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Synthesis and thermal decomposition of potassium tetraamidoboranealuminate, K[Al(NH$_2$BH$_3$)$_4$]

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ABSTRACT

A new potassium tetraamidoboranealuminate, K[Al(NH$_2$BH$_3$)$_4$], has been synthesized by a mechanochemical reaction between KAlH$_4$ and NH$_3$BH$_3$. The compound, K[Al(NH$_2$BH$_3$)$_4$], crystallizes in a triclinic unit cell with space group symmetry $P-1$. The crystal structure consists of [K(NH$_2$BH$_3$)$_6$]$^{5-}$ octahedra which facilitate the bridging between K$^+$ in 1D chains, while also bridging K$^+$ to Al^{3+} to connect the 1D chains in a 3D network. Thermal analysis reveals that K[Al(NH$_2$BH$_3$)$_4$] decomposes in two exothermic steps at $T \sim$ 94 and 138 °C and releases primarily hydrogen. The total gas release amounts to ~6.0 wt% H$_2$. The decomposition products are investigated *ex situ* by powder X-ray diffraction, infrared spectroscopy, and ^{11}B and ^{27}Al NMR and identified as KBH$_4$ and amorphous phases, possibly BN$_3$, N$_2$BH, and/or NBH$_2$ whereas aluminum is found in four-, five-, and six-fold coordination. Unfortunately, the decomposed sample shows no hydrogen absorption at $T = 260$ °C and $p(\text{H}_2) = 110$ bar.

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Introduction

Hydrogen has a great potential as an energy carrier [1–6]. Thus, research within hydrogen storage materials has primarily focused on the discovery of possible successors for liquid fuels, diesel and gasoline, appropriate for mobile applications [7–11]. Initially, aluminum-based hydrides attracted significant attention as the reversible system NaAlH$_4$–TiCl$_3$ was discovered [12]. However, KAlH$_4$ has the advantage over NaAlH$_4$ that no additives are needed to promote the reversible hydrogen release and uptake at low pressures (<10 bar) and moderate temperatures (250–300 °C) [13]. Yet, the detailed decomposition mechanism of KAlH$_4$ is

still debated and the possible intermediates remain not fully characterized [14,15]. Additionally, the reversibility conditions for $KAlH_4$ are too harsh for mobile applications, hence optimization of $KAlH_4$ is required if utilization is to be realized.

Nitrogen-boron containing compounds have also been extensively studied [16−19]. A compound which has received great attention is ammonia borane, NH_3BH_3, owing to its high gravimetric hydrogen density, $\rho_m = 19.6$ wt% H_2 [20−23]. However, for mobile applications, NH_3BH_3 has several drawbacks. The decomposition occurs in two steps below 200 °C, with release of toxic gasses, e.g. ammonia (NH_3), diborane (B_2H_6) and borazine ($N_3B_3H_3$) whilst the first decomposition step is exothermic ($\Delta H_{dec} = -21.7$ kJ/mol H_2) and hence irreversible [20,24−26]. Many attempts have been made to improve these properties, especially through metal amidoboranes, which often have high gravimetric hydrogen densities, fast kinetics, and low decomposition temperatures, whereas the purity of hydrogen released is improved [16,27−32]. Moreover, metal borohydride−ammonia borane complexes, $M(BH_4)_x(NH_3BH_3)_x$ (M = Li, Mg, Ca), have been reported, however, they maintain the drawbacks of molecular NH_3BH_3 [33−36]. Finally, complexes combining aluminum, boron, and nitrogen have received increasing interest [37]. Especially, the combination of an aluminum atom bonded to multiple NH_3BH_3 residues may enable reversibility by combining the efficiency of NH_3BH_3 dehydrogenation with an aluminum-mediated hydrogenation process [38,39].

Recently, the first aluminum-based amidoborane, $Na[Al(NH_2BH_3)_4]$, was reported and found to decompose in two steps at 120 and 160 °C into $NaBH_4$ and amorphous products [40,41]. Interestingly, a partial reversibility of 1.7 mol H_2 was found between the two amorphous decomposition states [40]. Additionally, a few potassium-containing amidoboranes have been reported, e.g. KNH_2BH_3 and $KNH(tBu)BH_3$ [28,30]. KNH_2BH_3 melts before an exothermic decomposition occurs at 80 °C and continues in two steps below 225 °C into an amorphous product which according to solid-state ^{11}B MAS NMR contains a branched polyiminoborane [30,42].

In this work, $K[Al(NH_2BH_3)_4]$ has been synthesized by mechanochemical treatment of $KAlH_4$ and NH_3BH_3. The new potassium-based amidoborane compound has been characterized by in-situ synchrotron radiation powder X-ray diffraction (SR-PXD), density functional theory (DFT), thermogravimetric analysis combined with differential scanning calorimetry and simultaneous mass spectrometry (TG-DSC-MS), temperature programmed photographic analysis (TPPA), Sieverts' method (PCT), and solid-state [11]B and [27]Al magic-angle spinning (MAS) NMR.

Experimental

Sample preparation

KH (Sigma−Aldrich, 30 wt% dispersed in mineral oil) was initially dried under vacuum and washed three times with diethyl ether. Subsequently, Al (Strem Chemicals, 99.7%) and KH in a 1:1 molar ratio were loaded into a 80 mL tungsten carbide (WC) vial with WC balls (o.d. 10 mm) in a ball-to-powder mass ratio of 30:1 and ball milled for 48 cycles

consisting of 10 min milling and a 2 min break, giving a total of 8 h milling, using a Fritsch Pulverisette 6 planetary mill.

