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Abstract

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Keywords

hydrogen, nh₄b₃h₈, structure, ammonium, properties, octahydrotriborate, storage, synthesis

Disciplines

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Ammonium Octahydrotriborate ($\text{NH}_4\text{B}_3\text{H}_8$): New Synthesis, Structure and Hydrolytic Hydrogen Release.

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ABSTRACT

A metathesis reaction between unsolvated NaB_3H_8 and NH_4Cl provides a simple and high-yield synthesis of $\text{NH}_4\text{B}_3\text{H}_8$. Structure determination through X-ray single crystal diffraction analysis reveals weak $\text{N-H}^+ \cdots \text{H}^- \cdots \text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8$ and strong $\text{N-H}^+ \cdots \text{H}^- \cdots \text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct. Pyrolysis of $\text{NH}_4\text{B}_3\text{H}_8$ leads to the formation of hydrogen gas with appreciable amounts of other volatile boranes below 160 °C. Hydrolysis experiments show that upon addition of catalysts, $\text{NH}_4\text{B}_3\text{H}_8$ releases up to 7.5 materials wt % hydrogen.

Introduction

The safe and efficient hydrogen storage is a major barrier to the use of hydrogen as a transportation fuel. Intensive efforts in recent years have been focused on boron hydrides such as metal borohydrides ($\text{Mg}(\text{BH}_4)_2$,¹ NaBH_4 ²) and amine boranes ($\text{NH}_3\text{B}_3\text{H}_7$,³ NH_3BH_3 ⁴) for hydrogen storage due to their high hydrogen contents. Various catalysts have been investigated to improve hydrogen release from these materials through either thermal decomposition or hydrolysis. However, none of these materials under investigation meets the multiple targets set forth by the US Department of Energy (DOE).

The great variety and distinct properties of boron compounds prompt us to search for a compound that could satisfy the requirements for hydrogen storage. In order to obtain a high hydrogen capacity, it is essential to find a suitable combination of light-weight cation and H-rich B_mH_n anion. High number of m in B_mH_n leads to a lower hydrogen content and also greater stability of the boron cluster.⁵ Ammonium octahydrotriborate, $\text{NH}_4\text{B}_3\text{H}_8$, has a high hydrogen content of 20.5 wt %. Unfortunately, the first synthesis reported 40 years ago involves pentaborane, B_5H_9 , which is highly volatile and inflames violently upon contact with air.^{6a,b} There are two pentaborane-free patents, but the procedures are complicated and require intermediate compounds and large amounts of solvents.^{6c,d} Probably due to the lack of suitable syntheses, there have been little explorations of its reactivities and properties in 40 years. Here we report (1) a simple and efficient synthesis of this compound; (2) a crystallographic study of the structure; (3) thermal decomposition; and (4) interesting hydrogen release properties through hydrolysis.

Experimental Section

General Procedures. All manipulations were carried out on a high-vacuum line or in a glove box filled with high purity nitrogen. Solvents were dried over sodium/benzophenone and freshly distilled prior to use. Ammonia (Matheson) was distilled from sodium immediately prior to use. NMR spectra were obtained on a Bruker Avance DPX 250 NMR. ¹¹B NMR spectra were obtained at 80.3 MHz and externally referenced to $\text{BF}_3 \cdot \text{OEt}_2$ in C_6D_6 at 0.00 ppm. ¹H NMR spectra were obtained at 250.1 MHz and

referenced to THF- d_8 . Unsolvated NaB_3H_8 was prepared following the procedure recently developed in our lab.⁷ NH_4Cl (Aldrich) was recrystallized from methanol. Mass spectra of the gas released from the hydrolysis and thermal decomposition were collected through a Balzer's Quadstar 422 Quadrupole mass spectrometer.

Synthesis of $\text{NH}_4\text{B}_3\text{H}_8$

The prepared unsolvated NaB_3H_8 (634 mg, 10 mmol) reacted with NH_4Cl (535 mg, 10 mmol) in liquid ammonia at $-78\text{ }^\circ\text{C}$. After 30 min stirring using a magnetic bar, ammonia was removed and the flask was warmed to room temperature. The desired $\text{NH}_4\text{B}_3\text{H}_8$ was extracted using dry THF followed by pumping off THF right away, leaving a white powder, $\text{NH}_4\text{B}_3\text{H}_8$ (555 mg, yield 95%). ^{11}B NMR: (THF- d_8) δ -29.9 ppm, ^1H NMR (THF- d_8): NH_4^+ , δ 6.8 ppm; $\text{B}_3\text{H}_8^\bullet$, δ 0.2 ppm.

