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Potassium(I) Amidotrihydroborate: Structure and Hydrogen Release

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Abstract: Potassium(I) amidotrihydroborate (KNH_2BH_3) is a newly developed potential hydrogen storage material representing a completely different structural motif within the alkali metal amidotrihydroborate group. Evolution of 6.5 wt % hydrogen starting at temperatures as low as 80 °C is observed and shows a significant change in the hydrogen release profile, as compared to the corresponding lithium and sodium compounds. Here we describe the synthesis, structure, and hydrogen release characteristics of KNH_2BH_3.

The need for safe and highly efficient hydrogen storage materials is a major concern for the further exploitation of hydrogen fuel cell technology.[1,2] In light of this, the discovery and development of new materials comprising light elements with a high hydrogen content has attracted much interest.[3−8] Ammonia borane (NH_3BH_3) is considered to be one of the most promising potential hydrogen storage materials. It is a stable, nonflammable, nonexplosive, and nontoxic molecular solid containing 19.6 wt % hydrogen. Thermal dehydrogenation of NH_3BH_3 takes place in three distinct steps within a broad temperature range.[9,10] Recent work shows several approaches to lower the decomposition temperature and improve the dehydrogenation properties of NH_3BH_3, including the use of various transition metals, iridium and base-metal catalysts, acid catalysis, nanoscaffolds, ionic liquids, and carbon cryogels.[11−18] Even though the above methods improve some of the dehydrogenation properties of NH_3BH_3, there is no single approach that can simultaneously achieve all the required improvements, such as reduced dehydrogenation temperatures, accelerated H_2 release kinetics, and minimized borazine release.

More recently, alkali metal amidoboranes, i.e., $LiNH_2BH_3$[19−25] and $NaNH_2BH_3$,[23,26] and alkaline-earth amidoborane, i.e., $Ca(NH_2BH_3)_2$[27,28] have been reported to show significantly enhanced dehydrogenation kinetics and suppressed borazine release. While the kinetics of hydrogen release from $LiNH_2BH_3$ are faster than for NH_3BH_3, the process still takes place in two separate steps, the first at 90 °C and the second at temperatures greater than 140 °C.

Recently we have reported a chemical route to synthesize such metal amidoboranes. One of the potential materials newly developed uses potassium amidoborane (KNH_2BH_3), which will evolve 6.5 wt % hydrogen if held isothermally at 80 °C for several hours. Here we report a detailed description of the synthesis, characterization, and hydrogen release of high-purity KNH_2BH_3.

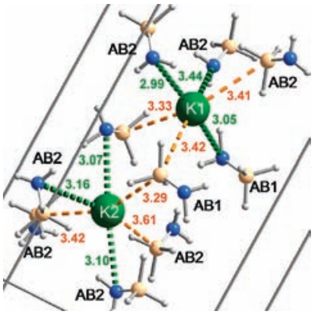

Figure 1. Schematic diagram of the structure of KNH_2BH_3, showing a close-up of the *mer*-octahedral coordination of both K^+ sites. Potassium, green; nitrogen, blue; and boron, cream. Distances are measured in angstroms.

The reaction of NH_3BH_3 in tetrahydrofuran with 1 equiv of KH for 4 h afforded KNH_2BH_3 (eq 1). [Yield 95%; mp 66−68 °C. ^{11}B NMR (96.29 MHz, diglyme, 22 °C): $\delta = -19.62$ (q, $^1J(B,H) = 84.0$ Hz, BH_3).] Single crystals were obtained from a mixture of diglyme and hexane at room temperature. It is also possible to obtain the same material, based upon thermogravimetric analysis, differential scanning calorimetry, NMR, and X-ray data, using benzene as a solvent.

$$KH + NH_3BH_3 \rightarrow KNH_2BH_3 + H_2 \qquad (1)$$

Crystal Structure. A single-crystal X-ray diffraction study was performed for the crystals grown from diglyme/hexane. X-ray powder diffraction patterns of the samples were collected, and the structure obtained from the single-crystal data was used as a starting point for refinement.

KNH_2BH_3 is an ionic salt consisting of $[M]^+$ ions and $[NH_2BH_3]^-$ molecular anions in an orthorhombic unit cell, lattice constants $a = 9.4304(1)$ Å, $b = 8.26112(1)$ Å, and $c = 17.3403(2)$ Å, with a *Pbca* space group. The structure of KNH_2BH_3 (Figure 1) differs substantially from those of the analogous compounds $LiNH_2BH_3$ and $NaNH_2BH_3$.[26] While all three compounds share the same space group, in isostructural $LiNH_2BH_3$ and $NaNH_2BH_3$ the Li/Na^+ ions are tetrahedrally coordinated by a strong electrostatic interaction with the N^- at the apex and three weaker van der Waals interactions with the closest BH_3 units. In KNH_2BH_3 there are two distinct K, N, and B atomic sites, and each K^+ ion is octahedrally coordinated in *mer* symmetry surrounded by three N atoms and three BH_3 units, analogous to KBH_4[29] and KNH_2.[30] This higher coordination number confers greater stability on the larger, more diffuse cation, and the *mer* symmetry is favorable as it minimizes the repulsion between like units.

