3 as well as on AB were conducted. The IR spectra of s2 and s3 exhibit characteristic bands for the B–H ($\tilde{v}$ = 1100–1150 and 2340–2420 cm$^{-1}$), N–H ($\tilde{v}$ = 1500–1650 and 3200–3430 cm$^{-1}$), and B–N ($\tilde{v}$ = 780 cm$^{-1}$) vibration modes similar to those for AB (Figure 4).[31] Although the IR spectrum of mixture s2 shows no significant changes compared to those of the pristine AB and NaAlH$_4$, the spectrum of mixture s3 contains new bands at $\tilde{v}$ = 630–673 cm$^{-1}$ assigned to the Al–N vibrational modes (similar to Na[Al(NH$_3$)$_4$] and aluminum nitride (AlN)).[30,32] Calculated values for the selected vibrational modes in Na[Al(NH$_2$BH$_3$)$_4$] are given in Figure S5 in the Supporting Information.
Temperature-programmed photographic analysis

As mentioned in the Introduction, one of the disadvantages of the practical application of AB for hydrogen storage arises from its spectacular foaming leading to a dramatic volume expansion during its thermolysis. With this in mind, we have applied the temperature-programmed photographic analysis to visually observe volume expansion of the mixtures s2 and s3 during thermal decomposition from room temperature to 275 °C. The mixture s2 showed a drastic volume expansion upon heating starting from about 70 °C and increasing up to approximately 110 °C (Figure 5). Under the applied experimental conditions with a heating rate of 5 °C min⁻¹, this observation can be explained by the decomposition of the unreacted AB, as its decomposition temperature is at about 107 °C. Indeed, at around 110 °C the foaming reaches its maximum. The volume of mixture s3 remained constant under the same experimental conditions (Figure 5), showing a remarkable difference between the starting composite NaAlH₄–4AB and the reaction product Na[Al(NH₂BH₃)₄]. On the other hand, the foaming of the unreacted AB can be decreased by keeping the temperature below the decomposition of AB, that is, at 76 °C, where Na[Al(NH₂BH₃)₄] is forming from s2 over about one hour. This is yet another evidence of the formation of Na[Al(NH₂BH₃)₄] at temperatures below the decomposition of AB.

Thermal analysis and mass spectrometry

A simultaneous thermogravimetric analysis–differential scanning calorimetry–mass spectrometry (TGA–DSC–MS) experiment has been conducted for mixture s2 aiming to characterize the hydrogen release through the formation of Na[Al(NH₂BH₃)₄], and for mixture s3 aiming to observe the decomposition properties of Na[Al(NH₂BH₃)₄]. Thermal decomposition of both samples is described mainly by two resolved steps of weight loss centered at about 120 and 160 °C (Figure 6). The first step in the TGA plot for s2 is seen as a sharp weight deviation due to the so-called “jet” effect, which is explained by a drastic volume expansion upon heating. This finding is in line with the spectacular foaming, which, in turn, is the result of the decomposition of unreacted AB, as it was observed by the temperature-programmed photographic analysis (Figure 5 and the description above).

Both decomposition steps were found to be exothermic and correspond to hydrogen evolution. An additional exothermic peak was found at about 75 °C for both samples (much less pronounced in the DSC plot of mixture s3), and can be explained by the reaction between NaAlH₄ and AB according to the reaction given in Equation (3). The exothermic peak at 115 °C in the DSC plot of mixture s2 is the result of the decom-
position of the unreacted AB, which is in agreement with our PXRD data (Figure S2 in the Supporting Information) and the thermal decomposition pathway of pristine AB.\textsuperscript{[19]}

According to the TGA–MS data, neither borazine nor diborane and only traces of ammonia were observed during the decomposition of the mixtures s2 and s3 (Figure 6). The total mass loss of approximately 9 wt% for s3 indicates a partial hydrogen release out of the theoretical 11.9 wt% in Na[Al(NH$_3$)BH$_4$]. Notably, the formation of Na[Al(NH$_3$)BH$_4$] from mixture s2 at a constant temperature of 71 °C results in hydrogen release without detectable impurities of ammonia, diborane, and borazine (Figure S6 in the Supporting Information). The calculated enthalpy of the reaction given in Equation (3) at room temperature was found to be about –25 and –30 kJ mol$^{-1}$ (Figure S7 in the Supporting Information), calculated with and without van der Waals interactions, respectively. These results are in agreement with the exothermic events in the DSC data (Figure 6).