Finally, the ball-milled mixture was hydrogenated at $p(H_2) = 120$ bar and $T = 270$ °C for 12 h providing the product potassium alanate, $KAlH_4$. $KAlH_4$ was then mixed with ammonia borane, NH_3BH_3 (Sigma−Aldrich, 97%), in the molar ratio 1:4 and ball milled in cycles consisting of 5 min milling and 2 min break with a ball-to-powder mass ratio of 30:1. Three samples were made using 96, 120, and 144 cycles giving a total milling time of 8, 10, and 12 h, respectively. The samples are denoted **S1**, **S2**, and **S3**, respectively.

Synchrotron radiation powder X-ray diffraction

High resolution, in-situ time-resolved SR-PXD data, used for crystal structure solution and refinement, were collected at beamline I11 at the Diamond Light source, Oxford, UK on a wide-angle position sensitive detector (PSD) based on Mython-2 Si strip modules, $\lambda = 0.8259$ Å. The powdered sample was packed in quartz capillaries (i.d. 0.5 mm, wall thickness 0.01 mm) in an argon-filled glovebox ($p(O_2, H_2O) < 1$ ppm). Subsequently, the sample was heated from RT to 500 °C ($\Delta T/\Delta t = 5$ °C min^{-1}), while rotated during data acquisition. The temperature was calibrated using a NaCl standard [43]. The in-situ SR-PXD data plot has been background subtracted to clearly show the Bragg reflections.

Structure solution and refinement

The in-situ SR-PXD data (sample **S3**) were indexed using the DICVOL routine implemented in the software FOX [44], which revealed a triclinic unit cell. Subsequently, the structure was solved by global optimization in direct space, also using FOX. Structural models were created with one potassium atom, one aluminum atom, and four $[NH_2BH_3]^-$ groups treated as rigid bodies with N−B, N−H, and B−H distances of 1.589, 1.029, and 1.226 Å, respectively, and a number of antibump restraints to assist the convergence. The structure of $K[Al(NH_2BH_3)_4]$ was solved in space group $P-1$ and the structural model was refined using the Rietveld approach implemented in the software Fullprof [45].

Density functional theory

The initial, Rietveld-refined structure of $K[Al(NH_2BH_3)_4]$ was optimized with the conjugated gradient (CG) method with respect to the internal atomic positions. This procedure provided equilibrium hydrogen sites. As the second step, the unit cell shape was optimized. These optimized structures were subject to simulated annealing. No constraints were imposed on the internal atomic positions and the unit cell parameters were kept fixed for this procedure. The symmetry of the final structures was analyzed, and systems with imposed symmetry were re-optimized with the CG method. The electronic configurations of for H ($1s^1$), B ($2s^22p^1$), N ($2s^22p^3$), K ($3p^64s^1$), and Al ($3s^23p^1$) were represented by projected augmented wave potentials [46]. The gradient-corrected (GGA) functional and the corrections for a weak dispersive interaction were applied [47,48]. The plane wave formulation of the DFT method implemented in Vienna Simulation Package (VASP) was used [49].

The NMR parameters were calculated within the gauge-including projector augmented waves (GIPAW) approach [50,51]. PAW pseudopotentials were used and the geometry of the system was fixed. The isotropic shielding of BPO_4 at -3.60 ppm was used as the reference for ^{11}B [52], and for ^{27}Al: 16.0 ppm of α-Al_2O_3 [53]. The quadrupolar coupling constant (C_Q) and the asymmetry parameter (η_Q) have been determined from the traceless electric field gradient (EFG), further details can be found elsewhere [54]. The nuclear quadrupole moments of 40.59 mb and 146.6 mb were used for the ^{11}B and ^{27}Al, respectively.

Thermal analysis

Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) of $KAlH_4$ and $KAlH_4-NH_3BH_3$ (1:4, **S3**) were performed on a PerkinElmer STA 6000 apparatus. The samples (approx. 4 mg) were placed in Al_2O_3 crucibles under protective argon atmosphere in a glovebox and heated from 40 to 300 °C ($\Delta T/\Delta t = 5$ °C min^{-1}) in an argon flow of 40 mL min^{-1}. Additionally, mass spectrometry data were simultaneously collected for H_2, B_2H_6, $B_3H_6N_3$ ($m/z = 80$), and NH_3 using a Hiden Analytical HPR-20 QMS sampling system.

Sieverts' measurement

The $KAlH_4-NH_3BH_3$ (1:4, **S3**) sample was transferred to a stainless steel high-temperature autoclave and connected to a custom-made Sieverts' apparatus [55]. Decomposition of the sample was performed by heating to $T = 200$ °C ($\Delta T/\Delta t = 3$ °C min^{-1}) for 1 h. Finally, the sample was cooled naturally to *RT*. Absorption was performed by heating the sample to $T = 260$ °C ($\Delta T/\Delta t = 5$ °C min^{-1}) at $p(H_2) = 110$ bar for 15 h. Subsequently, the sample was decomposed as described above.

Solid-state ^{11}B and ^{27}Al MAS NMR spectroscopy

The solid-state ^{11}B and ^{27}Al MAS NMR spectra were obtained on a Varian Direct-Drive VNMRS-600 spectrometer (14.1 T) using a custom-made CP/MAS NMR probe for 4 mm outer diameter rotors. The spectra employed a 0.5 μs excitation pulse for rf field strengths of $\gamma B_1/2\pi = 58$ kHz (^{11}B) or $\gamma B_1/2\pi = 70$ kHz (^{27}Al), relaxation delays of 4 s, 30 s (^{11}B) or 4 s (^{27}Al) and ^1H decoupling (TPPM, $\gamma B_2/2\pi = 42$ kHz). The experiments were performed at ambient temperature using airtight end-capped zirconia rotors packed with the samples in an argon-filled glovebox. Isotropic ^{11}B and ^{27}Al chemical shifts are relative to neat $F_3B\cdot O(CH_2CH_3)$ and an aqueous 1.0 M $AlCl_3\cdot 6H_2O$ solution, respectively. Simulations and least-squares optimizations to the manifold of spinning sidebands, observed for the ^{11}B and ^{27}Al satellite transitions, were performed using the STARS simulation software [56].

