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Weidong Chen
Chinese Academy Of Sciences

Guotao Wu
Chinese Academy Of Sciences

Teng He
Chinese Academy Of Sciences

Zhao Li
Chinese Academy Of Sciences

Zaiping Guo
University of Wollongong, zguo@uow.edu.au

See next page for additional authors

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Abstract

Octahydrotriborates are potential hydrogen storage materials and chemical vapor deposition precursors to boride films. Their syntheses have been quite challenging, however. In this paper, an improved facile route for the preparation of unsolvated sodium octahydrotriborate (NaB₃H₈), which is an important precursor to other octahydrotriborates and derivatives, is reported. The key steps in the synthesis involve dispersing Na finely in inert media and preparing fresh tetrahydrofuran (THF)·BH₃ at room temperature. High purity unsolvated NaB₃H₈ can be obtained in tens of grams or more in one batch, depending on the reactor size. Using NaB₃H₈ as the precursor, sodium dodecaborate (Na₂B₁₂H₁₂) has been successfully synthesized. Both octahydrotriborates and dodecaborates have been observed as intermediates during the thermal dehydrogenation of borohydrides, and their facile syntheses would facilitate mechanistic studies on the hydrogen storage of borohydrides, among other potential applications.

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Authors

Weidong Chen, Guotao Wu, Teng He, Zhao Li, Zaiping Guo, Hua-Kun Liu, Zhenguo Huang, and Ping Chen

An improved synthesis of unsolvated NaB_3H_8 and its application in preparing $\text{Na}_2\text{B}_{12}\text{H}_{12}$

Weidong Chen^{ab}, Guotao Wu^a, Teng He^a, Zhao Li^{ab}, Zaiping Guo^c, Huakun Liu^c, Zhenguo Huang^{c*}, and Ping Chen^{a*}

^a Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023 (China). E-mail: pchen@dicp.ac.cn

^b University of the Chinese Academy of Sciences, Beijing 100039 (China)

^c Institute for Superconducting and Electronic Materials, University of Wollongong, Squires Way, North Wollongong, New South Wales 2522 (Australia). E-mail: zhenguo@uow.edu.au

Abstract

Octahydrotriborates are potential hydrogen storage materials and chemical vapor deposition precursors to boride films. Their syntheses have been quite challenging, however. In this paper, an improved facile route for the preparation of unsolvated sodium octahydrotriborate (NaB_3H_8), which is an important precursor to other octahydrotriborates and derivatives, is reported. The key steps in the synthesis involve dispersing Na finely in inert media and preparing fresh tetrahydrofuran (THF)· BH_3 at room temperature. High purity unsolvated NaB_3H_8 can be obtained in tens of grams or more in one batch, depending on the reactor size. Using NaB_3H_8 as the precursor, sodium dodecaborate ($\text{Na}_2\text{B}_{12}\text{H}_{12}$) has been successfully synthesized. Both octahydrotriborates and dodecaborates have been observed as intermediates during the thermal dehydrogenation of borohydrides, and their facile syntheses would facilitate mechanistic studies on the hydrogen storage of borohydrides, among other potential applications.

Introduction

Various compounds with high hydrogen content have recently attracted intense attention for hydrogen storage.[1-5] Metal octahydrotriborates ($\text{M}(\text{B}_3\text{H}_8)_n$), sometimes known as metal triboranes, have therefore aroused attention.[6-8] $\text{Mg}(\text{B}_3\text{H}_8)_2$, an intermediate during the thermal decomposition of $\text{Mg}(\text{BH}_4)_2$, has shown a cycling capacity of 2.5 wt %.[8] They have been observed during the thermal decomposition of borohydrides.[9, 10] Metal dodecaborates ($\text{M}(\text{B}_{12}\text{H}_{12})_m$) have also been observed as intermediates among others during the thermal decomposition of borohydrides.[8, 11] Their high thermal stability makes complete dehydrogenation of borohydrides difficult, so it may be desirable to change the reaction pathway to avoid their formation. The availability of metal octahydrotriborates and metal dodecaborates is important for in-depth investigations of the borohydrides' hydrogen storage mechanism.[11, 12]

