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# Calcium Amidotrihydroborate: A Hydrogen Storage Material\*\*

Himashinie V. K. Diyabalanage, Roshan P. Shrestha, Troy A. Semelsberger, Brian L. Scott, Mark E. Bowden, Benjamin L. Davis, and Anthony K. Burrell\*

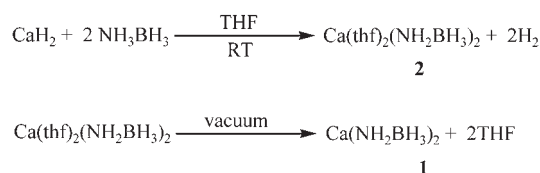
The promise of the hydrogen economy, while great, will only be realized when many major scientific challenges are overcome. One of primary challenges is the need to find a safe and economic method for storing and transporting H<sub>2</sub>. Conventional storage systems include classical high-pressure tanks, insulated liquid-hydrogen systems, and storage in hydrocarbons.<sup>[1]</sup> Chemical methods, such as the use of metal hydrides (for example, MgH<sub>2</sub>),<sup>[2]</sup> imides (such as LiNH<sub>2</sub>),<sup>[3]</sup> organic frameworks (Zn<sub>4</sub>O(1,4-benzenedicarboxylate)),<sup>[4,5]</sup> alkali-metal tetrahydroboride (such as LiBH<sub>4</sub>),<sup>[6]</sup> alanates (for example, NaAlH<sub>4</sub>),<sup>[7]</sup> and chemical hydrides all show promise. There are several advantages of chemical H<sub>2</sub> storage over compressed H<sub>2</sub>; an important advantage is that the H<sub>2</sub> density available in chemical systems significantly outweighs even liquid H<sub>2</sub>.

Among the potential candidates for effective chemical H<sub>2</sub> storage, ammonia–borane (NH<sub>3</sub>BH<sub>3</sub>) has garnered much interest owing to its ideal combination of low molecular weight and high H<sub>2</sub> storage capacity of 19.6 weight %, which exceeds the current capacity of gasoline.<sup>[8–15]</sup> The chemical nature of the NH<sub>3</sub>BH<sub>3</sub> molecule, with both hydridic and protic hydrogen atoms in close proximity, provides a unique environment for the release of H<sub>2</sub>. Ultimately, NH<sub>3</sub>BH<sub>3</sub> can be dehydrogenated completely, forming ceramic BN, but only at temperatures in excess of 500 °C.<sup>[15–19]</sup> Recently, catalytic hydrogen release from NH<sub>3</sub>BH<sub>3</sub> has also achieved significant attention.<sup>[11,20–23]</sup>

Herein we report a derivative of NH<sub>3</sub>BH<sub>3</sub>, Ca(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub> (**1**), in which a new covalent bond between the nitrogen atom of NH<sub>3</sub>BH<sub>3</sub> and calcium has been formed. Compound **1** has thermal properties that differ significantly from solid NH<sub>3</sub>BH<sub>3</sub>, and undergoes loss of H<sub>2</sub> without significant foaming, which is a common problem with NH<sub>3</sub>BH<sub>3</sub>. The H<sub>2</sub> loss from **1** is also not as exothermic as in ammonia–borane,

and the steady release of H<sub>2</sub> in the solid state is spread over much wider temperature and time ranges (see Supporting Information).

The reaction of NH<sub>3</sub>BH<sub>3</sub> with calcium hydride in THF leads to calcium amidotrihydroborate as the bis(thf) adduct (**2**) in excellent yield (Scheme 1). Compound **2** loses THF



**Scheme 1.** Synthesis of **1** from calcium hydride and ammonia–borane.

once it is removed from solution, giving **1**. In most samples of **1**, small amounts of THF are still detected, yet the amounts present are well below stoichiometric ratios. Calcium amidotrihydroborate is relatively stable in air, with no observable decomposition over two days in the solid state or in solution.