Fourier-transformed infrared spectroscopy

The sample $KAlH_4-NH_3BH_3$ (1:4, **S3**) was characterized by infrared absorption spectroscopy using a NICOLET 380 FT-IR instrument from Thermo Electron Corporation. The sample was briefly exposed to air (~10 s) during transfer to the instrument.

Temperature-programmed photographic analysis

Two pellets of **S1** and **S3** (~10 mg) were pressed and sealed under argon in a glass tube and placed in a custom-made aluminum heating block [57]. The samples were heated from *RT* to 200 °C ($\Delta T/\Delta t = 5$ °C min^{-1}) while photos of the sample were collected every six seconds.

Results

Initial sample analysis

Mechanochemical treatment of the reactants, $KAlH_4-NH_3BH_3$ (1:4), results in the appearance of a new set of Bragg reflections in the PXD pattern for all three samples, which was indexed in a triclinic unit cell: $a = 9.7151(3)$ Å, $b = 7.8221(3)$ Å, $c = 7.8750(3)$ Å, $\alpha = 95.358(3)°$, $\beta = 109.944(3)°$, and $\gamma = 89.629(3)°$, $V = 559.74(4)$ Å^3, and $Z = 2$. This diffraction data originates from a new compound, $K[Al(NH_2BH_3)_4]$, formed by the chemical reaction (1):

$$KAlH_4 \text{ (s)} + 4NH_3BH_3 \text{ (s)} \rightarrow K[Al(NH_2BH_3)_4] \text{ (s)} + 4H_2 \text{ (g)} \quad (1)$$
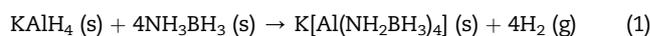
Rietveld refinement of the diffraction data of **S1** reveals a sample composition of $K[Al(NH_2BH_3)_4]$ (~67 wt%), $KAlH_4$ (~12 wt%), and NH_3BH_3 (~21 wt%). To enhance the formation of the new $K[Al(NH_2BH_3)_4]$ compound the ball-milling time was extended. Sample **S2** contains a major fraction of $K[Al(NH_2BH_3)_4]$ (~91 wt%) whereas only minor fractions of the reactants, $KAlH_4$ (~1.7 wt%) and NH_3BH_3 (~0.10 wt%) are present. However, Bragg reflections belonging to KBH_4 are now appearing and the amount was determined to be ~7.5 wt%. Longer ball-milling time, **S3**, results in additional formation of KBH_4 (~26 wt%), thus the $K[Al(NH_2BH_3)_4]$ decomposes under extensive ball milling (see later section on decomposition products). Furthermore, **S3** contains $K[Al(NH_2BH_3)_4]$ (~67 wt%), NH_3BH_3 (~3.6 wt%), and $KAlH_4$ (~3.1 wt%), see also Table 1 for an overview of the approximate sample composition. However, the structural solution was carried out on *in-situ* SR-PXD data collected for **S3** and the Rietveld refinement on the SR-PXD data is seen in Fig. 1. The quartz capillary contributes significantly to the background at low 2θ values.

For all three samples, the observed Bragg reflections can be assigned to either the reactants, $KAlH_4$ or NH_3BH_3, the reaction product, $K[Al(NH_2BH_3)_4]$, or the decomposition product, KBH_4. The contrast between the presence of NH_3BH_3 in **S1** and KBH_4 in **S3** is further evident from TPPA in which the foaming of NH_3BH_3 is clearly observed in **S1** whereas only a minor volume change is observed for **S3** due to the gas release following decomposition (see Figs. S1 and S2).

Structural analysis

The Rietveld refined structure was optimized using DFT owing to multiple options for hydrogen positions. Three

Table 1 – Overview of sample compositions determined by Rietveld refinement of the SR-PXD data.

Sample	Compound				
	$K[Al(NH_2BH_3)_4]$ (wt%)	NH_3BH_3 (wt%)	$KAlH_4$ (wt%)	KBH_4 (wt%)	Milling time [h]
S1	67	21	12	0	8
S2	91	0.1	1.7	7.5	10
S3	67	3.6	3.1	26	12
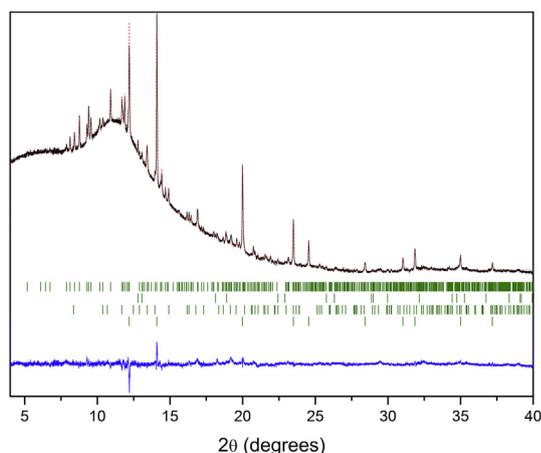
Fig. 1 – Rietveld refinement of the SR-PXD diffractogram of $KAlH_4$–NH_3BH_3 (1:4, S3, RT) containing $K[Al(NH_2BH_3)_4]$ (upper green marker), NH_3BH_3 (second green marker), $KAlH_4$ (third green marker), and KBH_4 (lower green marker) ($\lambda = 0.8259$ Å). Observed data (Y_{obs}, red curve), Rietveld refinement profile (Y_{calc}, black curve), and difference plot ($Y_{obs} - Y_{calc}$, blue curve). Agreement factors, corrected for background, are $\chi^2 = 2.64$, $R_{exp} = 14.1\%$, $R_{wp} = 22.9\%$, and $R_p = 40.0\%$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2 – Comparison of crystallographic data for the isostructural compounds $Na[Al(NH_2BH_3)_4]$ and $K[Al(NH_2BH_3)_4]$, using data collected at $T = 100$ °C [40] and RT, respectively.