Both metal octahydrotriborates and metal dodecaborates could be used in other fields. For instance, metal octahydrotriborates have been studied as chemical vapor deposition (CVD) precursors for metal boride thin films.[13, 14] NaB_3H_8 is a potential anodic fuel for direct liquid fuel cell.[15] Owing to its good solubility in ethyl ether, NaB_3H_8 can be used as a precursor for the further synthesis of other octahydrotriborates.[13, 16] $\text{Na}_2\text{B}_{12}\text{H}_{12}$ has recently attracted great interest as solid electrolyte for solid battery applications due to its outstanding ionic conductivity.[17-19] A dual-cation dodecaborate, $\text{LiNaB}_{12}\text{H}_{12}$, possesses ion conductivity approximately 8 and 11 times higher than $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Li}_2\text{B}_{12}\text{H}_{12}$, respectively.[20] Additionally, dodecaborates have long

been studied as effective drug delivery vehicles for neutron capture therapy, which is one of the minimally invasive cancer therapies.[21, 22]

Unsolvated NaB_3H_8 was first synthesized from the direct reaction between B_2H_6 and Na[23-25] or Na/Hg amalgam,[26, 27] but the high toxicity and high flammability of B_2H_6 make these methods hard to repeat. Reacting sodium borohydride with oxidation reagents such as I_2 , metal halides or dichloromethane, can also yield NaB_3H_8 but with a small amount of impurities.[28-30] Furthermore, in most cases, it is hard to remove the solvents due to the strong coordination between the solvents and the Na^+ ions.[9, 28, 30-35] Sodium borohydride or sodium hydride would react with B_4H_{10} leading to NaB_3H_8 . [36] B_4H_{10} , however, is highly toxic and unstable, and not commercially available. Based upon an early report on the reactions between alkali metal and $\text{THF}\cdot\text{BH}_3$, solvent-free NaB_3H_8 was recently obtained by the reacting Na/Hg amalgam with tetrahydrofuran ($\text{THF}\cdot\text{BH}_3$). [37] Subsequently, an innovative modification was made to replace Na/Hg amalgam with Na dispersed on silica gel through heating.[38] These demonstrate that a good dispersion of Na is the key to improve the synthesis.

$\text{Na}_2\text{B}_{12}\text{H}_{12}$ is commercially available but with a very high price. $\text{MgB}_{12}\text{H}_{12}$ can be directly synthesized via a gas-solid reaction between $\text{Mg}(\text{BH}_4)_2$ and B_2H_6 . [39] $\text{MgB}_{12}\text{H}_{12}$ is also known to form during the dehydrogenation of $\text{Mg}(\text{B}_3\text{H}_8)_2$, but only as a small fraction of the products and never in an isolated form.[8, 11] One pot synthesis of metal $\text{B}_{12}\text{H}_{12}^{2-}$ from metal borohydrides and alkyl or aryl halides were reported but further purification process were needed to obtain pure and unsolvated metal $\text{B}_{12}\text{H}_{12}^{2-}$ salts.[40] Solid-state reaction between metal borohydrides and $\text{B}_{10}\text{H}_{14}$ leads to solvent-free metal $\text{B}_{12}\text{H}_{12}$. [12, 41], but $\text{B}_{10}\text{H}_{14}$ is a rarely available. Small scale $[\text{NEt}_3\text{H}]_2\text{B}_{12}\text{H}_{12}$ was prepared through the decomposition of corresponding B_3H_8 salt and further be used as precursor for preparing metal $\text{B}_{12}\text{Cl}_{12}^{2-}$ salts.[42] Therefore, a convenient and high purity synthetic method for $\text{Na}_2\text{B}_{12}\text{H}_{12}$ is worth to be investigated.

