The First Halide-Free Bimetallic Aluminum Borohydride: Synthesis, Structure, Stability, and Decomposition Pathway

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Supporting Information

ABSTRACT: Interaction of solid KBH₄ with liquid Al(BH₄)₃ at room temperature yields a solid bimetallic borohydride KAl(BH₄)₄. According to the synchrotron X-ray powder diffraction, its crystal structure (space group Fddd, a = 9.7408(3), b = 12.4500(4), and c = 14.6975(4) Å) contains a substantially distorted tetrahedral [Al(BH₄)₄]⁻ anion, where the borohydride groups are coordinated to aluminum atoms via edges. The η²-coordination of BH₄⁻ is confirmed by the infrared and Raman spectroscopies. The title compound is the first aluminum-based borohydride complex not stabilized by halide anions or by bulky organic cations. It is not isostructurally to bimetallic chlorides, where more regular tetrahedral AlCl₄⁻ anions are present. Instead, it is isomorphous to the LT phase of TbAsO₄ and can be also viewed as consisting of two interpenetrated dia-type nets where BH₄⁻ ligand is bridging Al and K cations. Variable temperature X-ray powder diffraction, TGA, DSC, and TGA-MS data reveal a single step of decomposition at 160 °C, with an evolution of hydrogen and some amount of diborane. Aluminum borohydride is not released in significant amounts; however, some crystalline KBH₄ forms upon decomposition. The higher decomposition temperature than in chloride-substituted Li-Al (70 °C) and Na-Al (90 °C) borohydrides suggests that the larger alkali metal cations (weaker Pearson acids) stabilize the weak Pearson base, [Al(BH₄)₄]⁻.

INTRODUCTION

During the recent years, metal borohydride complexes and their derivatives are among the most exciting materials for potential hydrogen storage due to their high hydrogen content.1 Regarding the hydrogen gravimetric and volumetric system targets, recently revised by the U.S. Department of Energy to 5.5 wt % and 40 g/L,² most of the alkali and alkali-earth metal borohydrides match them. However, metal borohydrides are quite stable for hydrogen release by thermolysis as they decompose at high temperatures (about 470 °C for LiBH₄ and 290–500 °C for Mg(BH₄)₂).³,⁴ The temperature of desorption can be dramatically reduced for bimetallic borohydride complexes, where the decomposition temperature decreases with increasing Pauling electronegativity for complex anions.⁵,⁶

The increasing covalence in M−H bonding weakens the B−H bond and improves thermal decomposition properties of bimetallic complexes. Among the so far published bimetallic borohydrides, there are several that match the temperature range of 60–120 °C applicable for fuel cells:⁷ “Li₃Al(Al(BH₄)₄)”, containing some chloride on a borohydride site,⁸ Na[Al(BH₄)₄−Cl]₉, NaZn₂(BH₄)₃, NaZn(NBH₄)₂,⁹ KCd(BH₄)₂, K₂Cd(BH₄)₄,¹⁰ K₃Cd(BH₄)₆.¹¹ All the mentioned bimetallic borohydrides evolve diborane (B₂H₆) as hydrogen desorption byproduct which prevents full reversibility and is undesirable for fuel cell applications. This disadvantage is absent for borohydrides which decompose at higher temperatures,¹² in particular for the bimetallic series (Li, Na, K)[(Sc, Y)-(BH₄)₄].¹³–¹⁶ Because of the widely used mechanochemical synthesis of novel borohydrides starting from metal borohydrides and halides, most bimetallic systems contain metal halides as secondary phases as well as halide substitution on the borohydride sites.¹⁷,¹⁸ Besides stabilizing new phases that may not exist in Cl-free systems,¹⁹ this considerably decreases gravimetric capacities of the novel hydrides. From this point of view, it is important to carry out synthesis of new borohydrides by addition with other complex forming borohydrides, like Al(BH₄)₃.²⁰