	$Na[Al(NH_2BH_3)_4]$	$K[Al(NH_2BH_3)_4]$
Space group	$P-1$	$P-1$
a (Å)	9.4352(2)	9.7151(3)
b (Å)	7.7198(1)	7.8221(3)
c (Å)	7.6252(1)	7.8750(3)
α (°)	97.211(1)	95.358(3)
β (°)	109.223(2)	109.944(3)
γ (°)	89.728(2)	89.629(3)
Z	2	2
V (Å^3)	518.86(2)	559.74(4)
ρ (g cm^{-3}) (calc.)	1.070	1.101
ρ_m (H_2) (wt%)	11.90	10.87
ρ_V (H_2) (kg H_2 L^{-1})	119.81	111.02

octahedrally coordinated to $[NH_2BH_3]^-$ through the BH_3 group in zig-zag 1D chains, see Fig. 2b and c. Four of the six $[NH_2BH_3]^-$ units in the octahedron facilitate the bridging between K^+ of the 1D chains, while all six $[NH_2BH_3]^-$ bridge the K^+ to an Al^{3+} to connect the 1D chains in a 3D network, see Fig. 2b.

Different from $Na[Al(NH_2BH_3)_4]$, our model suggests alternating bridging of the K^+ ions in the structure of $K[Al(NH_2BH_3)_4]$, between corner-/corner-interactions and edge-/corner-interactions with the BH_3 group and results in two different $K-K$ distances of 4.314(6) Å and 5.030(6) Å. The $K-B$ distances range from 3.131(8) Å to 3.602(9) Å (3.17 Å to 3.59 Å from DFT) comparable to the $K-B$ distance in KBH_4 of approximately 3.36 Å [58]. Furthermore, $N-H^{\delta+}...^{\delta-}H-B$ distances as short as 1.969(9) Å (1.95 Å from DFT) indicate that the structure is partially stabilized by dihydrogen bonds.

In-situ synchrotron radiation powder X-ray diffraction

In-situ SR-PXD data of $KAlH_4$–NH_3BH_3 (1:4, S3) are presented in Fig. 3. Initially, diffraction from the new compound $K[Al(NH_2BH_3)_4]$, the reactants $KAlH_4$ and NH_3BH_3, and the decomposition product, KBH_4, are present. Only the most intense Bragg reflection from NH_3BH_3 is visible in the data and it disappears at $T = 75$ °C, which is low compared to the reported decomposition temperature at 110–120 °C [25,59]. However, no change in the diffracted intensity of the other compounds is observed, hence no reaction appears to occur. The diffracted intensity of $K[Al(NH_2BH_3)_4]$ is reduced at $T = 95$ °C and disappears completely at $T = 105$ °C, apparently in a single-step decomposition reaction, which does not produce crystalline products. In this case, there is no observable change in intensity of KBH_4 after decomposition of $K[Al(NH_2BH_3)_4]$, though at $T > 115$ °C there is a significant, almost threefold, increase in the full width at half maximum (FWHM) from 0.0738° at $T = 115$ °C to 0.2008° at $T = 170$ °C, which may be due to a reduction in particle size. However, in-situ SR-PXD data of $KAlH_4$–NH_3BH_3 (1:4, S1) ball milled for only 8 h, shown in Fig. S3, clearly show an increase in diffracted intensity of KBH_4 after decomposition of $K[Al(NH_2BH_3)_4]$. Weak Bragg reflections from $KAlH_4$ are observed during the

independent structures were obtained by DFT optimization procedures, which all can be assigned to $P-1$ symmetry, the main difference being the unit cell orientation and density (within 1.5%). Also the positions of the hydrogen atoms are different in these three structures. Normal mode analysis at the gamma point revealed no instabilities in these structures. The ground state energy was within 5 meV per formula unit (structure with the highest density was less stable by 20 meV). Considering the accuracy of the calculations, the obtained results do not allow the selection of one optimal structure, thus the Rietveld refinement of calculated models was decisive in the selection of a model.

The new compound, $K[Al(NH_2BH_3)_4]$, is isostructural to $Na[Al(NH_2BH_3)_4]$ [40]. Indeed, introduction of the larger potassium cation leads to an increased unit cell while the α-angle becomes smaller, see Table 2. The Al^{3+} ions are tetrahedrally coordinated to $[NH_2BH_3]^-$ through the nitrogen lone pair, see Fig. 2a, with Al–N distances ranging from 1.838(9) Å to 1.909(9) Å (Al–N bond lengths of 1.90 Å to 1.91 Å are obtained from the DFT structural optimization). The K^+ ion is