X-ray Crystallography

X-ray quality crystals of the $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct were grown from 1:1 (molar ratio) mixtures of $\text{NH}_4\text{B}_3\text{H}_8$ and 18-crown-6 in THF. $\text{NH}_4\text{B}_3\text{H}_8$ single crystals were grown from anhydrous CH_3CN . *Words of caution: at room temperature, signs of decomposition (bubbles) were observed after a few days for both the $\text{NH}_4\text{B}_3\text{H}_8/18\text{-crown-6}/\text{THF}$ and $\text{NH}_4\text{B}_3\text{H}_8/\text{CH}_3\text{CN}$ mixtures.*

X-ray single crystal diffraction data were collected on a Nonius Kappa CCD diffractometer which employs graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.71073\text{ \AA}$). Due to the sensitivity of the compound, single crystals were picked up from the mother solution in a nitrogen filled glove box and stored in Fomblin oil until data collection. A single crystal coated with Fomblin oil was mounted on the tip of a glass fiber. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package.⁸ Absorption correction for the structure was accounted for by using SCALEPACK.⁸ The structure was solved by direct method using the SHELXTL-97 (full-matrix least-squares refinements) structure solution package.⁹ All nonhydrogen atoms were

located and refined anisotropically. Hydrogen atoms on boron and nitrogen atoms were located and refined isotropically, and other hydrogen atom positions were calculated by assuming standard geometries.

Table 1. Crystallographic information

empirical formula	H ₁₂ B ₃ N	C ₁₆ H ₄₄ B ₃ NO ₇
formula weight	58.54	394.95
crystal system	Orthorhombic	Monoclinic
space group	<i>Cmcm</i>	<i>Pc</i>
<i>Z</i>	4	4
<i>a</i> , Å	7.1530(14)	16.407(3)
<i>b</i> , Å	8.2648(17)	11.215(2)
<i>c</i> , Å	8.3895(17)	13.841(3)
α , deg	90	90
β , deg	90	107.76(3)
γ , deg	90	90
<i>T</i> , K	150	150
<i>V</i> , Å ³	495.97(17)	2425.4(9)
<i>D</i> _{calcd} (g·cm ⁻³)	0.784	1.082
μ (mm ⁻¹)	0.038	0.079
λ , Å	0.71073	0.71073
no. reflns collected	1617	8313
no. unique reflns	251 (<i>R</i> _{int} = 0.0245)	4286 (<i>R</i> _{int} = 0.0258)
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0370	0.0420
w <i>R</i> 2(all data) ^b	0.1153	0.1043

$$^a R1 = \sum \|F_0\| - |F_c| / \sum |F_0| \cdot ^b wR2 = [\sum w(F_0^2 - F_c^2)]^2 / \sum w(F_0^2)^2]^{1/2}$$

Thermal decomposition studies

Thermal stability of NH₄B₃H₈ was studied using a Mettler Toledo high-pressure differential scanning calorimeter (DSC27HP) in an argon glove box with a ramp rate of 5 °C/min. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 analyzer. Powder was loaded onto a quartz crucible and heated to 400 °C at a heating rate of 5 °C/min under an Ar flow of 40 cm³/min. The gaseous

decomposition products were semi-quantified through a calibrated vacuum line. After freezing out the gaseous products at -196 °C, hydrogen content was determined; after removing hydrogen and then raising the temperature to -78 °C, diborane was quantified; the residual product, pentaborane and borazine, were analyzed after diborane was removed and temperature was raised to ~25 °C.¹⁰

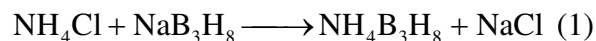
Hydrolytic H₂ release Measurements

In a two-neck flask connected to a vacuum line, 1 mmol NH₄B₃H₈ was mixed with 0.04 mmol CoCl₂. After evacuating all the gases via dynamic vacuum, the flask was sealed and 18 mmol water was injected. After the reaction completion, the flask was opened to a vacuum line, and the evolved gas passed through a liquid nitrogen trap in order to isolate any non-hydrogen products, including water. The hydrogen was then quantitatively measured using a Toepler pump. About 8.80 mmol H₂ was obtained through the reaction.