The boron chemical shift in NH<sub>3</sub>BH<sub>3</sub>, **1**, and **2** are effectively identical in the <sup>11</sup>B NMR spectrum, with the only difference being the B–H coupling constants (<sup>1</sup>J<sub>BH</sub> = 93.0 Hz for NH<sub>3</sub>BH<sub>3</sub> and <sup>1</sup>J<sub>BH</sub> = 86.0 Hz for **1**). The characteristic differences between **1** and **2** are observed in the <sup>1</sup>H NMR spectrum. Two signals are observed for **1** in [D<sub>8</sub>]THF, namely a quartet at δ = 1.39 ppm and a broad singlet at δ = –0.64 ppm, corresponding to BH<sub>3</sub> and NH<sub>2</sub> protons, respectively. On the other hand, the <sup>1</sup>H NMR of **2** in C<sub>6</sub>D<sub>6</sub> shows two multiplets, at δ = 3.58 ppm and 1.38 ppm, indicating the presence of thf ligands, in addition to two broad peaks corresponding to the BH<sub>3</sub> and NH<sub>2</sub> protons (at about δ = 1.22 ppm and 0.88 ppm, respectively).

In the single-crystal X-ray analysis (Figure 1) of the crystals obtained from a THF/hexane mixture containing **1**, two thf ligands coordinate to each Ca(NH<sub>2</sub>BH<sub>3</sub>)<sub>2</sub> molecule, forming **2**. Intermolecular interactions of 2.368 Å are observed between the Ca<sup>II</sup> ion and hydridic hydrogens of BH<sub>3</sub>. This gives rise to an extended structure with a chain-like arrangement in the solid state structure of **2**.

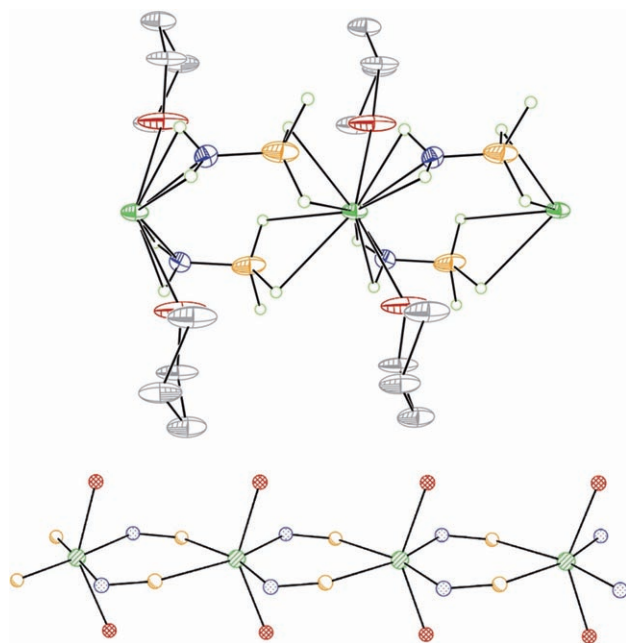
The thermal properties of **1** are of primary importance if it is to be useful as a H<sub>2</sub> storage material. The thermal gravimetric analysis (TGA) of **1** shows several weight-loss events (Figure 2). The initial loss, which begins at 70 °C, is attributed to THF. This loss was also observed at this temperature by mass spectrometry (MS). The amount of THF that remains in **1** varies depending on the surface area of the sample. Elemental analysis of a typical sample of **1**, dried