### Reaction pathways, volumetric analysis, and reversibility tests

The mixture s2 heated to 85 °C releases about 3.5 mol of hydrogen per one mole of aluminum (Figure 7). This value is close to the calculated four moles of hydrogen according to the reaction given in Equation (3), and, together with the diffraction, thermal, and mass spectrometry analyses, proves the formation of Na[Al(NH$_3$)BH$_4$] during the heating of the NaAlH$_4$–4AB composite.

Volumetric studies of the decomposition of mixture s3 and of the TiCl$_3$-doped but otherwise identical sample s4 (Table 1) were performed from room temperature up to 250 °C. The decomposition profiles of the samples s3 and s4 differ slightly, showing a total hydrogen release of about 6.2 and 6.6 mol per one mole of Na[Al(NH$_3$)BH$_4$] for samples s3 and s4, respectively (Figure 7).

We have also applied a volumetric technique to study the two decomposition steps centered at about 120 and 160 °C (Figure 6), by fast heating of mixture s3 to 120 °C, followed by keeping the mixture at this temperature for 60 h, and then by the complete decomposition at 250 °C for about 30 h. Complete separation of these two steps seems impossible due to their partial overlap as evidenced from the TGA–DSC–MS experiments (Figure 6). However, the two decomposition steps are clearly visible on the volumetric curve (Figure S8 in the Supporting Information). The first decomposition step at 120 °C yields approximately 5.3 mol of hydrogen, whereas the total amount of about 8.0 mol is desorbed at 250 °C. These data confirm the prevalent formation of hydrogen: the weight loss of about 9 wt% in the TGA is in agreement with eight mole of hydrogen gas found volumetrically.

The absence of crystalline Al and NaAlH$_3$ (the decomposition products of NaAlH$_4$)\textsuperscript{[40]} of the boron nitride (BN), which can be formed during the decomposition of AB,\textsuperscript{[20,101]} as well as of AlN, which hypothetically can form through the decomposition of Na[Al(NH$_3$)BH$_4$] at 250 °C has been shown by XRPD (Figure S9 in the Supporting Information). The only crystalline phase present there is NaBH$_4$. However, the FTIR spectrum of the final residue reveals all characteristic bands of NaBH$_4$ and a number of additional bands suggesting the presence of the Al–N, B–N, B–H, and N–H groups. The latter two bands are similar to those observed upon thermal decomposition of the pristine AB with the formation of polymeric (NH$_3$)BH$_4$\textsubscript{x} (1 ≤ x ≤ 2) species (Figure S10 in the Supporting Information).\textsuperscript{[35,32]} Furthermore, in resemblance to binary amidoboranes M(NH$_3$)BH$_4$\textsubscript{x} (n = 1, M = Li$^+$, Na$^+$, K$^+$; n = 2, M = Ca$^{2+}$, Mg$^{2+}$)\textsuperscript{[35–36]} and to the Li$_3$AlH$_4$–4AB\textsuperscript{[25]} system, we observed the formation of amorphous product(s), most likely, of the hydrogen-poor Al-N-B-H composition(s). Interestingly, recent theoretical calculations of the decomposition mechanism of Al(NH$_3$)BH$_4$ propose the formation of Al(NBH$_3$)$_2$.\textsuperscript{[37]} However, to the best of our knowledge, no experimental evidence of the existence of Al(NH$_3$)BH$_4$ was reported so far. Taking into account all the data on the decomposition pathway of Na[Al(NH$_3$)BH$_4$] obtained in this work, the following simplified total decomposition reaction can be suggested [Eq. (4)]:

\[
\text{Na[Al(NH$_3$)BH$_4$]} \rightarrow \text{NaBH}_4 + \text{AlN}_x\text{B}_y\text{H}_z(0.3–0.6) + (6.2 – 8.0) \text{H}_2 \quad (4)
\]

Two regeneration tests were performed for the samples s3 and s4 by applying 150 bar of hydrogen: one at 85 °C, to check for a hypothetical transformation back to the starting NaAlH$_4$–4AB composite, and another at 250 °C, to attempt a rehydrogenation of AlN$_x$B$_y$H$_z$. It was found that Na[Al(NH$_3$)BH$_4$] does not take up hydrogen at temperatures up to 85 °C but instead decomposes slowly (Figures S11a and e in the Supporting Information). Thus, the final uptake was negative for both samples s3 and s4. This behavior is expected, because the reaction given in Equation (3) is slightly exothermic according to the DSC data (Figure 6) and the DFT calculations (Figure S7 in the Supporting Information).