For catalyst screening, a gas buret was set up to measure the amount of H₂ gas and to determine the rates of H₂ release.^{3a} Pt/C (10 wt % Pt), Ru/Al₂O₃ (5 wt % Ru), RuCl₃, CoCl₂, NiCl₂ and FeCl₃ were all tested as received. For the catalyst loading, 1 mol % (with reference to NH₄B₃H₈) of noble metal (Pt or Ru) was loaded, while 4 mol % of transition metal (Co, Ni or Fe) was employed.

Results and Discussions

A simple and efficient method has now been developed to synthesize NH₄B₃H₈ via a metathesis reaction between unsolvated NaB₃H₈ and NH₄Cl in liquid ammonia (eq 1).



This reaction proceeds rapidly and the desired product can be efficiently extracted using THF after removing the liquid ammonia. Furthermore, the yield is ~95 %, higher than 79.5 % reported for the previous methods.⁶ The unsolvated NaB₃H₈ was prepared via a route recently developed in our lab⁷,

which eliminates the use of dangerous starting materials such as B_2H_6 and BF_3 ¹¹ and enables a high yield. Therefore, a large-scale and simple synthesis of $NH_4B_3H_8$ is now possible.

The metathesis reaction has also been explored in several other solvents and it was found that the solvent had an influence on the course of the reaction. In addition to $NH_4B_3H_8$, $NH_3B_3H_7$ and other boron compounds were also observed for the reaction in THF and DME, with the latter resulting in more $NH_3B_3H_7$.

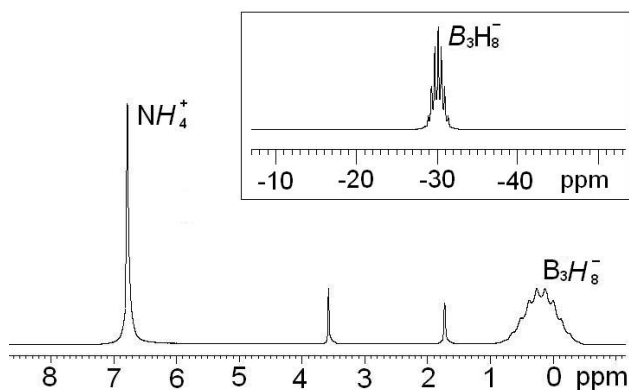


Figure 1. ¹H NMR spectrum of $NH_4B_3H_8$ recorded in $THF-d_8$ at room temperature. Inset is the ¹¹B NMR spectrum.

The successful synthesis in liquid ammonia is corroborated by NMR spectrum (Figure 1). After extracting $NH_4B_3H_8$ using THF and then pumping off the THF immediately via dynamic vacuum, pure desired product was obtained. $NH_4B_3H_8$ exhibits a ¹¹B NMR resonance at -29.9 ppm, which is assigned to $B_3H_8^-$.⁷ The ¹H NMR spectrum of $NH_4B_3H_8$ reveals the existence of both NH_4^+ (6.8 ppm) and $B_3H_8^-$ (0.2 ppm).

Table 2. Selected bond distances and angles of H₁₂B₃N^a

N(1)-H(5)	0.85(3)
N(1)-H(6)	0.79(4)
B(1)-B(2)	1.779(2)
B(1)-B(2) [#]	1.779(2)
B(1)-H(4)	1.475(18)
B(1)-H(1)	1.079(17)
B(2)-B(2) [#]	1.813(3)
B(2)-H(3)	1.096(13)
B(2)-H(4)	1.137(17)
H(5)-N(1)-H(6)	113(2)
B(2)-B(1)-B(2) [#]	61.27(11)
B(2)-B(1)-H(4)	39.5(7)
B(2) [#] -B(1)-H(4)	100.8(7)
B(2)-B(1)-H(1)	117.3(7)
B(2) [#] -B(1)-H(1)	117.3(7)
H(4)-B(1)-H(1)	100.4(4)
B(1)-B(2)-B(2) [#]	59.37(5)
B(1)-B(2)-H(3)	121.5(6)
B(2) [#] -B(2)-H(3)	108.5(7)
B(1)-B(2)-H(4)	55.7(9)
B(2) [#] -B(2)-H(4)	115.0(9)
H(3)-B(2)-H(4)	104.2(8)

^a Symmetry transformations used to generate equivalent atoms: # = $x, y, -z+3/2$