In this paper, we report an improved synthesis method for unsolvated NaB_3H_8 , which involves an improved method to disperse Na and a refined procedure to produce fresh $\text{THF}\cdot\text{BH}_3$. The procedure avoids toxic reagents such as Hg and B_2H_6 , employs simple setup, and thus facilitates large-scale production of NaB_3H_8 . Using NaB_3H_8 as the precursor, we have successfully synthesized $\text{Na}_2\text{B}_{12}\text{H}_{12}$ by isolating it from the decomposition residue of NaB_3H_8 .

Experimental

Reagents

Sodium borohydride (NaBH_4) ($\geq 97\%$), sodium fluoride (NaF) ($\geq 99.5\%$), sodium chloride (NaCl) ($\geq 99.5\%$), sodium bromide (NaBr) ($\geq 99.5\%$), sodium sulfate (Na_2SO_4) ($\geq 99.5\%$), dichloromethane (CH_2Cl_2) ($\geq 99.5\%$), and diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$) ($\geq 99.5\%$) were purchased from Kermel. NaF , NaCl , NaBr , and Na_2SO_4 were dried at $400\text{ }^\circ\text{C}$ for 4 h under flowing argon before they were used. Sodium (Na) ($\geq 99.7\%$), silicon powder (Si) (99.9%, $1\text{ }\mu\text{m}$), and cuprous chloride (CuCl) ($\geq 97\%$) were purchased from Aladdin and used as received. Bismuth fluoride (BiF_3) (99%), bismuth chloride (BiCl_3) (99.9%), chromium chloride (CrCl_3) (99%), tin chloride (SnCl_2) (99%), lead fluoride (PbF_2) (99%), and lead chloride (PbCl_2) (99%) were purchased from Alfa Aesar and used as received. Tetrahydrofuran was purchased from Merck ($\geq 99.9\%$). All the organic solvents were dried over 5 \AA molecule sieves before use. All the manipulations were carried out under argon protection to avoid air contamination.

Instruments and characterization

Solvent nuclear magnetic resonance spectroscopy (NMR) was performed on a Bruker Avance 500 MHz spectrometer equipped with a liquid detector. Solution ^{11}B NMR was externally referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$. Ball milling was performed on a Retsch planetary ball-mill (PM400) machine. Powder X-ray diffraction (XRD) characterization was performed on a PANalytical X'Pert diffractometer (Cu $K\alpha$, 40 kV, 40 mA) with a home-made sample holder that protects the samples from exposure to air. The closed system for the synthesis of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ consists of a sealed reactor coupled with a pressure detector. All the manipulations were carried out in an air-free environment.

Results and Discussions

Synthesis of unsolvated NaB_3H_8

1. Preparation of $\text{THF}\cdot\text{BH}_3$ and well-dispersed Na

Commercial $\text{THF}\cdot\text{BH}_3$ is expensive and tends to decompose over time. Additives are therefore normally introduced to stabilize the solution. $\text{THF}\cdot\text{BH}_3$ is synthesized from the reaction between boron tri-halides (BF_3 or BCl_3) and NaBH_4 , or from the oxidation of NaBH_4 by certain oxidants such as I_2 . [28, 32, 43] These methods are not cost effective and/or require special care when dealing with these highly reactive/corrosive reagents. Inspired by a previous report, [30] we have thus developed an economical and efficient way to produce fresh $\text{THF}\cdot\text{BH}_3$ without additives according to the equation shown below:



($\text{M} = \text{Bi}^{3+}$, Cr^{3+} , Sn^{2+} , Pb^{2+} , and Cu^+ , $\text{X} = \text{Halides}$)

The choice of metal halides depends on their oxidation capability, which should be neither too weak so to form metal borohydrides, nor too strong so to remove all the hydrogens on B. For example, stirring NaBH_4 (0.3 mol) and CuCl (0.36 mol, 20% excess) in THF at 40 °C for 4 h leads to high purity $\text{THF}\cdot\text{BH}_3$ (Fig. 1). Low-pressure evaporation and condensation (liquid nitrogen cold trap) were employed to isolate the product. 500 mL of 1 M $\text{THF}\cdot\text{BH}_3$ can be produced in one batch. High purity $\text{THF}\cdot\text{BH}_3$ was also obtained after reacting other halides respectively with NaBH_4 for 4 h (Fig. 1).