Herein we report on the synthesis, crystal structure, and Raman vibrational spectra together with thermal analysis of K[Al(BH₄)₄] which was first obtained by Semenenko et al.²¹ The synthesis was performed with liquid Al(BH₄)₃ and KBH₄ with the aim to prevent formation of possible halide-containing...
phases, common in case of metathesis reactions between borohydrides and halides. The crystal structure was determined by synchrotron powder diffraction, and further structural characterization was performed with Raman and IR spectroscopy. The thermal stability of the title compound up to 160 °C is considerably higher than 70 and 90 °C for the related Li[Al(BH$_4$)$_4$]$_3$ and Na[Al(BH$_4$)$_4$-Cl]$_3$. Unlike the Li-based phase, the title compound does not desorb Al(BH$_4$)$_3$; however, it eliminates diborane as a decomposition byproduct with 20.8 wt % mass loss at 12.7 wt % theoretical hydrogen content.

**EXPERIMENTAL DETAILS**

**Synthesis.** Caution! Al(BH$_4$)$_3$ is highly pyrophoric and explosive in contact with moisture and air. In order to prevent explosive reaction of Al(BH$_4$)$_3$ with air, all manipulations were carried out in nitrogen-filled Plexiglas glovebox. The starting materials are AlCl$_3$ (95% Sigma-Aldrich), KBH$_4$ (99% Sigma-Aldrich), and LiBH$_4$ (95% Sigma-Aldrich and 96% Boss Chemical Industry Co.). The first stage of the synthesis is the preparation of Al(BH$_4$)$_3$ from AlCl$_3$ and LiBH$_4$ according to the reaction

\[
\text{AlCl}_3 + 3\text{LiBH}_4 \rightarrow \text{Al(BH}_4)_3 + 3\text{LiCl}
\]

We have developed a modified procedure of those described in refs 20 and 22. The grinded mixture with 5% excess of LiBH$_4$ (Boss Chemical Industry Co.) relative to stoichiometry was condensed in the traps. The pumping was ended when the system was pumped down to 10$^{-7}$ mbar, and the product with some AlCl$_3$ impurity is condensed in the traps. The pumping was ended when the mixture stopped boiling. The content of the first trap was unfrozen and purified by distillation at ambient pressure, all in the nitrogen-filled glovebox. The distillation was carried out with Teflon-coated greaseless ground glass joints using a water cooled Liebig condenser. Only the fraction boiling at $>$ 44.5 °C is considerably higher than 70 and 90 °C, while the fraction boiling at 44.5 °C considerably depends on the purity of Al(BH$_4$)$_3$; however, it eliminates diborane as a decomposition byproduct with 20.8 wt % mass loss at 12.7 wt % theoretical hydrogen content.

After the first stage of the synthesis, 1–2 mL of the fresh Al(BH$_4$)$_3$ was transferred via a syringe to a bottle with 200 mg of grinded KBH$_4$ powder with continuous stirring. Reaction 2 took place over 4–6 days:21

\[
\text{Al(BH}_4)_3 + \text{KBH}_4 \rightarrow \text{K[Al(BH}_4]_2}
\]

The excess of volatile Al(BH$_3$)$_2$ was removed by pumping with an oil pump for a few minutes. The final products of the reaction were identified by X-ray powder diffraction (XRD). The thermal stability of the title compound up to 160 °C is considerably higher than 70 and 90 °C, and Na[Al(BH$_4$)$_4$-Cl]$_3$. Unlike the Li-based phase, the title compound does not desorb Al(BH$_4$)$_3$; however, it eliminates diborane as a decomposition byproduct with 20.8 wt % mass loss at 12.7 wt % theoretical hydrogen content.

**IR and Raman Spectra.** These spectra were recorded at room temperature respectively with a FTIR-8400S Shimadzu spectrophotometer in the 400–4000 cm$^{-1}$ range and with a Bruker RFS 100/s FT-Raman spectrometer ($I$ = 200 mW) in 100–4000 cm$^{-1}$ using a diode-pumped, air-cooled Nd:YAG laser for 1064 nm excitation. For the IR measurements the sample was mixed with KBr matrix and XENOCs focusing mirror.