Table 3. Selected bond distances and angles of C₁₆H₄₄B₃NO₇

N(1)-H(2)	0.82(5)
N(1)-H(1)	0.92(4)
N(1)-H(3)	0.87(4)
N(1)-H(4)	0.99(6)
B(1)-B(3)	1.758(6)
B(1)-B(2)	1.796(7)
B(2)-B(3)	1.762(6)
B(1)-H(9)	1.14(4)
B(1)-H(15)	1.27(5)
B(2)-H(11)	1.10(4)
B(2)-H(12)	1.08(5)
B(3)-H(16)	1.41(4)
H(2)-N(1)-H(3)	111(4)
H(1)-N(1)-H(3)	108(3)
H(2)-N(1)-H(4)	111(4)
H(1)-N(1)-H(4)	110(4)
B(3)-B(1)-B(2)	59.4(3)
B(1)-B(3)-B(2)	61.3(3)
B(3)-B(2)-B(1)	59.2(2)
B(3)-B(1)-H(9)	121.4(18)
B(3)-B(1)-H(10)	126(2)
B(2)-B(1)-H(15)	115(2)
B(1)-B(3)-H(16)	102.0(17)
B(2)-B(3)-H(16)	40.6(17)
B(1)-B(3)-H(15)	45.1(19)
B(1)-B(3)-H(14)	115.2(18)

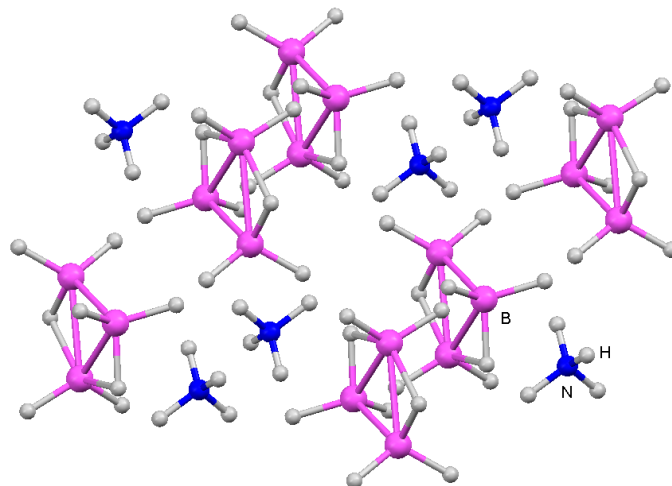


Figure 2. Crystal structure of the $\text{NH}_4\text{B}_3\text{H}_8$. B: pink, H: light grey, N: blue.

The structures of $\text{NH}_4\text{B}_3\text{H}_8$ and $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct were determined through single crystal X-ray diffraction analysis. Selected bond distances and angles are given in Tables 2 and 3, respectively. Figure 2 shows a separate ion pair structure of $\text{NH}_4\text{B}_3\text{H}_8$, with the shortest $\text{N-H}^+ \cdots \text{H}^- \text{-B}$ distance being $2.37(3) \text{ \AA}$, very close to the sum of van der Waals radii between two hydrogen atoms, 2.4 \AA . All other $\text{N-H}^+ \cdots \text{H}^- \text{-B}$ distances are more than 2.47 \AA . This seems unusual since B-N compounds tend to have close $\text{N-H}^+ \cdots \text{H}^- \text{-B}$ contacts,^{12a} as observed in $\text{NH}_3\text{B}_3\text{H}_7$ ^{3a} and NH_3BH_3 ^{12b}. This structure differs from the reported metal octahydrotriborates, where B_3H_8 can coordinate with a metal center such as for $\text{Cr}(\text{B}_3\text{H}_8)_2$,^{11c} $(\text{CO})_4\text{Mn}(\text{B}_3\text{H}_8)$,¹³ $\text{Mg}(\text{B}_3\text{H}_8)_2(\text{Et}_2\text{O})_2$ ¹⁴, and $\text{Ru}(\text{B}_3\text{H}_8)(\text{PPh}_3)\{\kappa^3\text{-HB}(\text{pz})_3\}$.¹⁵