For the synthesis of unsolvated NaB_3H_8 , Na/Hg amalgam or Na on silica gel was used to maximize the reaction surface of Na and consequently to improve the reaction rate and final yield. [37, 38] Na on silica gel is a better way to disperse Na, since Hg is expensive and environmentally unfriendly, but the high temperature (160 °C) used could be a concern when dealing with highly reactive melted Na. Ball milling at room temperature is well known as an effective way to reduce the particle size and create highly reactive surfaces. Na is a soft material, however, and unsuitable to be ball milled alone. We found that if Na is ball milled together with a chemically inert medium (towards Na), for instance NaCl, it will be mixed homogeneously with NaCl as extremely fine particles (Fig. 2a). The inert media that we have tried include Si, NaF, NaCl, NaBr, and Na_2SO_4 . Since ball milling is simple and efficient, large amounts of Na/NaCl powder can be acquired in one batch, which will help with scaling up. In all cases, the weight ratio between Na and the dispersion medium is about 1:10 and the milling speed is 150-200 rpm.

(Caution! Freshly dispersed Na powders are highly reactive in air and may catch fire and be explosive. They must be handled under inert atmosphere.)

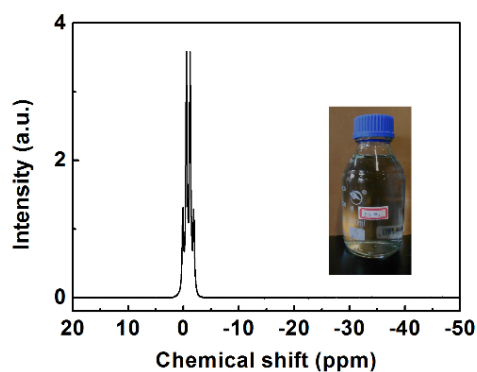


Fig. 1 A representative solution ^{11}B NMR spectrum of $\text{THF}\cdot\text{BH}_3$ prepared by reacting NaBH_4 with metal halides, including BiF_3 , BiCl_3 , CrCl_3 , SnCl_2 , PbF_2 , PbCl_2 , and CuCl . (Inset is a digital photograph of a 500 mL bottle filled with 1 M $\text{THF}\cdot\text{BH}_3$ that was synthesized in one batch.).

2. Synthesis and characterization of unsolvated NaB_3H_8

Well-dispersed fine Na/NaCl (28.5 g, 50% excess) powder (Fig. 2a) was mixed with 0.1 M fresh $\text{THF}\cdot\text{BH}_3$ (300 ml) and stirred at room temperature for 12 h. The following reaction (Eq 2) occurs according to the literature.[37, 44]



The detailed isolation procedure can be found in our previous report.[37] Briefly, filtration (to remove NaCl and other insoluble residue) and rotary evaporation (to remove THF) were carried out first. After introducing diethyl ether, filtration (to remove NaBH_4) and rotary evaporation (to remove diethyl ether) were conducted again. Upon adding dry CH_2Cl_2 to the oily products, white unsolvated NaB_3H_8 powder precipitates out. The yield was determined to be 67.3 % based on $\text{THF}\cdot\text{BH}_3$. ^{11}B NMR and ^1H NMR spectra (Fig. 2b, c) and the XRD pattern (Fig. 2d) are in good agreement with the previous reports,[37, 38] attesting to the high quality of the as-prepared NaB_3H_8 . Depending on the volume of the reactor, this process can be scaled up to obtain tens of grams or a larger quantity.