Fig. 3 − *In-situ* SR-PXD data of KAlH$_4$−NH$_3$BH$_3$ (1:4, S3) measured in the temperature range RT to 270 °C (ΔT/Δt = 6 °C min^{-1}, λ = 0.8259 Å). Symbols: K[Al(NH$_2$BH$_3$)$_4$] black circle; NH$_3$BH$_3$ blue square; KAlH$_4$ purple triangle; KBH$_4$ orange diamonds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
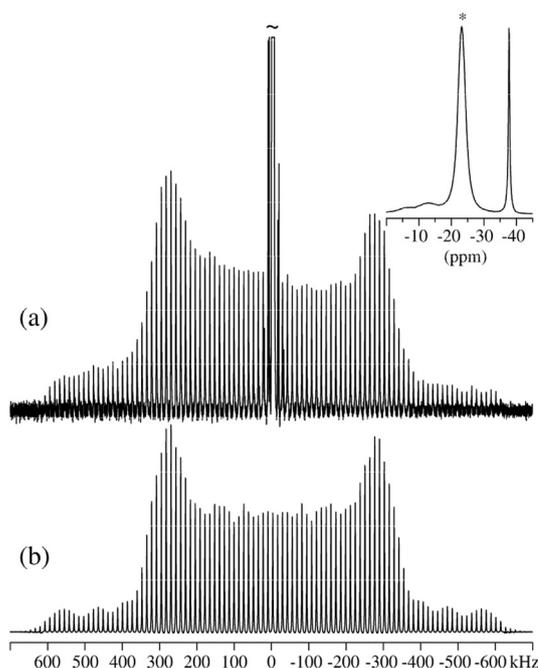
Fig. 4 − (a) ^{11}B MAS NMR spectrum (14.1 T) of the central and satellite transitions for K[Al(NH$_2$BH$_3$)$_4$] (sample S2), obtained with a spinning frequency of ν_R = 13.0 kHz and a 4-s relaxation delay. The inset illustrates the resonances from the central transitions. (b) Optimized simulation of the ssbs from the satellite transitions in (a), employing the ^{11}B parameters in **Table 3** and a deviation from the magic angle of ΔΘ = 0.0365°.

Fig. 2 − The crystal structure of K[Al(NH$_2$BH$_3$)$_4$]. (a) Coordination of the [Al(NH$_2$BH$_3$)$_4$]$^-$ complex. Color scheme: K, dark blue; Al, red; N, light blue; B, dark yellow. (b) The K$^+$ ions are organized as chains in the structure, illustrated as green dashed lines) and the linkage between these chains through the [Al(NH$_2$BH$_3$)$_4$]$^-$ complex (purple, dotted line). For simplicity, this is only shown in one case and hydrogen atoms have been omitted. Hence, the three chains shown are connected by the [Al(NH$_2$BH$_3$)$_4$]$^-$ complexes marked as

light red tetrahedra. (c) The unit cell of K[Al(NH$_2$BH$_3$)$_4$] highlighting the coordination between K$^+$ and the BH$_3$ group via edge and corner interactions of hydrogen (purple, dotted lines). Additionally, a di-hydrogen bond is emphasized (orange, dotted line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
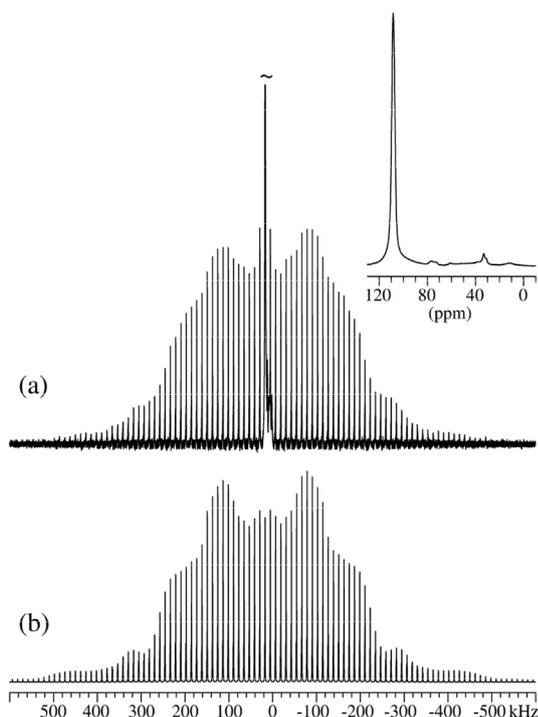
Fig. 5 — (a) ^{27}Al MAS NMR spectrum (14.1 T) of the central and satellite transitions for K[Al(NH$_2$BH$_3$)$_4$] (sample S2), obtained with a spinning frequency of ν_R = 12.0 kHz and a 4-s relaxation delay. The inset illustrates the spectra region for the central transitions. (b) Optimized simulation of the ssbs from the satellite transitions in (a), corresponding to the ^{27}Al parameters in Table 3.

Fig. 6 — (a) ^{11}B and (b) ^{27}Al MAS NMR spectra (14.1 T) showing the central transition region for the decomposed sample of K[Al(NH$_2$BH$_3$)$_4$]. The ^{11}B spectrum is acquired with a spinning speed of ν_R = 12.0 kHz and a relaxation delay of 30 s, whereas the ^{27}Al NMR spectrum, employed ν_R = 13.0 kHz and a 4-s relaxation delay. Asterisks indicate spinning sidebands.

entire *in-situ* SR-PXD experiment as decomposition does not occur before $T > 300$ °C [14].

