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Potassium(I) Amidotrihydroborate: Structure and Hydrogen Release

Himashinie V. K. Diyabalanage,[†] Tessui Nakagawa,[†] Roshan P. Shrestha,[†] Troy A. Semelsberger,[†] Benjamin L. Davis,[†] Brian L. Scott,[†] Anthony K. Burrell,[*,†] William I. F. David,[‡,§] Kate R. Ryan,[§] Martin Owen Jones,[‡,§] and Peter P. Edwards[§]

Materials Physics and Applications Division, Los Alamos National Laboratory, Mail Stop J514, Los Alamos, New Mexico 87545, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot OX11 0QX, U.K., and Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 0ER, U.K.

Received January 20, 2010; E-mail: Burrell@lanl.gov

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.

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.

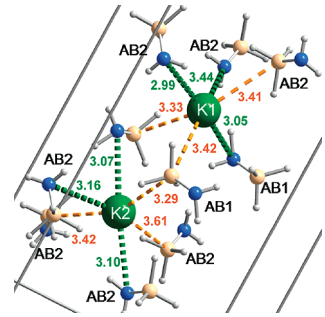

Figure 1. Schematic diagram of the structure of KNH_2BH_3, showing a close-up of the *mer*-octahedral coordination of both K^+ sites. Potassium, green; nitrogen, blue; and boron, cream. Distances are measured in angstroms.

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

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

[†] Los Alamos National Laboratory.
[‡] Rutherford Appleton Laboratory.
[§] University of Oxford.

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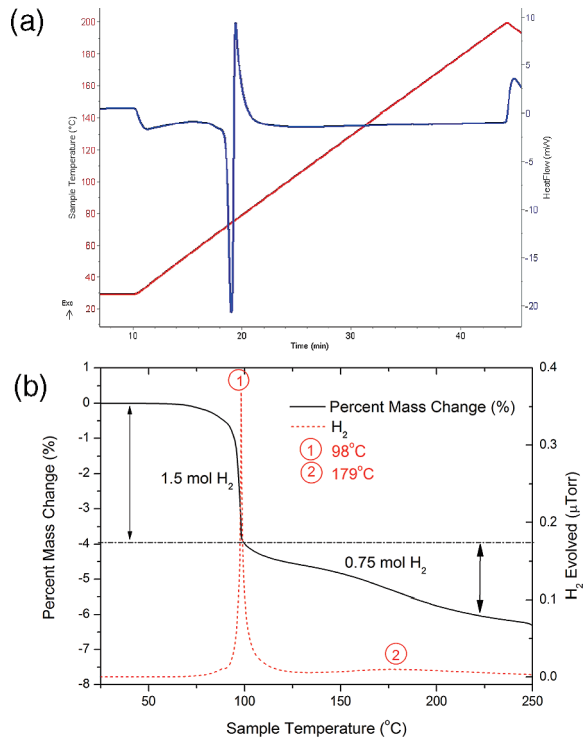

Figure 2. (a) DSC and (b) IGA data for KNH_2BH_3.

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.

References

(1) Grochala, W.; Edwards, P. P. *Chem. Rev.* **2004**, *104*, 1283–1315.
(2) Schlapbach, L.; Zuttel, A. *Nature* **2001**, *414*, 353–358.
(3) Hamilton, C. W.; Baker, R. T.; et al. *Chem. Soc. Rev.* **2009**, *38*, 279–293.
(4) Stowe, A. C.; Shaw, W. J.; Linehan, J. C.; Schmid, B.; Autrey, T. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831–1836.
(5) Wolf, G.; Baumann, J.; Baltalow, F.; Hoffmann, F. P. *Thermochim. Acta* **2000**, *343*, 19–25.
(6) Hu, M. G.; Geanangle, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1978**, *23*, 249–255.
(7) Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T.; Autrey, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7493–7496.
(8) Bluhm, M. E.; Bradley, M. G.; Butterick, R., III; Kusari, U.; Sneddon, L. G. *J. Am. Chem. Soc.* **2006**, *128*, 7748–7749.
(9) Sit, V.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta* **1987**, *113*, 379–382.
(10) Baitalow, F.; Baumann, J.; Wolf, G.; Jaenicke-Rössbler, K.; Leitner, G. *Thermochim. Acta* **2002**, *391*, 159–168.
(11) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.* **2007**, 2613–2626.
(12) Jaska, C. A.; Temple, K.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434.
(13) Denney, M. C.; Pons, V.; Hebden, T. J.; Heinekey, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049.
(14) Keaton, R. J.; Blacquiere, J. M.; Baker, R. T. *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845.
(15) Stephens, F. H.; Baker, R. T.; Matus, M. H.; Grant, D. J.; Dixon, D. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 746–749.
(16) Gutowska, A.; Li Liyu, S. Y.; Wang, C. M.; Li, X. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3578–3582.
(17) Clark, T. J.; Lee, K.; Manners, I. *Chem. Eur. J.* **2006**, *12*, 8634–8648.
(18) Feaver, A.; Sepehri, S.; Shamberger, P.; Stowe, A.; Autrey, T.; Cao, G. *J. Phys. Chem. B* **2007**, *111*, 7469–7472.
(19) Myers, A. G.; Yang, B. H.; Kopecky, D. J. *Tetrahedron Lett.* **1996**, *37*, 3623–3626.
(20) Graham, K. R.; Kemmitt, T.; Bowden, M. E. *Energy Environ. Sci.* **2009**, *2*, 706–710.
(21) Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 14834–14839.
(22) Xiong, Z.; Chua, Y. S.; Wu, G.; Xu, W.; Chen, P.; Shaw, W.; Karkamkar, A.; Linehan, J.; Smurthwaite, T.; Autrey, T. *Chem. Commun.* **2008**, 5595–5597.
(23) Xiong, Z.; Yong, C. K.; Wu, G.; Chen, P.; Shaw, W.; Karkamkar, A.; Autrey, T.; Jones, M. O.; Johnson, S. R.; Edwards, P. P.; David, W. I. F. *Nat. Mater.* **2008**, *7*, 138–141.
(24) Kang, X.; Fang, Z.; Kong, L.; Cheng, H.; Yao, X.; Lu, G.; Wang, P. *Adv. Mater.* **2008**, *20*, 2756–2759.
(25) Ramzan, M.; Silvearv, F.; Blomqvist, A.; Scheicher, R. H.; Lebègue, S.; Ahuja, R. *Phys. Rev. B* **2009**, *79*, 132102-1–132102-4.
(26) Xiong, Z.; Wu, G.; Chua, Y. S.; Hu, J.; He, T.; Xub, W.; Chen, P. *Energy Environ. Sci.* **2008**, *1*, 360–363.
(27) Spielmann, J.; Jansen, G.; Bandmann, H.; Harder, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6290–6295.
(28) Diyabalanage, H. V. K.; Shrestha, R. P.; Semelsberger, T. A.; Scott, B. L.; Bowden, M. E.; Davis, B. L.; Burrell, A. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 8995–8997.
(29) Renaudin, G.; Gomes, S.; Hagemann, H.; Keller, L.; Yvon, K. *J. Alloys Compd.* **2004**, *375*, 98–106.
(30) Zalkin, A.; Templeton, D. H. *J. Phys. Chem.* **1956**, *60*, 821–823.

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