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Dehydrogenation Tuning of Ammine Borohydrides Using Double-Metal Cations

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S *Supporting Information*

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, $Li_2Al(BH_4)_5\cdot 6NH_3$, which forms a novel structure with ordered arrangement of $Al(NH_3)_6^{3+}$ ammine complexes and $Li_2(BH_4)_5^{3-}$ 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.[1] After several excellent initial efforts,[2−12] a potentially workable approach for developing these systems has been proposed, which it is believed may play a significant role in the field of hydrogen storage. Among these booming candidates, ammine borohydrides, $M(BH_4)_m\cdot n NH_3$ (M = Li, Mg, Ca, Al), which dehydrogenate on the basis of a simple recombination of the $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ dihydrogen bonds, show favorable hydrogen storage properties, competitive with those of ammonia borane.[7,11,12] Practically, $Al(BH_4)_3\cdot 6NH_3$ 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.[13]

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.[14−17] 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 an ammine double-cation borohydride, $Li_2Al(BH_4)_5\cdot 6NH_3$. This compound possesses a completely novel structure with an ordered arrangement of hexaamminealuminum(III) complex anions, $Al(NH_3)_6^{3+}$ and $Li_2(BH_4)_5^{3-}$, 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.

$Li_2Al(BH_4)_5\cdot 6NH_3$ crystallizes in a hexagonal $P\bar{3}c1$ (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 $Li_2Al(BH_4)_5\cdot 6NH_3$ structure is that each cation is coordinated completely by the same type of ligands, in contrast to the known monometallic borohydride ammoniates such as $Li(NH_3)BH_4$,[9,10] $Mg(BH_4)_2\cdot 2NH_3$,[6] $Ca(BH_4)_2\cdot 2NH_3$,[11] and $Al(BH_4)_3\cdot NH_3$,[18] where the cation is surrounded by both BH_4^- and NH_3 groups.

In $Li_2Al(BH_4)_5\cdot 6NH_3$, Al atoms are octahedrally coordinated exclusively by six NH_3 molecules with Al—N distance of 2.05 Å, longer than those in ammine aluminum halides such as $Al(NH_3)_5X_3$,[19] $Al(NH_3)_3X_3$,[20] $Al(NH_3)_2F_3$,[21] $Al(NH_3)X_3$,[19] and $Al(NH_3)_6Cl_6$ (X = Cl, Br, and I)[22] and also longer than those in $Al(BH_4)_3\cdot NH_3$.[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 $Al(BH_4)_3\cdot NH_3$ is 1.95 Å. It should be noted that in these compounds Al is coordinated by both NH_3 ligands and halogen anions or BH_4^- ions. In such a configuration, N donates its lone-pair electrons to Al, and Al donates its valence electrons to anions ($N\rightarrow Al\rightarrow X$). 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 NH_3's and forms hexaamminealuminum(III), $Al(NH_3)_6^{3+}$, the interaction between Al and the neutral NH_3 becomes weaker due to the milder ligand strength of NH_3 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 $Al(NH_3)_6I_3(NH_3)$,[23] where Al—N is 2.044 Å.

As for the Li surroundings, Li atoms are tetrahedrally coordinated by four BH_4 groups via ionic bonding, with Li—B distances of approximately 2.52 and 2.68 Å, similar to those in

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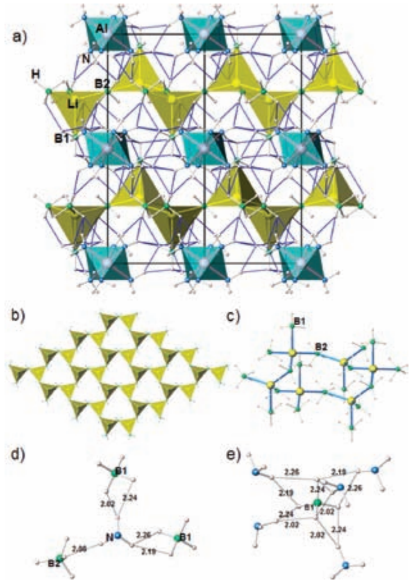

Figure 1. (a) (110) view of the crystal structure of $Li_2Al(BH_4)_5 \cdot 6NH_3$. The dihydrogen bonds are highlighted in blue. (b) A 2D sheet of $Li[BH_4]_4$ tetrahedra framework viewed from (001). $Li[BH_4]_4$ tetrahedra are linked by bridging BH_4^- units (B2 site). (c) Local coordination of the Li and BH_4^- network. Li tetrahedrally coordinates to four BH_4^- units with three bridging BH_4^- (B2 site) and one vertex BH_4^- (B1 site). BH_4^- units are strongly associated to Li^+, forming the $Li_2(BH_4)_5^{3+}$ complex anion. (d,e) NH···HB dihydrogen bonding around (d) NH_3 and (e) BH_4. The NH···HB distances are measured in angstroms.

lithium borohydride complexes.[24−26] These $Li[BH_4]_4$ tetrahedra are then vertex-linked through three bridging BH_4 units (B2, 6f site) with the fourth BH_4 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 zeolites[27] 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 BH_4^- units are strongly associated with Li^+, such a 2D network is actually an anionic complex of $Li_2[BH_4]_5^{3+}$ (Figure 1b, c). As a result, $Li_2Al(BH_4)_5 \cdot 6NH_3$ adopts an intriguing ordered arrangement with alternating layers of $Al[NH_3]_6$ octahedra and $Li[BH_4]_4$ tetrahedra and thus should be formulated as $[Al(NH_3)_6][Li_2(BH_4)_5]$, which is comprised of $Al(NH_3)_6^{3+}$ ammine complexes and $Li_2(BH_4)_5^{3-}$ complex anions.