Slow hydrogen absorption was observed at 250 °C for the completely decomposed samples s3 and s4 (Figures S11b and f in the Supporting Information). Surprisingly, about 1.7 out of 6.2 mol (≈27%) of the released hydrogen have been absorbed by the amorphous residue during approximately 225 h (Figures S11c and g in the Supporting Information). The absorbed amount can be readily released (Figures S11d and h in the
Supporting Information). This reversible absorption can be due to the hydrogen uptake with the formation of the amorphous intermediate(s) observed between the two decomposition steps at 120 and 160 °C (Figure 1). This scenario is likely, because in situ XRPD done at 250 °C and 150 bar of hydrogen did not show any crystalline phases forming upon the rehydrogenation during 26 h of the decomposed sample 3s (Figure S9 in the Supporting Information). This rehydrogenation can be a result of a continuous hydrogen absorption in the amorphous compound AlN₃B₃H₉₋₁₆ to phases with a higher hydrogen content.

Conclusions

The new NaAlH₄–4AB composite, combining complex and chemical hydrides, releases pure hydrogen and produces the first Al-based amidoborane, Na[Al(NH₂BH₄)₃]. The reaction proceeds already at 70 °C or under mechanochemical treatment at room temperature. This is the first example of a reaction where a complex hydride anion is deprotonated AB. Until now only binary metal hydrides were reacted with AB, forming amidoboranes [see the equation given in Equation (2)]. Breaking of the Al–H bonds in the AlH₄⁻ ion is, apparently, easier than the breaking of the B–H bonds in the BH₄⁻ ion as the latter one does not deprotonate AB. Therefore, alkali and alkali-earth metal borohydrides (M = Li⁺, Mg²⁺, and Ca³⁺) merely form adducts with AB [Eq. (5)]..

\[
M[\text{BH}_4]^n + m \text{NH}_2\text{BH}_3 \rightarrow M[\text{BH}_4]^n \cdot (\text{NH}_2\text{BH}_3)_m
\]

The formation of Na[Al(NH₂BH₄)₃] by the reaction given in Equation (3) is not reversible at 150 bar of hydrogen, which is in line with the observed exothermic dehydrogenation. Therefore, an RHC based on this reaction [Eq. (3)] cannot be used as a reversible hydrogen store.

Na[Al(NH₂BH₄)₃] decomposes in two steps with the formation of NaBH₄ up to eight equivalents of pure hydrogen and an amorphous product AlN₃B₃H₉₋₁₆. The latter reversibly reabsorbs about 27% of hydrogen. This re-absorption regenerates neither NaAlH₄ nor Na[Al(NH₂BH₄)₃] but occurs between the amorphous product and the intermediate(s) of the dehydrogenation. Further in-depth studies of AlN₃B₃H₉₋₁₆ that is, its chemical structure and an optimization of the rehydrogenation process, are required.

During the recent years, Al-based complex hydrides attract an ever-growing attention as potential hydrogen storage media. Indeed, the reaction given in Equation (3) is possible not only because the Al–H bonds are less stable than the B–H ones, but also due to the strong Lewis acidity of the Al⁺³ ion forming the tetraamidoborane complex. The title system opens an avenue to a series of aluminum tetraamidoboranes, M[Al(NH₂BH₄)₃], with improved hydrogen storage properties, such as the hydrogen storage density, the hydrogen purity and reversibility. Our preliminary experiments, not presented in this work, show that the reaction given in Equation (3) easily proceeds in THF solution at room temperature, and these conditions are successfully applied to the reaction in the LiAlH₄–4AB system, uncontrollable in the solid state.

Future works can also exploit the combination of amidoborane and borohydride ligands in the same Al-based compound, tuning their stability through different electron donor–acceptor properties of the ligands. Recent discovery of the M[Al(BH₄)₃] series allows this goal to be achieved in a one-step reaction with M[Al(NH₂BH₄)₃].

Experimental Section

Materials and synthesis: All samples were obtained from commercially available LiAlH₄, NaAlH₄, TiCl₄, and NH₂BH₄ (95, 93, 99.99, and 98% purity, respectively) purchased from Alfa Aesar, Sigma Aldrich Co, and Katchem. All operations were done in gloveboxes with a high purity argon atmosphere. The starting materials were placed into stainless steel vials and milled in a planetary ball mill Fritsch Pulverisette 7, by using Easy GTM gas pressure and a temperature detection system for monitoring the reaction. The gas release measured during the ball milling for the NaAlH₄–4AB composite is shown in Figure S12 in the Supporting Information. The rotation speed was set to 600 rpm and the ball to the powder mass ratio to 30:1. Synthetic approaches for different samples are listed in Table 1.