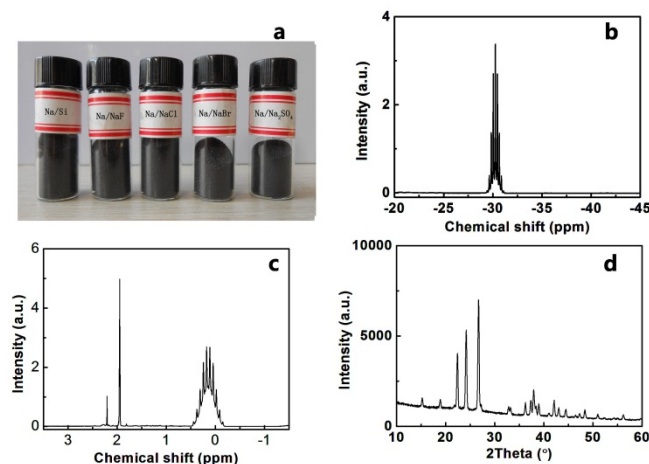


Fig. 2 (a) Digital photographs of ball-milled fine powders of Na/Si , Na/NaF , Na/NaCl , Na/NaBr , and $\text{Na}/\text{Na}_2\text{SO}_4$ (from left to right). Solution ^{11}B (b) and ^1H NMR (c) spectra of the as-prepared NaB_3H_8 in

CD₃CN. (d) Powder XRD pattern of the as-prepared NaB₃H₈. The ¹H NMR resonances at 2.2 ppm and 1.9 ppm are associated with water and CH₃CN residue, respectively.

Compared with NaBH₄ for hydrogen storage via hydrolysis, unsolvated NaB₃H₈ has higher solubility and much improved stability in water.[7] In addition, the higher Na to B ratio (1:3) in NaB₃H₈ compared with NaBH₄ (1:1) also affords highly soluble hydrolytic products. These merits have made NaB₃H₈ an interesting liquid-phase hydrogen carrier.[45] We have also found that the unsolvated form is not flammable in air.

Synthesis of Na₂B₁₂H₁₂

NaB₃H₈ (5 g) was placed in a tubular furnace with an argon flow of 10 mL/min. The temperature was elevated to 150 °C and the sample was held at this temperature for 24 h. The temperature was then raised to 500 °C, and held for 1 h. Solid samples were collected and characterized by ¹¹B NMR. The results indicate that the thermal decomposition of NaB₃H₈ at 150 °C produces NaBH₄, Na₂B₁₂H₁₂, Na₂B₁₀H₁₀, and other minor impurities (Fig. 3a). Heat treatment at 500 °C for 1 h eliminates Na₂B₁₀H₁₀. When higher temperatures were chosen, Na₂B₁₀H₁₀ will decompose completely. Lower temperatures will also eliminate Na₂B₁₀H₁₀ but with extended time (Fig. 4). Since Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂ are both soluble in diethyl ether and NaBH₄ is not, once Na₂B₁₀H₁₀ consumed, Na₂B₁₂H₁₂ can be isolated from NaBH₄ by ethyl ether. Therefore, 500 °C was chosen. Diethyl ether was employed to extract Na₂B₁₂H₁₂ from the solid products. After removing the diethyl ether, Na₂B₁₂H₁₂ was obtained as a white powder, as clearly evidenced by ¹¹B NMR (Fig. 3b).

