Dehydrogenation Tuning of Ammine Borohydrides Using Double-Metal Cations

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ABSTRACT: The strategy of using double-cations to tune the temperature and purity of dehydrogenation of ammine borohydrides is reported. The first double-cation ammine borohydride, Li₂Al(BH₄)₅·6NH₃, which forms a novel structure with ordered arrangement of (NH₃)₆⁺ ammine complexes and Li₂(BH₄)₅⁻ complex anions, is found to release over 10.0 wt % hydrogen below 120 °C with favorable kinetics and high H-purity (>99%).

Research on B−N−H systems, e.g. ammonia borane, as potential hydrogen storage materials has intensified to become a highly active and exciting area today. After several excellent initial efforts, a potentially workable approach for developing these systems has been proposed, which is believed may play a significant role in the field of hydrogen storage. Among these booming candidates, ammine borohydrides, M-(BH₄)₃·nNH₃ (M = Li, Mg, Ca, Al), which dehydrogenate on the basis of a simple recombination of the N−H⁻⁺·⋯·H⁻⁻→B dihydrogen bonds, show favorable hydrogen storage properties, competitive with those of ammonia borane. Practically, Al-(BH₄)₃·6NH₃ is one of the most promising candidates as an advanced solid-state hydrogen storage substrate due to its high hydrogen capacity, encouraging dehydrogenation performance, lasting stability in air, and tunable hydrogen storage properties.

Although single-cation ammine borohydrides have been demonstrated to be compelling candidates for hydrogen storage, further improvements in dehydrogenation temperature, purity of gas released, etc. are still required for these materials to be practical. The dehydrogenation temperatures of metal borohydrides have been found to show a certain correlation with Pauling electronegativities and can be tuned extensively with double- or multiple-cation substitutions. It is of great interest if the same strategy may be applicable to the ammine complexes of borohydrides, which could consequently lead to a greatly extended modification of the hydrogen storage properties of this class of materials. To the best of our knowledge, there has been no such investigation of this approach thus far.

Herein we report the first example of a ammine double-cation borohydride, Li₂Al(BH₄)₃·6NH₃. This compound possesses a completely novel structure with an ordered arrangement of hexaamminealuminum(III) complex anions, Al(NH₃)₆³⁻ and Li₂(BH₄)₅⁻, distinct from all known ammonia complexes of borohydrides. More importantly, the dehydrogenation properties are significantly improved in terms of dehydrogenation temperatures, hydrogen capacity, and the purity of gas released compared to the monometallic ammine borohydrides. The finding of mixed-cation ammine borohydrides provides general guideline to chemical control of the hydrogen storage properties of ammine borohydrides as well as an easy synthesis route to prepare other new compounds.

Li₂Al(BH₄)₅·6NH₃ crystallizes in a hexagonal P6₃mc (No. 165) structure with lattice parameters of a = 7.79779(5) Å and c = 15.9693(1) Å, as shown by high-resolution X-ray diffraction. The structure is illustrated in Figure 1a, the detailed crystallographic data are listed in Table S1, and the Rietveld fit to the diffraction pattern is shown in Figure S1. A noticeable feature of the Li₂Al(BH₄)₅·6NH₃ structure is that each cation is coordinated completely by the same type of ligands, in contrast to the known monometallic borohydride ammoniates such as Li(NH₃)BH₄⁹,¹⁰ Mg(BH₄)₂·2NH₃⁶, Ca(BH₄)₂·2NH₃¹¹ and Al(BH₄)₃·NH₃¹⁸ where the cation is surrounded by both BH₄− and NH₃ groups.