**TGA and DSC Analysis.** This analysis was made on powder samples after preliminary X-ray powder diffraction analysis. The data were obtained independently with a TGA/SDTA 851 Mettler and a DSC 821 Mettler instrument with the heating rate of 5 °C/min from 25 to 500 °C. The samples for the TGA and DSC analyses were sealed under an inert atmosphere. The decomposition was performed using a MAR345 diffractometer, rotating anode MoKα radiation, and XENOCS focusing mirror. The decomposition was performed using a MAR345 diffractometer, rotating anode MoKα radiation, and XENOCS focusing mirror.

**X-ray Powder Diffraction Analysis.** Samples were filled into 0.5 mm thin-walled glass capillaries and sealed under an inert atmosphere. Laboratory diffraction data were obtained with a MAR345 diffractometer, rotating anode MoKα radiation, and XENOCS focusing mirror.
and DSC analysis were loaded in the argon inert glovebox into crucibles with caps or sealed into aluminum pans, respectively. The experiments were done under 10 mL/min nitrogen flow to prevent the oxidizing reactions.

**TGA Coupled with Mass Spectrometry (MS).** TGA-MS was measured using two independent setups: (1) ThermoStar GSD 301T spectrometer coupled with simultaneous TGA/DTA 851 Mettler and (2) Omnistar GSD 301C-Pfeiffer Vacuum spectrometer coupled with SETARAM Setsys Ev 1750 TGA instrument. The measurements were done under 10 mL/min argon flow with the heating rate of 2 °C/min in 25–300 and 20–500 °C temperature ranges, respectively.

**RESULTS AND DISCUSSION**

**Phase Analysis of in Situ Synchrotron Powder Diffraction Data.** The X-ray powder diffraction analysis was performed for ternary Li−K−Al and binary K−Al borohydride systems; the details are given in the Supporting Information, Figure S3. The trimeritic Li−K−Al−BH₄ system contains LiBH₄ as LT and HT polymorphs (within their stability ranges), KBH₄, LiK(BH₄)₂, and a new bimetallic phase, K[Al(BH₄)₄]. The formation of K[Al(BH₄)₄] is more favorable than that of LiAl₃[BH₄]₁₃ or a hypothetical Li[Al(BH₄)₄] because the Li atom is a weaker donor of electrons compared to K. In other words, K stabilizes better the [Al(BH₄)₄]⁻ complex. The known bimetallic LiK(BH₄)₂ forms readily at room temperature, in contrast to the 120 °C annealing required for the LiBH₄/KBH₄ sample. Formation of LiK(BH₄)₂ in the mild conditions is thus mediated by Al(BH₄)₃. It can be explained by partial solubility of solid LiBH₄ and KBH₄ borohydrides in liquid Al(BH₄)₃ facilitating the addition reaction. Notably, LiK(BH₄)₂ in our sample decomposes into the LiBH₄ + KBH₄ mixture at much lower temperatures than reported previously, namely at 95 °C against 240 °C attributed to melting and 380 °C for the decomposition. The disappearance of diffraction peaks from LiK(BH₄)₂ correlates nicely with increasing intensities from LiBH₄ and KBH₄. This observation confirms the theoretical conjecture that LiK(BH₄)₂ is unstable with respect to decomposition into LiBH₄ and KBH₄ as the decomposition temperatures apparently do not reflect the equilibrium state but the kinetic barriers intrinsic to a particular multicomponent system, in particular by the presence of the Al-based complex, K[Al(BH₄)₄].