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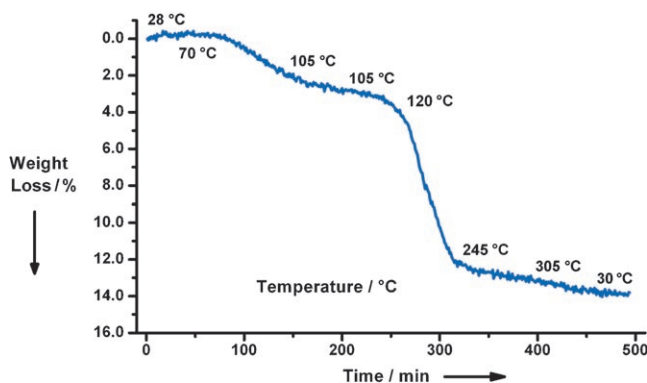
[\*\*] We thank Tom Autrey (PNNL) for very helpful discussions. We would like to acknowledge the support of the IPHE collaboration “Combination of Amine Boranes with MgH<sub>2</sub> & LiNH<sub>2</sub> for High Capacity Reversible Hydrogen Storage” in the development of this work and the US Department of Energy, Office of Energy Efficiency and Renewable Energy for providing funding.



Supporting Information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

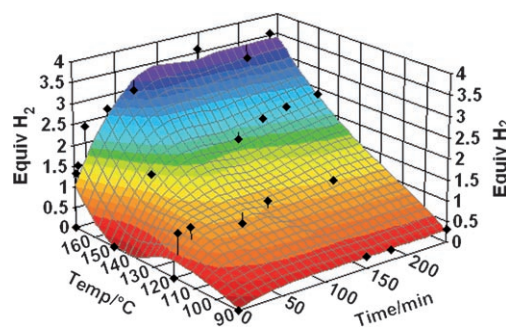


**Figure 1.** X-ray crystal structure of **2**, with thermal ellipsoids set at 35% probability, and hydrogen atoms attached to thf carbon atoms omitted for clarity. A section of the chain (top) showing interactions involving the hydrogen atoms from the  $\text{NH}_2\text{BH}_3$  unit, and (bottom) the full chain with hydrogen and carbon atoms omitted for clarity. B yellow, Ca green, O red, N blue, C gray, H small green open circles. Selected distances ( $\text{\AA}$ ):  $\text{Ca}(1)\cdots\text{Ca}(1a) = 3.147(6)$ ,  $\text{Ca}(1)-\text{B}(1) = 2.349(12)$ ,  $\text{Ca}(1)-\text{B}(1a) = 2.829(13)$ ,  $\text{Ca}(1)-\text{N}(1) = 2.069(7)$ ,  $\text{Ca}(1)-\text{N}(1b) = 2.362(7)$ ,  $\text{Ca}(1)-\text{O}(1) = 2.438(4)$ . Symmetry operations: a:  $-x+1, -y, -z+1$ ; b:  $-x+1, -y, -z$ .



**Figure 2.** Thermogravimetric analysis of **1**; initial loss of THF begins at 70 °C. THF loss is also accompanied by a small release of  $\text{H}_2$  before the major hydrogen release begins at 120 °C.

under a stream of argon, shows less than 10% THF remaining. Upon heating to 120 °C, the onset of the most significant mass loss is observed. Analysis of the mass loss was carried out by mass spectrometry, and hydrogen was quantified below 170 °C by calibrated gas chromatography (GC; Figure 3). The majority of the mass loss is hydrogen gas. Small amounts of ammonia and borazine can be detected, but these contribute to less than 0.1% of the weight change below