^{11}B and ^{27}Al MAS NMR

^{11}B and ^{27}Al MAS NMR spectra of the central and satellite transitions for K[Al(NH$_2$BH$_3$)$_4$] (sample **S2**) are shown in Figs. 4 and 5, respectively. The ^{11}B MAS NMR spectrum is dominated by the central transition at −22.3 ppm, and the associated spinning sidebands (ssbs) from the satellite transitions, which is assigned to the ^{11}B sites in the K[Al(NH$_2$BH$_3$)$_4$] structure. This ^{11}B chemical shift is in agreement with a recent solution-state ^{11}B NMR study of K[Al(NH$_2$BH$_3$)$_4$] [60]. In addition, minor centerband resonances at −6.3 ppm, −12.9 ppm, and −37.8 ppm are observed. The latter peak originates from KBH$_4$, according to the ^{11}B chemical shift of −37.8 ± 0.2 ppm reported for this compound [61], which constitutes 9.9% of the ^{11}B intensity in the spectrum. The peaks with lower intensity at −6.3 ppm and −12.9 ppm can been assigned to [N$_3$BH] and [N$_2$BH$_2$] species, respectively, according to a recent ^{11}B MAS NMR study of lithium and potassium amidoboranes [42].

Least-squares optimization of simulated to experimental ssb intensities for the ^{11}B satellite transitions results in the ^{11}B isotropic chemical shift and quadrupole coupling parameters listed in Table 3 and the optimized simulation shown in Fig. 4b. The δ_{iso} and C$_Q$ values for ^{11}B in K[Al(NH$_2$BH$_3$)$_4$] are very similar to those reported for the two ammonia borane sites in

Mg(BH$_4$)$_2$(NH$_3$BH$_3$)$_2$ [35], where the isotropic chemical shift reflects the tetrahedral coordination of boron to three H$^-$ and one N atom. However, only a single centerband resonance and ssb manifold are observed, despite the crystal structure

Table 3 — Experimental and calculated ^{11}B and ^{27}Al isotropic chemical shifts (δ_{iso}) and quadrupole coupling parameters (C$_Q$, η_Q) for K[Al(NH$_2$BH$_3$)$_4$].[a]

	δ_{iso} (ppm)	C$_Q$ (MHz)[b]	η_Q[c]
^{11}B	−22.3 ± 0.2	1.26 ± 0.04	0.12 ± 0.02
B1	(−22.9)	(1.41)	(0.12)
B2	(−22.7)	(1.51)	(0.07)
B3	(−22.0)	(1.56)	(0.12)
B4	(−23.6)	(1.48)	(0.21)
^{27}Al	109.6 ± 0.3	2.41 ± 0.04	0.41 ± 0.02
	(110.7)	(1.83)	(0.21)

[a] The numbers in brackets are calculated values from DFT calculations of the optimized structure.
[b] Quadrupole coupling constant, C$_Q$ = eQV_{zz}/h, where e is the charge of the electron, Q the nuclear quadrupole moment, h Planck's constant, and V$_{zz}$ the principal element of the electric-field gradient tensor at the nuclear site, $|V_{zz}| \geq |V_{xx}| \geq |V_{yy}|$.
[c] Quadrupole asymmetry parameter, η_Q = $(V_{yy} - V_{xx})/V_{zz}$.

for K[Al(NH$_2$BH$_3$)$_4$] contains four crystallographically distinct ^{11}B sites. The absence of four resolved sites in the ^{11}B MAS NMR spectrum (Fig. 4a) may reflect dynamics in the structure and/or nearly identical chemical environments of the four sites, as reflected in the very similar δ_{iso}, C_Q and η_Q values calculated by DFT for the four sites (Table 3). In this context, we note that the calculated ^{11}B chemical shifts vary by only 1.6 ppm and are very close to the experimental values and that this similarity also holds for the C_Q and η_Q parameters.

The ^{27}Al central transition from KAlH$_4$ should be observed at 106 ppm [62], however, a close inspection of the line shape for the 109 ppm resonance from K[Al(NH$_2$BH$_3$)$_4$] gives no indications of such a peak, thereby showing that the amount of KAlH$_4$ in the **S2** sample must be very small, if present at all, which is in good agreement with the Rietveld refinement (Table 1), see Fig. 5a. Least-squares fitting to the intensities of the manifold of ssb's gives the δ_{iso}, C_Q, and η_Q parameters for the unique Al site in K[Al(NH$_2$BH$_3$)$_4$] along with the simulated spectrum in Fig. 5b, which convincingly reproduces the experimental manifold of ssb's from the satellite transitions. Furthermore, the DFT calculated isotropic chemical shift (Table 3) agrees very well the experimental value and the calculated C_Q and η_Q values are of the same magnitude as those determined experimentally.

The ^{11}B MAS NMR spectrum of the decomposed K[Al(NH$_2$BH$_3$)$_4$] sample, Fig. 6a, reveals a broad resonance at 26 ppm in addition to the narrow resonance at −37.8 ppm from KBH$_4$. The featureless character of the peak at 26 ppm indicates a less-ordered/amorphous phase with a local ^{11}B coordination sphere that differs significantly from those of four-fold boron in BH$_4^-$ and N$_{4-x}$BH$_x$ borane units. Similar resonances have been observed at 22 and 24 ppm by

decomposition of ammonia borane (NH$_3$BH$_3$) and potassium amidoborane (KNH$_2$BH$_3$), respectively, at elevated temperature [42], and are ascribed to the presence of trigonal boron coordinated to N and H (i.e., BN$_3$, N$_2$BH, and/or NBH$_2$ units). The chemical shift of 26 ppm is in accord with boron in trigonal coordination, thereby suggesting that BN$_3$, N$_2$BH, and/or NBH$_2$ species are formed in addition to KBH$_4$ during decomposition of K[Al(NH$_2$BH$_3$)$_4$]. The presence of less-ordered phases in the decomposition product is also in agreement with the ^{27}Al MAS NMR spectrum, Fig. 6b, which includes a number of rather broad and featureless resonances at approx. 96, 76, 61, 34 and 7 ppm. The peaks at 96, 76, and 61 ppm are ascribed to tetrahedrally coordinated Al whereas the resonances at 34 and 7 ppm are in accord with five-fold and octahedrally coordinated Al, respectively. The narrowest peak with lowest intensity at 76 ppm may originate from an AlO$_4$ impurity, whereas the other major resonances are ascribed to Al coordinated to H and/or N.