X-ray powder diffraction analysis (XRPD): Samples were filled into 0.5 mm thin-walled glass capillaries and sealed under an argon atmosphere. Laboratory diffraction data were obtained with a MAR345 diffractometer, rotating anode MoKα radiation, and a XENOCS focusing mirror. Sample 3s was tested for rehydrogenation by using a sapphire-based cell for in situ XRPD. The starting powder was kept in a single-crystal sapphire capillary with an outer diameter of 1.09 mm. Decomposition of Na[Al(NH₂BH₄)₃] under 5 bar of hydrogen was performed by heating the capillary from room temperature to 250 °C with a heating rate of 1 °C min⁻¹. The decomposed sample was heated to 250 °C under 150 bar of hydrogen, whereas powder diffraction data was continuously collected for approximately 26 h.

Variable-temperature in situ synchrotron X-ray powder diffraction (SRXRPD): SRXRPD data were collected with a PILATUS®SNBL diffractometer (SNBL, ESRF, Grenoble, France) equipped with a Dectris PILATUS 2M single-photon counting pixel area detector (λ = 0.823065 Å). Temperature was increased linearly in time by using an Oxford Cryostream 700 + with a heating rate of 5 °C min⁻¹ from room temperature to 150 °C. Powder patterns were obtained by using raw and integrated data preprocessed by the SNBL Toolbox software and data of the LaB₆ standard.

Crystal structure determination: The SRXRPD data for mixture s1 at 100 °C were indexed in a triclinic crystal lattice and the structure of Na[Al(NH₂BH₄)₃] was solved in the P1 space group by using the program FOX. The ADDSYM procedure did not reveal a higher symmetry. The obtained crystal structure was further optimized by DFT calculations (see below) in order to obtain accurate hydrogen atom positions. The final structure, obtained from the DFT calculations, was refined by using bond distance restraints for the hydrogen atoms by the Rietveld method by using Fullprof (Figure 8). The Supporting Information contains the experimental and DFT-optimized crystal structures as CIF files.

DFT optimization: The structure of Na[Al(NH₂BH₄)₃] was optimized by simulated annealing within the plane wave formulation of the DFT method. Electronic configurations of 1s¹ for H, 2s²2p² for B, 2s²2p² for N, 2p³ for Na, and 3s³ for Al were represented by...
The gradient-corrected $pV$ at $100\degree C$ for mixture \textbf{s1} at 100 \degree C (SNBL/SRF synchrotron, $\lambda = 0.8230565\AA$; \text{NaAl[NH$_3$H$_4$]}$_2$: triclinic; space group $P1$: $a = 9.4352(2)$, $b = 7.7198(1)$, $c = 7.6252(1)$ \AA; $\alpha = 97.211(1)$, $\beta = 109.223(2)$, $\gamma = 89.728(2)$; \text{NaAlH$_4$}: tetragonal; space group $I4/ma$: $a = 5.0398(1)$, $b = 11.4319(1)$ \AA; $\beta = 67.9\%$.

Figure 8. Rietveld refinement profile ($R_p = 12.7\%$) for mixture \textbf{s1} at 100 \degree C (SNBL/SRF synchrotron, $\lambda = 0.8230565\AA$; \text{NaAl[NH$_3$H$_4$]}$_2$: triclinic; space group $P1$: $a = 9.4352(2)$, $b = 7.7198(1)$, $c = 7.6252(1)$ \AA; $\alpha = 97.211(1)$, $\beta = 109.223(2)$, $\gamma = 89.728(2)$; \text{NaAlH$_4$}: tetragonal; space group $I4/ma$: $a = 5.0398(1)$, $b = 11.4319(1)$ \AA; $\beta = 67.9\%$.

projected augmented wave potentials.\textsuperscript{58} The gradient-corrected \textsuperscript{(GGA) functionals} and the correction for weak dispersive interac-
tions were applied.\textsuperscript{59} The initial structure from the Rietveld refine-
ment was optimized with respect to the internal atomic positions and the unit cell shape. This optimized structure was heated to $T = 400\degree C$ with a rate of 100 Kps$^{-1}$ and cooled down to $T = 0\degree C$ with a rate of 20 Kps$^{-1}$. No constraints were imposed on the internal atomic positions and the unit cell parameters were kept fixed. A Nose–Hoover thermostat\textsuperscript{58,59} was applied for this procedure, and the time step for integration of equations of motion was 0.6 fs. Six independent structures with the lowest energy from the temperature range below 50 K were optimized with respect to internal atomic positions with a conjugated gradient method; then the symmetry was determined to be $P1$ for five structures with the lowest ground state energy. For these structures the symmetry was imposed and the unit cell shape, together with the atomic positions, was re-optimized. Within the accuracy of the GGA calculations all five structures were identical with the following lattice parameters at the ground state: $a = 9.435$, $b = 7.719$, $c = 7.625$ \AA; $\alpha = 97.213$, $\beta = 109.219$, $\gamma = 89.725$. The total energy of the optimized structure was 0.03 eV per formula unit lower than that for the initial guess. The normal mode analysis was performed with finite displacement method for the $1^\text{st}$ point; atoms were displaced by $\pm 0.25$ \AA along each Cartesian direction. All modes are real positive.