**Figure 3.** Thermal hydrogen-release profile for **1**. The colored surface is fitted to the black data points.

170 °C. A small amount of hydrogen release ( $< 0.3$  equivalents of  $\text{H}_2$ ) is observed at 90 °C. However, prolonged heating at 90 °C does not result in further release of hydrogen or any other detectable mass loss (for thermal gravimetric analysis and differential scanning calorimetry results, see the Supporting Information). GC experiments indicate that 1.1 equivalents of  $\text{H}_2$  can be released from **1** at 120 °C, 2.4 equivalents at 150 °C, and  $(3.6 \pm 0.2)$  equivalents at 170 °C. This is a 90% yield at 170 °C based upon the four equivalents of  $\text{H}_2$  expected from the combination of four protic ( $-\text{NH}_2-$ ) and four of the six hydridic ( $-\text{BH}_3$ ) hydrogen atoms, and corresponds to a gravimetric concentration of 7.2 weight%  $\text{H}_2$ . Both the rate and volume of  $\text{H}_2$  release for **1** varies with temperature, which is in contrast to solid  $\text{NH}_3\text{BH}_3$ , where any temperature above 120 °C results in the release of about two equivalents of  $\text{H}_2$ . This is presumably a consequence of the endothermic hydrogen release from **1**, which was estimated to have an enthalpy of  $3.5 \text{ kJ mol}^{-1}$  after accounting for the overlapping THF endotherm in the DSC trace (Supporting Information). Hydrogen release from  $\text{NH}_3\text{BH}_3$  is exothermic with an enthalpy of  $-22.5 \text{ kJ mol}^{-1}$  for the release of the first equivalent of  $\text{H}_2$ .<sup>[17,18]</sup>

After about four equivalents of hydrogen are released from **1** by the facile combination of the boron hydrogen atoms and ammonia hydrogen atoms, the remaining hydrogen atoms in the residue ascribed to be  $\text{Ca}(\text{NBH})_2$  must be lost in an alternative mechanism at higher temperatures. As the sample is heated to from 170–245 °C, more hydrogen release is observed by mass spectrometry. Elemental analysis of the residue that remained after heating **1** to 170 °C indicates an elemental composition of  $\text{CaN}_2\text{B}_2\text{H}_2\text{C}_{0.2}$ . Elemental analysis of samples heated to greater than 245 °C show steady loss of nitrogen. Unfortunately, the residue that is formed as **1** is heated is amorphous and X-ray data cannot be obtained. Further studies on the high temperature decomposition of the residue formed after hydrogen release from **1** are underway.

In summary, we have described a straightforward route to obtain the calcium derivative of ammonia borane, which possesses different thermal properties than ammonia–borane and has a lower propensity for borazine release. As a potential hydrogen storage material, **1** offers some advantages in that the thermal hydrogen release does not suffer from the induction period present in ammonia–borane.

## Experimental Section

**1:** Ammonia–borane (0.20 g, 6.48 mmol) was dissolved in tetrahydrofuran (30.0 mL). This mixture was slowly added to a suspension of calcium hydride (0.14 g, 3.24 mmol) in tetrahydrofuran (20.0 mL) and allowed to stir overnight. The solvents were removed under vacuum to obtain the white solid product,  $\text{Ca}(\text{NH}_2\text{BH}_3)_2$  (0.31 g). X-ray quality crystals of the THF adduct **2** were obtained from a THF/hexane solution of **2** at  $-22^\circ\text{C}$ . Compound **1** was obtained by vacuum-drying **2** overnight at room temperature. Yield of **1**: 96%; m.p.:  $98-100^\circ\text{C}$  (dec);  $^1\text{H}$  NMR (300.13 MHz,  $[\text{D}_8]\text{THF}$ ,  $22^\circ\text{C}$ , TMS):  $\delta = 1.39$  (q,  $^1J(\text{H},\text{B}) = 86.0$  Hz, 3H,  $\text{BH}_3$ ),  $-0.64$  ppm (br.s, 2H,  $\text{NH}_2$ );  $^{11}\text{B}$  NMR (96.29 MHz,  $[\text{D}_8]\text{THF}$ ,  $22^\circ\text{C}$ ):  $\delta = -23.62$  ppm (q,  $^1J(\text{B},\text{H}) = 86.0$  Hz,  $\text{BH}_3$ ); IR (neat):  $\tilde{\nu} = 2977.7$  &  $2879.6$  (N-H),  $2196.7$  &  $2146.2$  (B-H),  $1533.0$ ,  $1459.8$ ,  $1260.6$ ,  $1168.1$ ,  $1041.8$ ,  $1010.5$ ,  $917.2$ ,  $884.6$ ,  $816.5$ ,  $671.9$ ,  $607.7$ ,  $597.0$   $\text{cm}^{-1}$ .