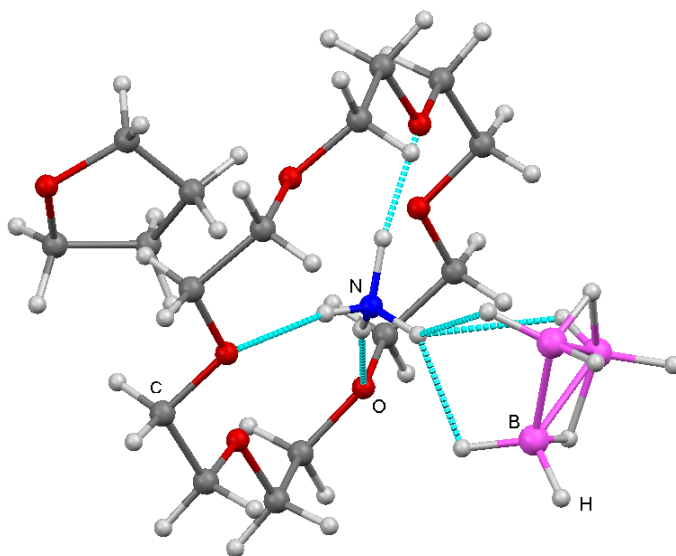


Figure 3. Fragment of the $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct. B: pink, H: light grey, N: blue O; red, C: grey.

The molecular structure of $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct is illustrated in Figure 3. Ammonium cation has been reported to connect to crown ether by three $\text{N-H} \cdots \text{O}$ hydrogen bonds between the hydrogen atoms of the ammonium and the oxygen atoms of the crown ether.¹⁶ We likewise found similar interaction present in $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-6} \cdot \text{THF}$ adduct. There is another independent fragment in the asymmetric unit, very similar to the one shown in Figure 3. THF molecule is packed into the structure with no interactions with other moieties. The average N-O distance is 2.94 \AA , longer than the standard N-O hydrogen bond length (2.87 \AA).¹⁷ The hydrogen atom on nitrogen that is not involved in bonding to an oxygen atom interacts with three terminal hydrogen atoms on the boron triangle, with the closest $\text{N-H}^+ \cdots \text{H}^- \text{-B}$ distance of $1.92(5) \text{ \AA}$ being shorter than $2.13(3) \text{ \AA}$ present in $\text{NH}_3\text{B}_3\text{H}_7$, determined by X-ray diffraction analysis,^{3a} significantly less than the sum of van der Waals radii between two hydrogen atoms, 2.4 \AA .

$\text{NH}_4\text{B}_3\text{H}_8$ in pure and solid form is stable at room temperature with no detectable signs of decomposition within one month. On the contrary, the adduct decomposes slowly at room temperature with the

evolution of hydrogen gas. The poor stability of the adduct is likely due to the stronger $\text{N-H}^+ \cdots \text{H}^- \text{-B}$ interactions.

NH_4BH_4 , an analogue of $\text{NH}_4\text{B}_3\text{H}_8$, decomposes at -78°C in THF.¹⁸ This is in stark contrast to the slow degradation of $\text{NH}_4\text{B}_3\text{H}_8$ in THF at ambient conditions. Since both compounds contain the same cation, the difference is likely due to the weaker hydridic H^- of $\text{B}_3\text{H}_8\cdot$ compared to that of $\text{BH}_4\cdot$. This is consistent with the findings that for boron hydrides the higher number of boron atoms in the structure, the less hydridic the hydrogen is.¹⁹

$\text{NH}_4\text{B}_3\text{H}_8$ has a high hydrogen content, 20.5 wt %. Unfortunately, thermal decomposition analysis shows that this compound gives off 10 wt % hydrogen below 160°C , but with appreciable amounts of diborane, pentaborane and borazine (Supporting Information). DSC and TGA results collectively indicate that melting and decomposition take place simultaneously at 120°C , with a substantial weight loss at this temperature. The presence of the boranes results in a $\sim 70\%$ final weight loss. It has been reported that NH_3BH_3 gives off the first equivalent H_2 below 120°C and further releases hydrogen at higher temperature but with a small fraction of borazine.²⁰ Compared with NH_3BH_3 , $\text{NH}_4\text{B}_3\text{H}_8$ produces less hydrogen and more undesired volatile compounds below 160°C . Thus, $\text{NH}_4\text{B}_3\text{H}_8$ is probably not a suitable candidate for hydrogen storage through thermal decomposition.