We focused our attention on the new bimetallic compound, which we first observed by diffraction in this ternary system. Our further attempts were to obtain and characterize this complex from the binary KBH₄ + Al(BH₄)₃ mixture. Two cycles of soaking in excess of Al(BH₄)₃ and its removal in vacuum resulted in samples containing ∼70 wt% of K[Al(BH₄)₄] with 30% of the remaining KBH₄. The yield can be increased to 90% by a third soaking—vacuum pumping cycle. The important intermediate step in the synthesis is grinding the sample before adding a new portion of Al(BH₄)₃.

**Crystal Structure of K[Al(BH₄)₄].** The title compound is the first halide-free bimetallic borohydride containing [Al(BH₄)₄]⁻. The other bimetallic Al-based complexes, such as “Li₄Al₃[BH₄]₁₃” and Na[Al(BH₄)₄]₉, Cl₉” are stabilized by Cl-substitution on the borohydride sites, as determined by structural refinements. The only Cl-free complex aluminum borohydride, [Ph₃MeP][(Al(BH₄)₄)], contains a bulky organic cation, making it inappropriate for hydrogen storage applications. Interestingly, a synthesis involving AlCl₃ results in the K[Al(BH₄)₄] phase with cell parameters very similar to those of the chlorine-free compound, indicating low or no substitution of Cl on the BH₄ sites (see Supporting Information).

**Figure 1.** (a) Low-angle part of the Rietveld refinement profile (extending up to 62° in 2θ) for the ESRF synchrotron data, λ = 0.682 525 Å, Rwp = 7.55%. K[Al(BH₄)₄]: space group Fddd, a = 9.740(3), b = 12.450(4), and c = 14.6975(4) Å, Rp = 3.8%; KBH₄: Fm-3m, a = 6.7256(1) Å, Rp = 3.2%. (b) Temperature evolution of powder diffraction patterns for K[Al(BH₄)₄]/KBH₄ mixture from 30 to 210 °C, λ = 0.815 60 Å, SLS. Red line highlights the pattern collected right after the decomposition of K[Al(BH₄)₄] at 180 °C, showing Bragg peaks of KBH₄ alone. The blue line shows the maximum intensity of KBH₄ at 160 °C.
K[Al(BH4)4] crystallizes in the orthorhombic space group Fddd, as the LT-TbAsO4 prototype,35 with BH4− anions in place of oxygen atoms. The LT phase of TbAsO4 (stable below 27.7 K) is an orthorhombic deformation of the tetragonal HT phase (I41/amd, ZrSiO4 type) caused by the Jahn–Teller effect. The orthorhombic structure of K[Al(BH4)4], stable until its decomposition, is far from a tetragonal prototype. This is certainly due to much stronger deformation of [Al(BH4)4]− from an ideal tetrahedron (see below) as compared to [AsO4]3−.

Metal cations have distorted tetrahedral environments formed by the BH4− groups. Aluminum atoms are coordinated to four anions via the BH2 edges: Al−H1 1.79(1) Å and Al−H3 1.96(1) Å, forming distorted tetrahedral [Al(BH4)4] complexes with B−Al−B angles ranging from 97.6(1)° to 135.4(1)°, very close to 100.0(1)°−103.8(2)° in Li4Al3(BH4)13.8 K+ coordinates the anion asymmetrically via an edge: K−H2 2.55(1) Å, K−H4 3.20(1) Å. The BH4− group is coordinated through the vertex to another potassium cation (K−H4 2.92(9) Å), forming T-shaped coordination for the anion and 4 + 4 coordination polyhedron for K with respect to the BH4− groups. Disregarding the more distant potassium atom, the borohydride group acts like a nearly linear bridging ligand with Al···B···K angle of 152.7(2)°, similar to Mg···B···Mg angles in Mg(BH4)2 framework structures.36,37