Thermal analysis

Simultaneous thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and mass spectrometry (MS) were measured for KAlH$_4$−NH$_3$BH$_3$ (1:4, **S3**), see Fig. 7. The DSC data reveal two exothermic thermal events. The first has onset at T ~ 92 °C and maximum at T ~ 104 °C which is associated with a mass loss of 1.3 wt% and a release of hydrogen, identified by MS. The second event initiates at T ~ 139 °C, peaks at T = 153 °C and is accompanied by a mass loss of 4.2 wt%, which is mainly assigned to hydrogen according to the MS data. The separation between the first and second event is not well defined and appears to be a smooth transition. Tiny amounts of NH$_3$,
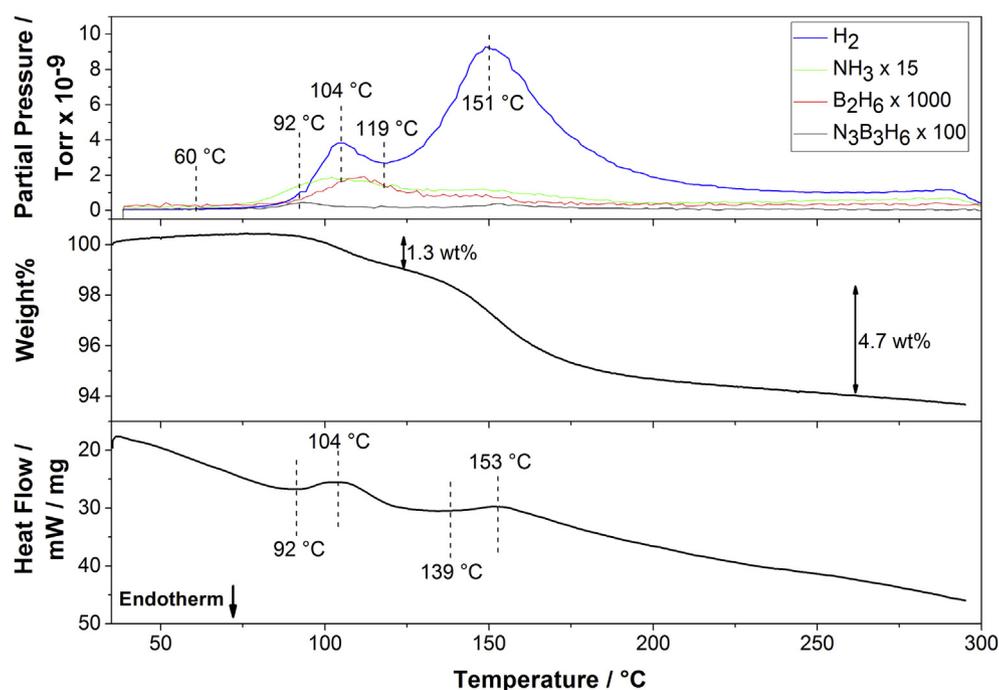
Fig. 7 − **Differential scanning calorimetry (bottom), thermogravimetric analysis (middle), and mass spectrometry (top) data measured from RT to 300 °C of KAlH$_4$−NH$_3$BH$_3$ (1:4, S3) (ΔT/Δt = 5 °C/min, Ar flow).**

$N_3B_3H_6$, and B_2H_6 (magnified 15, 100, and 1000 times, respectively, in Fig. 7) is also observed by MS in the two decomposition steps. MS data further reveal a minor H_2, NH_3, and $N_3B_3H_6$ release between $T \sim 60–92\ °C$, which is not readily observed in TG-DSC. A total mass loss of 6.0 wt% is observed at ~262 °C.

Fourier-transformed infrared spectroscopy

From FT-IR (Fig. 8) of $KAlH_4–NH_3BH_3$ (1:4, **S3**) two bands from N···H stretching modes are observed between 3350 and 3250 cm^{-1} and three bands from B···H stretching modes between 2350 and 2200 cm^{-1}. These stretching modes are very similar to those observed for NH_3BH_3. The B···H stretching modes probably have contributions from KBH_4 which were identified by PXD of the sample. However, the Al···H stretching mode observed in $KAlH_4$ at 1860–1460 cm^{-1} is no longer present, which is in agreement with the structure. Bands at 680–630 cm^{-1} are assigned to Al···N bending modes as reported for $Na[Al(NH_2BH_3)_4]$ [40]. Between 1600–1540 and 1100–1000 cm^{-1} N···H bending modes are present. Finally, B···H bending modes are located at 1380 and 1160 cm^{-1}. A calculated phonon spectrum (Fig. S4) is in good agreement with the FT-IR data, especially the Al···H stretching modes at 1860–1460 cm^{-1} are not present in the optimized $K[Al(NH_2BH_3)_4]$ structure.