The interaction between the M^+ ions and $[NH_2BH_3]^-$ results in strong, directional M−N bonds. The K−N bond distances range between 3.0207 and 3.1345 Å and are close to the K−N bond distance seen in KNH_2 (3.083 Å)[29] They are more than 2.0 Å longer than the H−N bond they replace, and this substitution therefore results in an expansion of the unit cell and the disappearance of dihydrogen bonding. The closest intermolecular $H^{\delta+}$---$H^{\delta-}$ distances increase from 1.96 (NH_3BH_3) to 2.2650 Å (KNH_2BH_3), which are close to the expected van der Waals distances (2.4 Å) and thus likely to be very weak

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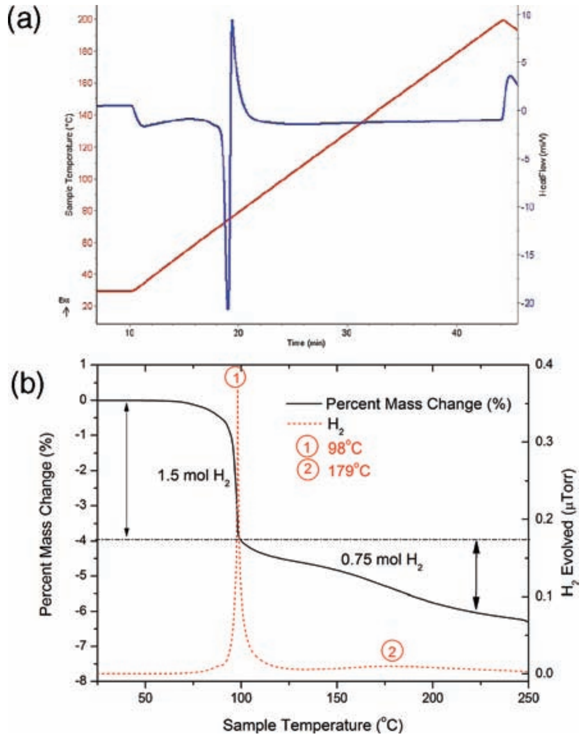

Figure 2. (a) DSC and (b) IGA data for KNH_2BH_3.

interactions. The $H^{\delta+}$---$H^{\delta-}$ distance is shorter than observed in $LiNH_2BH_3$ and $NaNH_2BH_3$ (2.372 and 2.717 Å, respectively) due to the change in coordination of the cation from tetrahedral to octahedral, thereby increasing the packing density of the $[NH_2BH_3]^-$ anions.

The next most significant interactions in the MNH_2BH_3 structure are the van der Waals interactions between M^+ and the three closest BH_3 units. The presence of these $BH^{\delta-}$---M^+ interactions supersedes the dihydrogen bonding seen in NH_3BH_3 as the stabilizing factor of the extended structure. These are of sufficient energy that the MNH_2BH_3 remains a solid at room temperature despite the removal of the dihydrogen bonding. The K−B distances of 3.3233, 3.3779, and 3.6131 Å are similar to that seen in KBH_4 (3.364 Å).[29] There are also a number of additional interactions between the cation and hydric hydrogens which further stabilize the larger, more diffuse cation.

Hydrogen Release. Typical thermal gravimetric analysis with mass spectroscopy (TGA-MS) indicates that only hydrogen is released. Differential scanning calorimetry (DSC) data for KNH_2BH_3 are shown in Figure 2a. The DSC data indicate the presence of a melt endotherm followed by a single exothermic event, which is associated with the hydrogen release. While DSC shows a very simple melt endotherm followed by a single exotherm, the pressure−composition−temperature (PCT) data indicate a much more complex hydrogen release mechanism. Intelligent gravimetric analysis (IGA) (Figure 2b), with a much greater sample mass, shows a single sharp release of 1.5 mol equiv of hydrogen at 80 °C, with a further 0.5 mol equiv of hydrogen released between 80 and 160 °C. Above 160 °C further hydrogen is released from the residue. No borazine was observed at any point, and no ammonia is detected during decomposition, using a 2 m IR flow cell with a 1 ppb detection limit.

An amorphous product is formed following hydrogen release. However, solid-state ^{11}B NMR indicates the presence of sp^2 borons. In addition, the IR spectra show stretching corresponding to B═N. Direct regeneration of this KNH_2BH_3 is not possible, but chemical regeneration, via ammonia borane, may be possible.

In conclusion, potassium amidoborane (KNH_2BH_3) was synthesized through the reaction of KH and NH_3BH_3. The structure has been determined, and the compound decomposes at 80 °C to release 6.5 wt % H_2 after 3 h. This material represents a completely new structural motif for the metal amidotrihydroborates, coupled with a significant change in the hydrogen release profile. This is apparent in two ways: melting prior to hydrogen release is currently unique to this material, and it is also the first alkali metal derivative that does not release ammonia.

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Supporting Information Available: Synthesis details and TGA-MS data (PDF); X-ray crystallographic file (CIF) for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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