$Li_2Al(BH_4)_5 \cdot 6NH_3$ contains oppositely charged $H^{\delta-}$ (in BH_4^-) and $H^{\delta+}$ (in NH_3). 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 NH_3 ligands have short separations, in a range of 2.02−2.26 Å (Table S2), to their neighboring H in BH_4^-, indicating rather strong dihydrogen bonding (Figure 1). This is remarkably different from the known monometallic ammine borohydrides because in these structures (i) not all H's in NH_3 participate in the dihydrogen bonding with BH_4 and (ii) the NH···HB distances are not as short as in the present mixed-cation ammine borohydride. The closest NH···HB interactions in $Li_2Al(BH_4)_5 \cdot 6NH_3$ are even shorter than those in the recently discovered metal amidoboranes[2] and are comparable to that in the solid ammonia borane, NH_3BH_3 (2.02 Å),[28] where the dihydrogen bonding is known to be primarily responsible for the stability of this molecular compound at room temperature and its predominate thermal dehydrogenation properties. Therefore, the strong dihydrogen bonding between all H's in NH_3 ligands and the H's in the BH_4^- groups, particularly the H's in the vertex BH_4^- in the *trans* positions, tightly stitches the layers of $Al[NH_3]_6$ octahedra and $Li[BH_4]_4$ tetrahedra together (Figure 1) and plays an important role in cohesion and the structural stability. Furthermore, similar to NH_3BH_3, the strong NH···HB interaction in such a structural motif is expected to have a great impact on the dehydrogenation properties of $Li_2Al(BH_4)_5 \cdot 6NH_3$.

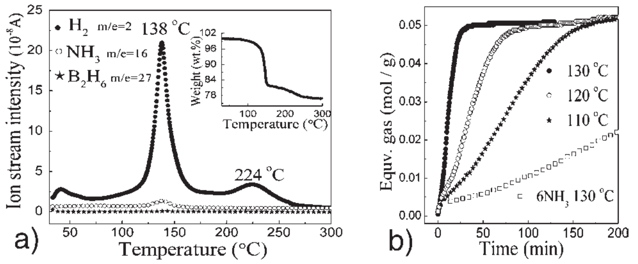

Figure 2. (a) MS and TG (inset) profiles of $Li_2Al(BH_4)_5 \cdot 6NH_3$ with a heating rate of 10 °C min^{-1} in argon. (b) Isothermal TPD curves for the decomposition of $Li_2Al(BH_4)_5 \cdot 6NH_3$ at 110, 120, and 130 °C and $Al(BH_4)_3 \cdot 6NH_3$ at 130 °C (noted as $6NH_3$).

Thermogravimetry/mass spectroscopy (TG/MS) measurements on $Li_2Al(BH_4)_5 \cdot 6NH_3$ (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 H_2, with a slight amount of NH_3, while the second step, from 190 to 250 °C, is purely from H_2 release. No B_2H_6 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$ is a weakly exothermic reaction, −5.8 kJ/mol H_2. Attempts to directly recharge the dehydrogenated samples under 6.9 MPa of H_2 at 170 and 350 °C for 10 h were unsuccessful. However, the decomposition is significantly less exothermic than that of AB (−21 kJ/mol),[1] indicating that a potential endothermic H_2 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$. On the basis of the volumetric and gravimetric results, $Li_2Al(BH_4)_5 \cdot 6NH_3$ released 15.5 wt % H_2 (~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 NH_3 starts at 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$ 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 H_2, with a purity of >99 mol %, can be achieved within 3 h and 2 h, respectively. Clearly, the dehydrogenation properties of $Li_2Al(BH_4)_5 \cdot 6NH_3$ are greatly improved compared to the $Al(BH_4)_3 \cdot 6NH_3$, 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

(130 °C), all the peaks assigned to $Li_2Al(BH_4)_5 \cdot 6NH_3$ 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$ was heated to 170 °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 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 two different B species in $Li_2Al(BH_4)_5 \cdot 6NH_3$. 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.[29,30] From the NMR, FTIR, and XRD results the structure of 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$ may be attributed to its unique structure characteristics and deliberately introduced $H^{\delta+}$ and $H^{\delta-}$. 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.[14,16,31] 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, $Al_3Li_4(BH_4)_{13}$.[15] However, $Al_3Li_4(BH_4)_{13}$ suffers from the common problem in metal borohydrides that the hydrogen released is contaminated by a significant amount of diborane. Introducing oppositely charge $H^{\delta+}$ through the formation of ammonia complexes of borohydrides $M(BH_4)_m \cdot nNH_3$ 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 $M(BH_4)_m \cdot nNH_3$. As a result, all the reported monometallic 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 difference 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$. Furthermore, the combination of cations with different ionicities/valences and the coexistence of $H^{\delta+}$ and $H^{\delta-}$ both have advantageous effects on reducing the dehydrogenation temperatures. In its unique crystal structure, $Li_2Al(BH_4)_5 \cdot 6NH_3$ 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 $Li_2Al(BH_4)_5 \cdot 6NH_3$ but also promotes the reaction between $H^{\delta+}$ and $H^{\delta-}$ and thus accelerates the release of hydrogen at much lower temperature and faster rate. If the rapid reaction between $H^{\delta+}$ and $H^{\delta-}$ 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.[32]

In summary, the first double-cation ammine borohydride, $Li_2Al(BH_4)_5 \cdot 6NH_3$, has been successfully synthesized. It forms a novel structure with an ordered arrangement of $Al(NH_3)_6^{3+}$ ammine complexes and $Li_2(BH_4)_5^{3-}$ complex anions. $Li_2Al(BH_4)_5 \cdot 6NH_3$ exhibits dramatically improved dehydrogenation properties over all known mixed-cation borohydrides and ammine complexes of monometallic 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

Ⓢ 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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