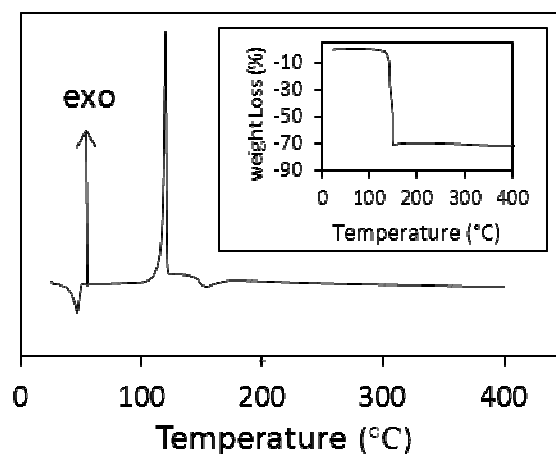


Figure 4. DSC and TGA curves of $\text{NH}_4\text{B}_3\text{H}_8$ ($5^\circ\text{C}/\text{min}$).

Hydrolytic studies, however, have demonstrated that $\text{NH}_4\text{B}_3\text{H}_8$ has advantages over NaBH_4 ² and NH_3BH_3 ,^{4c,d} the most studied chemical hydrides for hydrogen storage via hydrolysis. At room temperature, $\text{NH}_4\text{B}_3\text{H}_8$ is more soluble in water (> 45 wt % through visual observation) than NH_3BH_3 (26 wt %²¹) and NaBH_4 (35 wt %²²). The lower solubility significantly limits the theoretical hydrogen density of the respective system to 5.1 wt % for NH_3BH_3 and 7.5 wt % for NaBH_4 . Quantitative measurements of H_2 released via hydrolysis using a Toepler pump and gas buret showed that upon adding catalysts, 1 mmol $\text{NH}_4\text{B}_3\text{H}_8$ releases a near theoretical value of 8.80 mmol H_2 . Based on eq 2, therefore, this system has a high theoretical hydrogen weight density [wt % = $\text{H}_2 / (\text{NH}_4\text{B}_3\text{H}_8 + \text{H}_2\text{O})$] of 10.8 wt %.

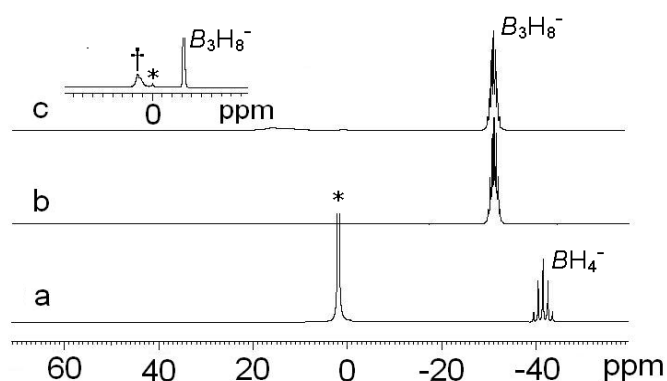
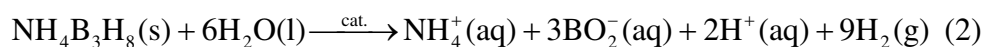


Figure 5. ^{11}B NMR spectra of 2 M aqueous solutions taken after a: 1 day for NaBH_4 ; b and c: 1 day and 7 days for $\text{NH}_4\text{B}_3\text{H}_8$. Inset is an expanded spectrum of c. *, $\text{B}_5\text{O}_6(\text{OH})_4^-$ □; †, $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$.

In addition, unlike NaBH_4 , which is stable only in strong alkaline solutions,² an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution is reasonably stable as shown by ^{11}B NMR studies (Figure 5). At 28 °C, for the same molar

concentration, i.e., 2 M, ^{11}B NMR studies show that more than 50 percent of NaBH_4 decomposed over a day, while less than 10 percent of $\text{NH}_4\text{B}_3\text{H}_8$ decomposed over a week.