In order to assess the enthalpy of the reaction given in Equation (3), the ground state and the vibrational properties were calculated for \text{AB} and \text{NaAlH$_4$} based on their crystal structures.\textsuperscript{34,35} For all systems two independent calculations were done with and without corrections for weak dispersive interactions. The enthalpy was calculated within an harmonic approximation.\textsuperscript{54} Thus, it consists of the electronic ground state energy and the contribution from the vibrational degrees of freedom.

For the phonon calculations the dynamical matrix was constructed from the forces exerted on atoms upon displacements. The dynamical matrix was diagonalized and the normal mode frequencies and polarization vectors were extracted. The enthalpy of the reaction given in Equation (3), $H(T) = E_T + H_{\text{vib}}(T)$, was calculated within the harmonic approximation as a sum of vibrational $H_{\text{vib}}(T) = \sum \omega_i^2 \hbar \pi + \sum \omega_i \left( \exp \left( \frac{\hbar \omega_i}{kT} \right) - 1 \right)^{-1}$ and electronic contributions at the ground state $E_T$ for each reactant and products ($\omega_i$ is the normal mode frequency at $T = 0\degree K$, $k$ is the Boltzmann constant). For the hydrogen in the gas-phase terms related to rotation-
al, translational, and $pV$ are added as $(7/2)kT$. The ground state energy normal modes were calculated for two independent cases: with and without weak van der Waals forces. For AB the later interactions are important. The lattice parameters calculated for the ground state are given in Table S3 in the Supporting Information.

**Fourier transform infrared spectroscopy (FTIR):** Infrared spectra were recorded with a NICOLET 380 FTIR spectrometer from Thermo Electron Corporation. Samples were exposed to air for about 15 s when transferring from the sample vial to the instrument. In order to determine the decomposition products of mixture \textbf{s3}, the same measurements were performed after its heating in a Schlenk tube under argon atmosphere at 250 \degree C for 3 h.

**Thermal analysis and mass spectrometry:** Thermogravimetric analysis and differential scanning calorimetry were measured by using a Perkin–Elmer STA 6000 apparatus simultaneously with mass spectrometry analysis of the residual gas with the use of a Hiden Analytical HPR-20 QMS sampling system. The samples ($\approx 2$ mg) were loaded into an $\text{Al}_2\text{O}_3$ crucible and heated from room temperature to 400 \degree C ($5\degree C\text{min}^{-1}$) in an argon flow of 20 mL min$^{-1}$. The released gases were analyzed for hydrogen, ammonia, diborane, and borazine.

**Temperature-programmed photographic analysis (TPPA):** Aliquots of samples \textbf{s2} and \textbf{s3} (10 mg) were sealed under argon in a glass tube placed in a home-built aluminum heating block as described recently.\textsuperscript{51} Samples were heated from room temperature to 300 \degree C ($\Delta T/\Delta t = 5\degree C\text{min}^{-1}$), sample \textbf{s2} was also heated from room temperature to 76 \degree C ($\Delta T/\Delta t = 3\degree C\text{min}^{-1}$) and kept at this temperature for 1 h. Photos of the samples were collected every five seconds.

**Volumetric analysis and reversibility tests:** Volumetric analysis was performed with using a Hiden Isochema IMI-SHP analyzer. Aliquots of samples \textbf{s2–s4} (40–50 mg) were heated from 30 to 85 and to 250 \degree C ($1\degree C\text{min}^{-1}$, $p(H_2) = 5$ bar). Subsequently, rehydroge-
nation was performed at $p(H_2) = 150$ bar by heating sample \textbf{s2} to 85 \degree C, and samples \textbf{s3} and \textbf{s4} to 250 \degree C ($0.1\degree C\text{min}^{-1}$). Gas release was calculated from the calibrated volumes of the system, excluding the volume of the glass wool (2.06 g cm$^{-3}$). The final uptake was calculated from the difference between the average start uptake at 30 \degree C (equal to the temperature of the manifold) and the decomposition uptake after cooling to the same temperature, in order to decrease uncertainties of calibrations. Usually, the uptake calculated by the manifold’s IMI software at 250 \degree C is about 3\% lower ($\approx 0.2$ mol) than at 30 \degree C.

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