The Al−B distance of 2.262(4) Å is slightly longer than 2.10−2.15 Å in α,β-Al(BH4)3 where Al coordinates three borohydrides38,39 and falls in the 2.22−2.35 Å range for the tetracoordinated Al in Al4[Li4(BH4)13], [Ph3MeP][Al(BH4)4], and Na4[Al(BH4)3Cl]4.8,34 Because of the smaller size of Al3+, the Al−B distances are slightly shorter than 2.27−2.38 Å Sc−B and Y−B bond distances in K[Sc(BH4)4] and K[Y(BH4)4].15,16 Remarkably, Y3+ and Sc3+ coordinate the BH4− groups via the tetrahedral faces, showing higher coordination numbers and longer metal—hydrogen distances. The short K−B distance of 3.285(4) Å in K[Al(BH4)4] (CN = 4 + 4) is similar to the 3.26(1) Å distance in K[Y(BH4)4] (CN = 6)16 and slightly shorter than 3.364 Å in the cubic KBH4 (CN = 6)31 or shorter than the short distance of 3.51(4) Å for CN = 8 in K[Sc(BH4)4].15 The longer K−B distance of 3.809(4) Å is comparable to the longest K−B distance of 3.95(2) Å15 for CN = 8 in K[Sc(BH4)4]. On the other hand, K′ with CN = 7 in LiK(BH4)2 shows more regular K−B distances, falling within 3.40−3.47 Å.32 K[Al(BH4)4] is not isomorphic to KAlCl4 and NaAlCl4, where much more regular tetrahedral AlCl4− anions are present, as well as different coordination polyhedra for alkali metal atoms are observed.25,40 The title structure can be seen as an ionocovalent compound containing complex anion [Al−(BH4)4]− located in the bicapped trigonal prismatic cage K8.  

Figure 2. Representations of the crystal structure of K[Al(BH4)4]. (a) Complex anion [Al(BH4)4]− located in the bicapped trigonal prismatic cage K8. (b) Coordination environment of K, Al atoms, and the BH4− group; the dashed lines depict elongated K···H distances completing the coordination for K to 4H + 8H. (c) Two interpenetrated dia-type nets; hydrogen atoms are omitted for clarity.
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Infrared and Raman Spectroscopy. The strongest bands in the 2100–2600 cm\(^{-1}\) range (Figure 3) correspond to B–H stretching, and less intense peaks from 990 to 1300 cm\(^{-1}\) can be attributed to B–H bending modes. Only the strongest peak of KBH\(_4\) at 2308 cm\(^{-1}\) can be recognized in stretching mode region in the Raman spectrum, the remaining peaks overlap with B–H stretching modes from K[Al(BH\(_4\))]\(_4\). The difference of intensities in spectra for different K[Al(BH\(_4\))]\(_4\)/KBH\(_4\) ratios is shown in the Supporting Information (Figure S4). The other two peaks at 2436 and 2476 cm\(^{-1}\) from Raman and 2419 and 2472 cm\(^{-1}\) from IR are related to the outward B–H stretching modes from [Al(BH\(_4\))]\(_4\) with respect to the observed in crystal structure bidentate coordination. The mentioned doublet in the 2400–2600 cm\(^{-1}\) range with 50–80 cm\(^{-1}\) splitting is typical for bidentately bridged borohydrides. Similar peaks were seen at 2440 and 2480 cm\(^{-1}\) for Al\(_2\)Li\(_4\)(BH\(_4\))\(_3\) in Raman and at 2420 and 2480 cm\(^{-1}\) in the infrared spectrum as well as 2444 and 2503 cm\(^{-1}\) for Na[Al(BH\(_4\))Cl\(_4\)] in Raman spectra.

In the region of B–H bending modes, a band at 1249 cm\(^{-1}\) corresponds to KBH\(_4\). The other peaks at 999, 1140, 1177, and 1450 cm\(^{-1}\) in Raman spectrum and 996, 1144, 1278, 1422 cm\(^{-1}\) in the IR can be assigned to the BH\(_2\) bending modes in [Al(BH\(_4\))]\(_4\), similar to Al\(_2\)Li\(_4\)(BH\(_4\))\(_3\) complex (near 1000, 1020, 1170, and 1450 cm\(^{-1}\) in the Raman spectrum). The sharp bands at 455 and 477 cm\(^{-1}\) in both spectra likely correspond to the Al–B stretching mode, also previously seen at 490 cm\(^{-1}\) for Li–Al and Na–Al complex borohydrides, as well as for the pure Al(BH\(_4\))\(_3\).