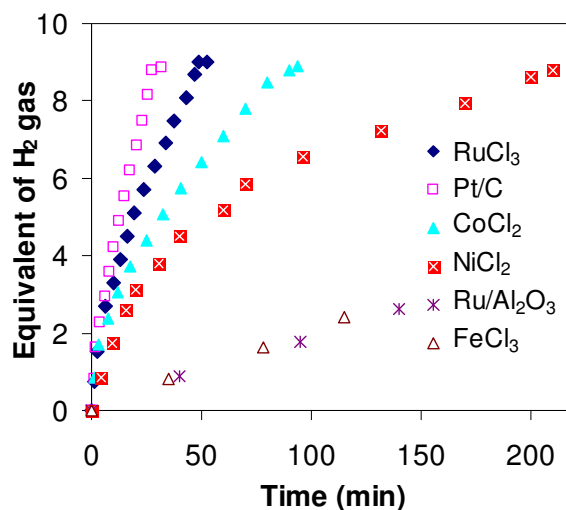


Figure 6. Hydrogen evolution at room temperature from an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution (molar ratio of $\text{NH}_4\text{B}_3\text{H}_8:\text{H}_2\text{O}$ being 1:18) containing 10 wt % Pt/C (1 mol % Pt); 5 wt % Ru/Al₂O₃ (1 mol % Ru), RuCl₃ (1 mol % Ru), CoCl₂ (4 mol % Co), NiCl₂ (4 mol % Ni) and FeCl₃ (4 mol % Fe). Molar ratios are referenced to $\text{NH}_4\text{B}_3\text{H}_8$.

Hydrolytic studies have shown that upon adding catalysts $\text{NH}_4\text{B}_3\text{H}_8$ rapidly releases pure H_2 (Figure 6). For an aqueous solution with a 1:18 molar ratio of $\text{NH}_4\text{B}_3\text{H}_8$ to H_2O , which represents a material density of 4.6 wt % H, the commercially available 10 wt % Pt/C catalyst (1 mol % Pt) shows the best catalytic activity, with complete hydrolysis in less than 30 min. RuCl₃ also displayed excellent catalytic activity, and this is likely associated with the in-situ formation of Ru (0) as indicated by the formation of a black powder, which was also observed during hydrolysis of both NaBH_4^2 and $\text{NH}_3\text{BH}_3^{4c}$. However, 5 wt % Ru/Al₂O₃ (1 mol % Ru) is much less active. The difference is probably associated with the degree of the dispersed catalytic sites. Lower-cost transition metal catalysts were also explored in our study and fairly good catalytic activity was observed for CoCl₂. With 4 mol % loading of CoCl₂, full hydrolysis was complete in about 100 min. A black powder appeared instantly when CoCl₂ was brought into contact with an aqueous $\text{NH}_4\text{B}_3\text{H}_8$ solution, suggesting the formation of cobalt boride (Supporting information)

as found during the hydrolysis of NaBH_4 . NiCl_2 is less effective and the full hydrolysis required ~200 min.

The “ BO_2^- ” product shown in eq 2 is only a hypothetical formulation, with the actual borate products of these reactions depending upon the final solution concentration and pH.^{3a} The ^{11}B NMR spectrum (Figure 7) of the catalyzed hydrolysis solution of $\text{NH}_4\text{B}_3\text{H}_8$ and H_2O (1: 18 ratio) reveals one broad peak centered at 16 ppm which is likely associated with $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$, along with another sharp peak situated at around 0 ppm that is also due to $\text{B}_5\text{O}_6(\text{OH})_4^-$.²³ Similar products were also formed during the hydrolysis of $\text{NH}_3\text{B}_3\text{H}_7$.^{3a}

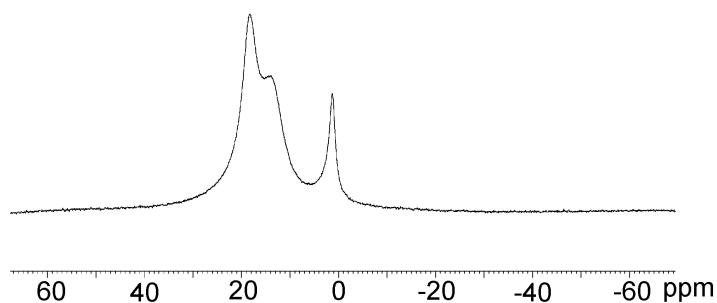


Figure 7. ^{11}B NMR spectrum of the catalyzed hydrolysis solution ($\text{NH}_4\text{B}_3\text{H}_8$: H_2O being 1: 18).

When an aqueous solution with 1:10 molar ratio of $\text{NH}_4\text{B}_3\text{H}_8$ to H_2O was subject to hydrolysis catalyzed by 4 mol % of CoCl_2 , full hydrolysis was achieved in ~200 min, which corresponds to a production of 7.5 wt % H_2 . US DOE recently modified vehicular hydrogen storage targets to 4.5 wt % by 2010, 5.5 wt % by 2015 and 7.5 wt % for the ultimate.²⁴ $\text{NH}_4\text{B}_3\text{H}_8$ thus could be a potential candidate to meet the 2010 target.