Sieverts' measurement

The Sieverts' data in Fig. 9 reveal a slow gas release initiated at $T = 60\ °C$ which continues up to $T \sim 102\ °C$ where 0.3 wt% has been released. This supports the minor gas release observed by MS in a similar temperature range. At $T \sim 102\ °C$, the first significant desorption step occurs, which releases an additional 1 wt% of gas between 102 and 128 °C. As observed in TGA-DSC, the second desorption step appears as a smooth transition from the first step and initiates at $T = 126\ °C$. Further gas release of 4.2 wt% is observed in the second step. As the sample is kept at isothermal conditions at 200 °C, the total gas release amounts to ~6.0 wt%. These observations are in excellent agreement with the observations in TGA-DSC. A second desorption measurement was performed after hydrogenation of the sample.
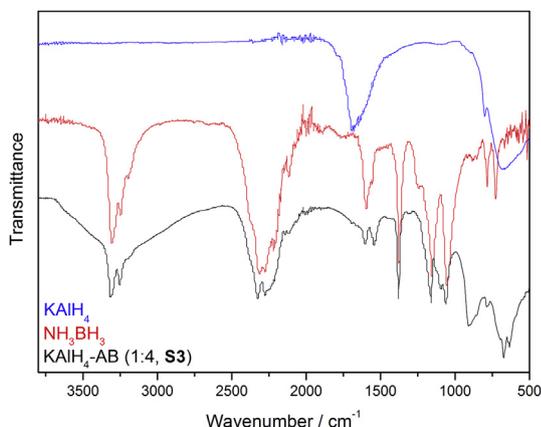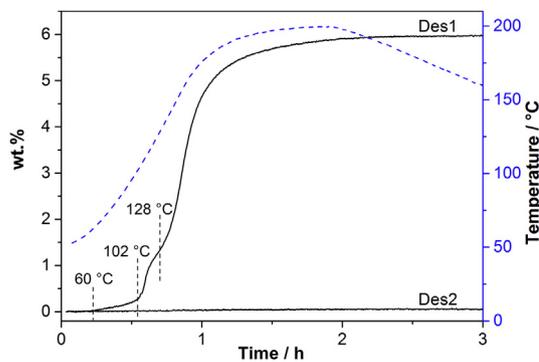
Fig. 9 – Sieverts' measurement of $KAlH_4–NH_3BH_3$ (1:4, S3) showing the two desorption experiments conducted in the temperature range RT to 200 °C ($\Delta T/\Delta t = 3$ °C/min, $p(H_2)_i = 10^{-3}$ bar).

However, the second measurement does not show any gas release, thus the sample did not absorb any hydrogen.

Discussion

The new potassium-containing aluminum-based amidoborane, $K[Al(NH_2BH_3)_4]$, differentiates from $Na[Al(NH_2BH_3)_4]$ in several ways. The structure contains two different $K^+···K^+$ ion bridging modes as the structural model indicates corner-/corner-interactions and edge-/corner-interactions with the BH_3 group of the $NH_2BH_3^-$ ion due to the different K–K distances. From TG-DSC-MS data the decomposition of $K[Al(NH_2BH_3)_4]$ appears to occur in two exothermic steps, similar to the decomposition of $Na[Al(NH_2BH_3)_4]$, which is supported by Sieverts' measurement. However, a small gas release of 0.3 wt% is observed in the temperature range ~60–95 °C, which may be related to slow kinetics in the first decomposition step. The observed decomposition temperatures in TG-DSC-MS are 10–15 °C lower compared to the ones for $Na[Al(NH_2BH_3)_4]$ [40]. On the contrary, the SR-PXD data only suggest one decomposition step, which may be explained by a second decomposition step between two amorphous phases, which is not visible by X-ray diffraction, similar to observations made for $Na[Al(NH_2BH_3)_4]$. MS reveals a tiny amount of NH_3, $N_3B_3H_6$, and B_2H_6. However, based on the relative intensities, the NH_3 is suppressed compared to the Na-analogue and especially NH_3BH_3. Finally, no hydrogen uptake is observed in the $K[Al(NH_2BH_3)_4]$ compound, which is contrary to $Na[Al(NH_2BH_3)_4]$ where hydrogen uptake was observed between the two amorphous phases at the same physical conditions as applied in this study. This suggests that the decomposition products of $K[Al(NH_2BH_3)_4]$ are more stable compared to those of $Na[Al(NH_2BH_3)_4]$, or that the decomposition is more exothermic, which is unfavorable. Further attempts to determine the decomposition products by PXD and FT-IR only support the formation of KBH_4 while a few Bragg reflections remain unassigned (see Fig. S5). Noticeably, the absence of Al Bragg reflections indicates that aluminum is chemically bound. This is supported by ^{27}Al MAS NMR which reveals the presence of four-, five-, and six-fold coordinated

Fig. 8 – Comparison of the FT-IR spectra of $KAlH_4$, NH_3BH_3, and $KAlH_4–NH_3BH_3$ (1:4, S3).

aluminum in the decomposed sample. Finally, this may explain the suppression of the release of boron and nitrogen species, as they may be found in coordination with aluminum.

Conclusion

The crystal structure of $K[Al(NH_2BH_3)_4]$ was determined in a triclinic unit cell with space group symmetry $P-1$. The crystal structure contains $[K(NH_2BH_3)_6]^{5-}$ octahedra, which link the structure in a 3D network. The decomposition occurs in two distinct steps and the total release of hydrogen amounts to ~6 wt% H_2. From ^{11}B and ^{27}Al MAS NMR and PXD, the decomposition mechanism has not been unambiguously determined due to its complexity. Hence, only KBH_4 can be identified as a decomposition product whereas aluminum is found in four-, five-, and six-fold coordination while boron is in three-fold coordination with nitrogen or hydrogen atoms as BN_3, N_2BH, and/or NBH_2 units. A tiny amount of NH_3, $N_3B_3H_6$, and B_2H_6, is observed by MS in the two decomposition steps. However, the NH_3 release often observed in metal amidoboranes seem suppressed in this study. Finally, the decomposition is irreversible as Sieverts' data show no gas release after hydrogen absorption experiments at $p(H_2) = 130$ bar.

Acknowledgement

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2017.11.080.

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