Previously reported results showed that H₂, B₂H₆, B₆H₁₀, and B₅H₉ could be detected as the gaseous products in the heat treatment.[46] It is reported that B₂H₆ could react with BH₄⁻ to produce B₁₂H₁₂²⁻. [39, 47] We also found that the back pressure of the reacting system affects the yield of Na₂B₁₂H₁₂. In a closed system, the yield of Na₂B₁₂H₁₂ is improved (~10 %, based upon NaB₃H₈), which indicates a more efficient reaction between the volatile boranes and the solid products forming Na₂B₁₂H₁₂. Although the yield is relatively low, the starting material, NaB₃H₈, could be efficiently synthesized in a large quantity according to the method developed above. Therefore, this method could be a facile way to prepare Na₂B₁₂H₁₂ for laboratory usage. Further optimizations are still necessary to increase the yield. This would include the adjustment of the back pressure using high-pressure system and introduction of extra boranes (B₂H₆, B₆H₁₀, and B₅H₉).

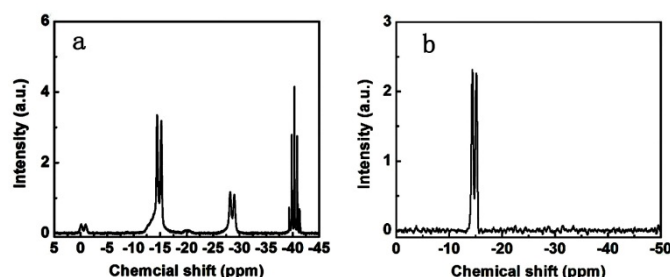


Fig. 3 Solution ¹¹B NMR spectra of a) the thermal decomposition products of NaB₃H₈ at 150 °C dissolved in CH₃CN, and b) the isolated Na₂B₁₂H₁₂ in CH₃CN.

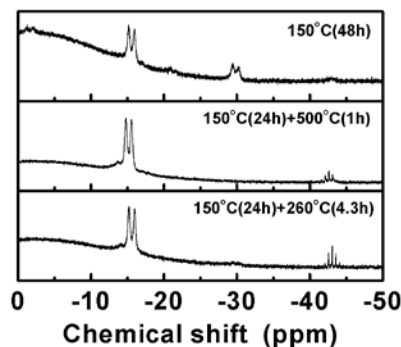


Fig. 4 Solution ^{11}B NMR spectra of the thermal decomposition products of NaB_3H_8 (in THF).

Conclusion

In this paper we report a scalable synthetic method for unsolvated NaB_3H_8 , which is based upon the reaction between well-dispersed Na in a chemically inert medium (towards Na) and freshly prepared $\text{THF}\cdot\text{BH}_3$. Additionally, no highly toxic reagents were employed in this procedure. Unsolvated NaB_3H_8 has been the key precursor to many other octahydrotriborates.[13, 16, 48-50] Its improved synthesis would enable the preparation of new octahydrotriborates. Benefiting from the facile synthesis of unsolvated NaB_3H_8 , a simple method to obtain $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was developed. $\text{Na}_2\text{B}_{12}\text{H}_{12}$ can be used to prepare other dodecaborates, which could contribute to further studies in relevant fields.

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An improved synthesis of unsolvated NaB_3H_8 and its applications in preparing $\text{Na}_2\text{B}_{12}\text{H}_{12}$

Weidong Chen^{ab}, Guotao Wu^a, Teng He^a, Zhao Li^{ab}, Zaiping Guo^c, Huakun Liu^c, Zhenguo Huang^{c*}, and Ping Chen^{a*}

^a Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023 (China). E-mail: pchen@dicp.ac.cn

^b University of the Chinese Academy of Sciences, Beijing 100039 (China)

^c Institute for Superconducting and Electronic Materials, University of Wollongong, Squires Way, North Wollongong, New South Wales 2522 (Australia). E-mail: zhenguo@uow.edu.au

High purity unsolvated NaB_3H_8 can be obtained in tens of grams or more in one batch by reactions between well dispersed Na and freshly prepared $\text{THF}\cdot\text{BH}_3$ at room temperature. Benefit from the large quantity of NaB_3H_8 , sodium dodecaborates ($\text{Na}_2\text{B}_{12}\text{H}_{12}$) has been successfully prepared by directly heat treatment of NaB_3H_8 . No high toxic reagent is involved in the whole process.