Thermal and Mass Spectrometry Analysis. The TGA and DSC curves of the K[Al(BH\(_4\))]\(_3\)/KBH\(_4\) (73.1/26.9 wt % from XRD) mixture are shown in Figure 4. Only one sharp endothermic peak with the maximum at 160 °C was detected by DSC analysis in the 25–500 °C temperature range. According to the thermogravimetric analysis and in situ XRD, a decomposition of K[Al(BH\(_4\))]\(_3\) complex starts at 135 °C and finishes at 175 °C (near 180 °C from XRD). This decomposition profile is significantly different from the previously reported decomposition of presumably pure K[Al(BH\(_4\))]\(_3\) by Semenenko et al., where two endothermic peaks were detected at 132 and 240 °C. According to ref 21, the evolution of diborane and hydrogen was also accompanied by considerable amounts of Al(BH\(_4\)) desorbing at 130 °C. The total mass losses of 20.8 wt % on our sample is equivalent to 28.5 wt % with respect to the pure K[Al(BH\(_4\))]\(_4\). Desorption of Al(BH\(_4\)) would lead to a much larger weight loss of 56.9 wt % for the pure K[Al(BH\(_4\))]\(_3\) or 41.8 wt % for our K[Al(BH\(_4\))]\(_3\)/KBH\(_4\) (73.1/26.9 wt %) sample. According to our diffraction data, the intensity of KBH\(_4\) peaks increases upon the decomposition of K[Al(BH\(_4\))]\(_3\) (Figure S5), providing ~0.6 mol of KBH\(_4\) upon decomposition of 1 mol of K[Al(BH\(_4\))]\(_3\). Taking together with the TGA data, all the observations can be described by the following hypothetic decomposition reaction 3:

\[
2\text{K[Al(BH}_4]\text{]}_3 \rightarrow \text{KBH}_4 + \text{amorphous } \text{KAl}_2\text{B}_3 + 2\text{B}_2\text{H}_6 + 8\text{H}_2
\]

This reaction gives 28.5 wt % loss of mass, as observed by the TGA. The absence of diffraction peaks in the decomposed products rules out the formation of the anticipated crystalline phases, such as AlB\(_2\), K–B borides, and KHI.

We additionally performed two independent mass spectrometry measurements on the evolving gas products, combined with the simultaneous TGA. Atomic mass units 26 and 27 corresponding to B\(_2\)H\(_6\) and 42, and 43, 56, 57 and 70–73 amu corresponding to Al(BH\(_4\))\(_3\) were chosen as characteristic fragments. From our data shown in Figure 5, diborane release is clearly observed at 160 °C, fully consistent with the maximum of the endothermic peak seen in DSC and weight losses in TGA and TGA-MS data in Figure 6. Due to the fact that 28 m/z signal in the diborane reference data amounts only to

Figure 3. Raman and infrared spectra of K[Al(BH\(_4\))]\(_4\)/KBH\(_4\) mixture (90.1/9.9 wt %) at room temperature.