In Li₂Al(BH₄)₅·6NH₃, Al atoms are octahedrally coordinated exclusively by six NH₃ molecules with Al−N distance of 2.05 Å, longer than those in ammine aluminum halides such as Al(NH₃)₃Xₙ (X = Br, I, n)¹⁹ Al(NH₃)₃X₉ Al(NH₃)₂F₇ Al(NH₃)₂X₅ and Al(NH₃)₃Cl₆ (X = Cl, Br, and I)²² and also longer than those in Al(BH₄)₃·NH₃.¹⁸ The Al−N distance(s) in these halides are in the range of 1.62−2.01 Å, and the Al−N distance in Al(BH₄)₃·NH₃ is 1.95 Å. It should be noted that in these compounds Al is coordinated by both NH₃ ligands and halogen anions or BH₄− ions. In such a configuration, N donates its lone-pair electrons to Al, and Al donates its valence electrons to anions (N→Al→X). Therefore, the anions are ultimately an electron drain, resulting in relatively strong interactions between Al and N and a shorter Al−N bond length. When Al is fully coordinated by six NH₃’s and forms hexaamminealuminum(III), Al(NH₃)₆³⁺, the interaction between Al and the neutral NH₃ becomes weaker due to the milder ligand strength of NH₃ compared to the anionic ligands, leading to a longer bond length. The longer Al−N bond lengths in hexaamminealuminum(III) complexes is also found in Al(NH₃)₃I₃(NH₃)³, where Al−N is 2.044 Å.

As for the Li surroundings, Li atoms are tetrahedrally coordinated by four BH₄ groups via ionic bonding, with Li−B distances of approximately 2.52 and 2.68 Å, similar to those in...
Figure 1. (a) (110) view of the crystal structure of Li2Al(BH4)5·6NH3. The dihydrogen bonds are highlighted in blue. (b) A 2D sheet of Li[BH4]4 tetrahedra framework viewed from (001). Li[BH4]4 tetrahedra are linked by bridging BH4− units (B2 site). (c) Local coordination of the Li and BH4− network. Li tetrahedrally coordinates to four BH4− units with three bridging BH4− (B2 site) and one vertex BH4− (B1 site). BH4− units are strongly associated to Li+, forming the Li3[BH4]4 complex anion. (d,e) NH···HB dihydrogen bonding around (d) NH3 and (e) BH4−. The NH···HB distances are measured in angstroms.

Lithium borohydride complexes.24–26 These Li[BH4]4 tetrahedra are then vertex-linked through three bridging BH4− units (B2, 6f site) with the fourth BH4− in the trans position (B1, 4d), leading to the formation of a two-dimensional honeycomb-patterned sheet that spreads along the ab plane (Figure 1b). This structural topology is similar to that of some porous silicate zeolites27 and is observed for the first time in the metal hydride systems. Notably, the framework is composed of three of the lightest elements, Li, B, and H. As BH4− units are strongly associated with Li+, such a 2D network is actually an anionic complex of Li2[BH4]53− (Figure 1b, c). As a result, Li2Al(BH4)5·6NH3 adopts an intriguing ordered arrangement with alternating layers of Al[NH3]6 octahedra and Li[BH4]4 tetrahedra and thus should be formulated as [Al(NH3)6][Li2(BH4)5], which is comprised of Al(NH3)63− ammine complexes and Li2(BH4)5− complex anions.

Li2Al(BH4)5·6NH3 contains oppositely charged H0− (in BH4−) and H3+ (in NH3). It would be interesting to check for the presence of dihydrogen bonding as addressed in other B−N hydrogenous compounds. The crystal structure shows that all H’s in the NH3 ligands have short separations, in a range of 2.02–2.26 Å (Table S2), to their neighboring H in BH4−, indicating rather strong dihydrogen bonding (Figure 1). This is remarkably different from the known monomeric ammine borohydrides because in these structures (i) not all H’s in NH3 participate in the dihydrogen bonding with BH4 and (ii) the NH···HB distances are not as short as in the present mixed-cation ammine borohydride. The closest NH···HB interactions in Li2Al(BH4)5·6NH3 are even shorter than those in the recently discovered metal amidoboranes28 and are comparable to that in the solid ammonia borane, NH3BH3 (2.02 Å),29 where the dihydrogen bonding is known to be primarily responsible for the stability of this molecular compound at room temperature and its predominant thermal dehydrogenation properties. Therefore, the strong dihydrogen bonding between all H’s in NH3 ligands and the H’s in the BH4− groups, particularly the H’s in the vertex BH4− in the trans positions, tightly stitches the layers of Al[NH3]6 octahedra and Li[BH4]4 tetrahedra together (Figure 1) and plays an important role in cohesion and the structural stability. Furthermore, similar to NH3BH3, the strong NH···HB interaction in such a structural motif is expected to have a great impact on the dehydrogenation properties of Li2Al(BH4)5·6NH3.