Compound **1** was weighed into glass vials in an argon-filled glove box and crimp sealed. The vials were heated isothermally in a stainless steel reactor vessel preheated to set temperatures for set durations of time. After quenching the reaction by cooling to  $0^\circ\text{C}$ , the gaseous contents were analyzed by GC at  $35^\circ\text{C}$ . Calibration curves were constructed using the ratio of the areas of Ar and  $\text{H}_2$  peaks in the chromatograph of standards having a known concentration. Percentage conversion of **1** to  $\text{H}_2$ , and consequently the number of equivalents of  $\text{H}_2$  released, were calculated from these calibration curves. No other gaseous species were detected by GC in the quenched samples. TGA of **1** was carried out in  $\text{N}_2$ . The temperature range for TGA was  $30-305^\circ\text{C}$  at a ramp rate of  $0.5-1^\circ\text{Cmin}^{-1}$ . Mass spectrometry (MS) of **1** was carried out using a Pfeiffer quadrupole spectrometer. The heated stainless steel capillary inlet was positioned in a stream of argon flowing across the sample, which was heated at  $1^\circ\text{Cmin}^{-1}$ .

Crystal Data for **2**:  $\text{C}_8\text{H}_{26}\text{B}_2\text{CaN}_2\text{O}_2$ ,  $M_r = 244.01$ , orthorhombic,  $a = 7.910(2)$ ,  $b = 17.570(4)$ ,  $c = 4.6700(9)$  Å,  $V = 649.0(2)$  Å<sup>3</sup>,  $T = 120$  K, space group  $Pnmm$  (No. 58),  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.249$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 0.47$  mm<sup>-1</sup>, 4461 reflections measured ( $2\theta_{\text{max}} = 50.0^\circ$ ), and 681 unique ( $R_{\text{int}} = 0.0889$ ). The final residuals were  $R(I > 2\sigma; \text{all data}) = 0.0906$ ;  $0.1161$ , and  $wR(I > 2\sigma; \text{all data}) = 0.2729$ ;  $0.2835$ , with residual electron density =  $0.484$  e Å<sup>-3</sup>. The data were collected on a Bruker D8, with APEX II CCD detector using  $\omega$  scans. The structure was solved using Direct Methods (SHELXS-97), and refined on  $F^2$  (SHELXL-97). The chain structure was disordered over two positions, and each atom was refined at one-half normal occupancy. The hydrogen atom positions were found on the difference map, and refined with fixed isotropic temperature factors ( $0.10$  Å<sup>2</sup>). The amine hydrogen atom positions were restrained. All non-hydrogen atoms were refined anisotropically. CCDC-646993 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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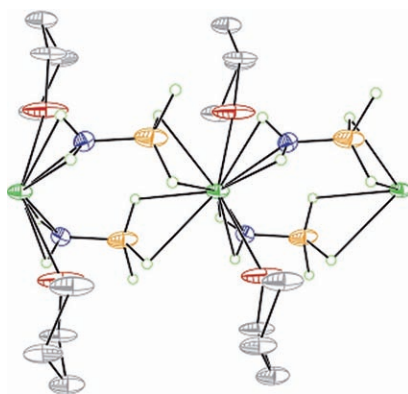
## Communications



### Hydrogen Storage

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Calcium Amidotrihydroborate: A  
Hydrogen Storage Material



**No foaming at the mouth here:** A calcium(II) derivative of ammonia–borane,  $\text{Ca}(\text{NH}_2\text{BH}_3)_2$  (see picture; green Ca, red O, blue N, yellow B, gray C, small green H), has thermal properties that are quite different from those of ammonia–borane.  $\text{Ca}(\text{NH}_2\text{BH}_3)_2$  releases hydrogen over a temperature range of 100 to 170 °C without foaming.