Figure 4. Thermal analysis of K[Al(BH\(_4\))]\(_3\)/KBH\(_4\) mixture.
that it stays in equilibrium with the starting compounds at temperatures close to ambient, forming a small partial pressure of aluminum borohydride. However, for potential applications in hydrogen storage it is important that this plausible reaction is not observed at elevated temperatures. This prompts further studies on reactive hydride composites capable of suppressing diborane release, and makes K[Al(BH₄)₄] a good candidate for a conversion of aluminum borohydride in a more stable form, to be used for example in reactive hydride composites.53

Assessment of Rehydrogenation by in Situ Synchrotron X-ray Powder Diffraction. The sample with ≈84 wt % of K[Al(BH₄)₄] was decomposed by heating up to 210 °C under 1 bar of H₂ using a single crystal sapphire cell shown in Figure 7a. It is the first system with [Al(BH₄)₄]⁻ anion, characterized for reversibility by this method. Its thermal decomposition behavior reproduces the one under argon (compare Figures 7b and 1b). The decomposed material was loaded with 100 bar of H₂ at 50 °C, but no changes were observed by diffraction during the first 70 min (Figure 1c). The sample was heated rapidly to 320 °C and slowly cooled to the room temperature under 100 bar of hydrogen. We did not observe neither significant changes of intensities from KBH₄ of decomposed sample nor a formation of the starting K[Al-(BH₄)₄] (Figure 1d). Nonreversible character of K[Al(BH₄)₄] decomposition is consistent with evolution of other gaseous species than hydrogen, such as gaseous B₂H₆ (see eq 3). Therefore, this composition alone is not suitable for direct rehydrogenation; its high hydrogen content allows for development of potentially reversible reactive hydride composites.53

Conclusions and Perspective. By direct interaction of potassium and aluminum borohydrides at room temperature, a complex borohydride, K[Al(BH₄)₄], was obtained. According to the synchrotron X-ray powder diffraction study as well as vibrational spectroscopy, it contains distorted tetrahedral [Al(BH₄)₄]⁻ anions, where the borohydride group is coordinated to aluminum via an edge. This is the first aluminum-based borohydride complex not stabilized by halide anions or by bulky organic cations. K[Al(BH₄)₄] is not isostructural to bimetallic chlorides, where much more regular tetrahedral AlCl₄⁻ anions are present. Instead, the complex borohydride is isomorphous to TbAsO₃ and reveals an anion [Al(BH₄)₄]⁻ located in the bicapped trigonal prismatic cage K₈. Neglecting four longer K−B₄H₁₀ distances, the structure can be also viewed as a framework built of two interpenetrated dia-type nets.

In situ X-ray powder diffraction, TGA, DSC, and TGA-MS data consistently show a single step of decomposition at ≈160 °C, with an evolution of hydrogen with some amount of diborane. Aluminum borohydride is not released in substantial amounts; however, some crystalline KBH₄ forms upon decomposition. This contrasts with the decomposition of chloride-containing Li−Al borohydride, producing Al(BH₄)₃. The higher decomposition temperature of K[Al(BH₄)₄] compared to the chloride-substituted Li−Al (70 °C) and Na−Al (90 °C) borohydrides suggests that the larger alkali metal cations (weaker Pearson acids) stabilize the weak Pearson base, [Al(BH₄)₄]⁻. The hypothetic alkali earth aluminum borohydrides, such as M[Al(BH₄)₄]₄, are therefore expected to be unstable. On the contrary, the heavier alkali metal aluminum borohydrides, such as the title compound, are good candidates for storage of aluminum borohydride in a more stable form. This prompts further studies on reactive hydride composites,
such as $\text{K[Al(BH}_4\text{)}_4]$ plus a binary metal hydride, potentially capable to suppress diborane release.

After initial submission of our work, an independent study by Knight et al. was published, reporting the crystal structure of $\text{K[Al(BH}_4\text{)}_4]$ in a noncentrosymmetric space group $\text{Fdd}_2$. They did solid-state NMR and volumetric studies, which complement well our MS study of the decomposition and the assessment of rehydrogenation via in situ diffraction. Knight et al. report higher TGA mass loss on the decomposition, attributing it to a release of $\text{Al(BH}_4\text{)}_3$.

**ASSOCIATED CONTENT**

* Supporting Information

Supplementary XRD data, Rietveld refinements, Raman spectra, temperature evolution of diffraction intensities, MS data, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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