Thermogravimetry/mass spectroscopy (TG/MS) measurements on Li2Al(BH4)5·6NH3 (Figure 2a) revealed a two-step decomposition, with a total weight loss of 23.2 wt % by 300 °C. Gas released in the first step, proceeding from ~75 to 150 °C, is predominantly H2, with a slight amount of NH3, while the second step, from 190 to 250 °C, is purely from H2 release. No B2H6 byproduct was detected at any point of the measured temperature range (Figure 2b). The differential scanning calorimeter (DSC) result (Figure S2) indicates that the first dehydrogenation step of Li2Al(BH4)5·6NH3 is a weakly exothermic reaction, −5.8 kJ/mol H2. Attempts to directly recharge the dehydrogenated samples under 6.9 MPa of H2 at 170 and 350 °C for 10 h were unsuccessful. However, the decomposition is significantly less exothermic than that of AB (−21 kJ/mol),3 indicating that a potential endothermic H2 release is possible with proper modification of the material. Volumetric temperature-programmed desorption measurements (Figure 2b, Figures S3 and S4) were performed to obtain more detailed decomposition information for Li2Al(BH4)5·6NH3. On the basis of the volumetric and gravimetric results, Li2Al(BH4)5·6NH3 released 15.5 wt % H2 (~88% of its calculated hydrogen content, 17.6%) with a purity of 97.0 mol % (see Table S3) from room temperature to 300 °C at a heating rate of 5°C/min. Given that the onset of evolution of NH3 starts around 125 °C, isothermal dehydrogenation from 100 to 130 °C was conducted to examine the kinetics and purity of hydrogen release. It revealed that the dehydrogenation of Li2Al(BH4)5·6NH3 proceeded slowly at 100 °C, releasing 9.8 wt % hydrogen within 7 h (Figure S3). Elevated temperature resulted in faster dehydrogenation; i.e., at 110 and 120 °C, >10 wt % hydrogen, corresponding to around 11 equiv of H2, with a purity of >99 mol %, can be achieved within 3 h and 2 h, respectively. Clearly, the dehydrogenation properties of Li2Al(BH4)5·6NH3 are greatly improved compared to the Al(BH4)3·6NH3, in which only 4.3 wt % hydrogen was released in 3 h at 130 °C (Figure 2b).

High-resolution in situ XRD revealed that no structure change occurred before 120 °C, and that after the first-step dehydrogenation...
At 130 °C, all the peaks assigned to Li$_2$Al(BH$_4$)$_3$·6NH$_3$ disappeared. No appearance of LiBH$_4$ or other unknown phases but a poorly crystalline product was observed (Figure S5). The limited number of XRD peaks and the poor crystallinity prevented the identification of the dehydrogenation products. Fourier transform infrared spectroscopy (FTIR) results (Figure S6) showed that, after Li$_2$Al(BH$_4$)$_3$·6NH$_3$ was heated to 130 °C, the intensity of the NH groups was greatly reduced while vibrations assigned to BH groups were still apparent, suggesting the consumption of N–H during the dehydrogenation. Further heat treatment to 300 °C resulted in the disappearance of both BH and NH groups. Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra showed an asymmetric N–H resonance centered at –36.6 and –38.1 ppm with peak area ratio about 2:3 in the as-synthesized sample (Figure S7), consistent with the population ratio of two B sites observed in the structure, further confirming the same B species in Li$_2$Al(BH$_4$)$_3$·6NH$_3$. After heat treatment at 170 °C, three kinds of B nuclei peaks appeared at 18.6, –1.3, and –39.8 ppm, indicating the formation of tricoordinated B$_{III}$ atoms (18.6 ppm) and tetracoordinated B$_{IV}$ atoms (–1.3 and –39.8 ppm), respectively, consistent with the partial consumption of BH$_4$ suggested by the IR results. From the NMR, FTIR, and XRD results, the intermediate phase is still not clear. Identification of the dehydrogenation product is necessary in the future, to enable the determination of reaction pathway and to promote further studies to achieve the possible reversibility of this type of material.