Calculations of the standard heat of hydrolysis from the standard enthalpies of formation indicate that H_2 release from $\text{NH}_4\text{B}_3\text{H}_8$ is much less exothermic (5.43 kcal/mol H_2 , Supporting information) than from either NaBH_4 (14.9 kcal/mol H_2), NH_3BH_3 (12.7 kcal/mol H_2), or $\text{NH}_3\text{B}_3\text{H}_7$ (18.9 kcal/mol H_2)^{3a}. The less exothermic nature favors $\text{NH}_4\text{B}_3\text{H}_8$ over the other candidates from the standpoint of heat management and system design.

As in the cases of NaBH_4 , NH_3BH_3 and $\text{NH}_3\text{B}_3\text{H}_7$, the formation of borates may affect the performance of the catalysts if the borate precipitates cover the active sites. It should be noted that the removal and transportability of the borates depend on the starting materials and reaction conditions,²⁵ and thus can be improved accordingly. Regeneration of these compounds from the borates has been challenging, but progress has been made in the regeneration of spent fuel back into NH_3BH_3 .²⁶ The final utility of $\text{NH}_4\text{B}_3\text{H}_8$ as a chemical hydrogen storage material will also hinge on the development of an efficient “off-board” regeneration of $\text{NH}_4\text{B}_3\text{H}_8$.

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Supporting Information Available: Structural information, calculation of the heat of the hydrolysis, mass spectra of gas from hydrolysis and thermal decomposition. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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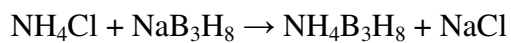
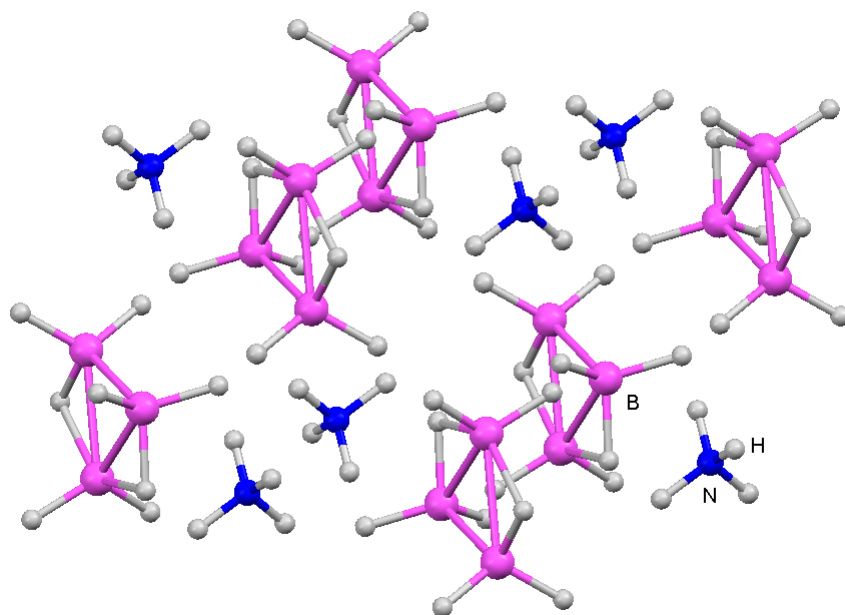
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A metathesis reaction between unsolvated NaB_3H_8 and NH_4Cl provides a simple and high-yield synthesis of $\text{NH}_4\text{B}_3\text{H}_8$. Structure determination through X-ray single crystal diffraction analysis reveals weak $\text{N}-\text{H}^+ \cdots \text{H}^- - \text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8$ and strong $\text{N}-\text{H}^+ \cdots \text{H}^- - \text{B}$ interaction in $\text{NH}_4\text{B}_3\text{H}_8 \cdot 18\text{-crown-}6 \cdot \text{THF}$ adduct. Pyrolysis of $\text{NH}_4\text{B}_3\text{H}_8$ leads to the formation of hydrogen gas with appreciable amounts of other volatile boranes below 160 °C. Hydrolysis experiments show that upon addition of catalysts, $\text{NH}_4\text{B}_3\text{H}_8$ releases up to 7.5 materials wt % hydrogen.