The dramatic improvement in the dehydrogenation of the Li$_2$Al(BH$_4$)$_3$·6NH$_3$ may be attributed to its unique structure characteristics and deliberately introduced H$^{3+}$ and H$^{5-}$. It has been proposed and experimentally confirmed that the decomposition temperatures of borohydrides can be tuned through adjusting the overall cation electronegativity with the combination of different elements. Stable LiBH$_4$ can be modified by the substitution of cations with higher electronegativity such as Zn$^{14+}$ and Al$^{15+}$. A very low dehydrogenation temperature (~70 °C) has been recently found in the Li–Al-based borohydride system, Al$_4$Li$_4$(BH$_4$)$_{13}$·15H$_2$O. However, Al$_4$Li$_4$(BH$_4$)$_{12}$ suffers from the common problem in metal borohydrides that the hydrogen released is contaminated by a significant amount of diborane. Introducing oppositely charge H$^{3+}$ through the formation of ammonia complexes of borohydrides M–(BH$_4$)$_m$·nNH$_3$ is another option to lower the decomposition temperature of M(BH$_4$)$_m$. Because ammonia is detrimental for fuel cell applications, the NH$_3$/BH$_4$ ratio (n/m) should be monitored so that no extra ammonia is released. It requires ingenious synthesis to control the exact ratio of N/B as the number of BH$_4$ is fixed by the valence of M in M(BH$_4$)$_m$·nNH$_3$. As a result, all the reported mononuclear ammine borohydride complexes still suffer from the problem of hydrogen purity. The synthesis of ammine complexes of mixed-cation borohydrides seems to provide an optimized solution by combining these two methods. Mixing cations with different valences enables the number of BH$_4$ to be also tunable so that accurate control of the M/B/N ratio becomes more facile and feasible. Therefore, minimization of NH$_3$ and other toxic volatile gases such as diborane is achieved in Li$_2$Al(BH$_4$)$_3$·6NH$_3$. Furthermore, the combination of cations with different ionicities/valences and the coexistence of H$^{3+}$ and H$^{5-}$ both have advantageous effects on reducing the dehydrogenation temperatures. In its unique crystal structure, Li$_2$Al(BH$_4$)$_3$·6NH$_3$ contains the closest NH···HB interactions in all known ammine complexes of borohydrides. The strong dihydrogen bonding not only plays an indispensable role in stabilization of the layered structure of Li$_2$Al(BH$_4$)$_3$·6NH$_3$ but also promotes the reaction between H$^{3+}$ and H$^{5-}$ and thus accelerates the release of hydrogen at much lower temperature and faster rate. If the rapid reaction between H$^{3+}$ and H$^{5-}$ exceeds the bond breaking between N–Al, this would be another factor contributing to the minimized NH$_3$ release, as observed in hydride–amide systems. 

In summary, the first double-cation ammine borohydride, Li$_2$Al(BH$_4$)$_3$·6NH$_3$, has been successfully synthesized. It forms a novel structure with an ordered arrangement of Al(NH$_3$)$_6$ ammine complexes and Li$_2$(BH$_4$)$_3$ complex anions. Li$_2$Al(BH$_4$)$_3$·6NH$_3$ exhibits dramatically improved dehydrogenation properties over all known mixed-cation borohydrides and ammine complexes of mononuclear borohydrides, with >10 wt % of hydrogen evolution easily achieved below 120 °C. This offers a promising route toward the chemical control of the dehydrogenation of ammine borohydrides.

**ASSOCIATED CONTENT**

2 Supporting Information. Materials and methods, crystallographic data, X-ray patterns, DSC, TPD, FTIR, and NMR results, including Figures S1–S7 and Tables S1–S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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