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An alternative approach to the synthesis of NaB_3H_8 and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ for solid electrolyte applications

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Abstract

Alkaline or alkaline earth octahydrotriborate $\text{M}(\text{B}_3\text{H}_8)_x$ and dodecahydro-*closo*-dodecaborate $\text{M}_x\text{B}_{12}\text{H}_{12}$ ($\text{M} = \text{Li}, \text{Na}, \text{Mg}$ or Ca with $x = 1$ or 2) have recently attracted a lot of interest for hydrogen storage and solid electrolyte applications. Nevertheless, their syntheses are still a roadblock for large scale applications. In this paper we propose a novel approach for their syntheses starting from the cheapest borohydride NaBH_4 . The process involves first the solvothermal synthesis of tetrabutylammonium octahydrotriborate $(\text{C}_4\text{H}_9)_4\text{NB}_3\text{H}_8$ (TBAB $_3\text{H}_8$) being the basis for the syntheses of the others boranes. Starting from TBAB $_3\text{H}_8$, we have synthesized pure and unsolvated NaB_3H_8 by salt metathesis reaction with sodium tetraphenylborate. Then, we have successfully obtained $\text{Na}_2\text{B}_{12}\text{H}_{12}$ by solvothermal decomposition of NaB_3H_8 . This approach has shown to be quantitative and reproducible, which could lead to the development of these boranes in real life applications.

Keywords

Octahydrotriborate, dodecaborate, solid electrolyte, hydrogen storage.

Introduction

Boron-hydrogen based materials have attracted a lot of interest since their discovery a hundred years ago. In the late 1990s, alkaline and alkaline earth borohydrides have been proposed as solid-state hydrogen storage materials due to their stability and high gravimetric hydrogen content [1-3] leading to a wealth of experimental and theoretical studies [4, 5]. To date, it appears that there remain important issues concerning reversibility and acceptable kinetics for efficient hydrogen storage applications. However, it was recently demonstrated that the system $\text{Mg}(\text{B}_3\text{H}_8)_2\text{-MgH}_2$ can be fully rehydrogenated to form $\text{Mg}(\text{BH}_4)_2$ under moderate conditions [6, 7]. Lately, a new possible application of boron-hydrogen based compounds has emerged as ionic conductor. For instance, sodium [8], lithium and mixed salt sodium lithium dodecahydro-*closo*-dodecaborate [9] have shown superionic conductivity for the HT-phase, above $10^{-1} \text{ S.cm}^{-1}$. Moreover, NaB_3H_8 was also proposed as liquid anodic fuel [10] or hydrogen storage material through hydrolysis [11]. Consequently, octahydrotriborate (for hydrogen storage and liquid anodic fuel) and dodecahydro-*closo*-dodecaborate (for solid state ionic conduction) salts are also worthy to be studied in depth.

In view of future applications, it is desirable to develop new synthetic approaches to compounds with B_3H_8^- or $\text{B}_x\text{H}_x^{2-}$ ions avoiding the use of dangerous (toxic, flammable etc) chemicals such as Na/Hg, B_2H_6 etc. which have been reported previously [12-17]. Further, in order to keep the price of the final product as low as possible, it is necessary to start with the cheapest borohydride available, i.e. NaBH_4 .

In this paper, we propose an alternative method to prepare NaB_3H_8 by the use of a simple and fast cation exchange, involving sodium tetraphenylborate (NaBPh_4) and TBAB $_3\text{H}_8$. The latter was synthesized using mechano-chemical and solvothermal techniques. One of the interests to start with

TBAB₃H₈ as precursor for Na₂B₁₂H₁₂ synthesis is its high stability in ambient conditions. Finally, we show that the thermal decomposition of NaB₃H₈ or mixture of TBAB₃H₈ and NaBH₄ in diglyme leads to the formation of Na₂B₁₂H₁₂ among other boranes.

Background on existing synthesis

Table 1 provides a non-exhaustive list of procedures found in the literature to synthesize NaB₃H₈. It can be seen from this table that, for most of the syntheses, unfriendly, toxic, unstable, not readily available and expensive chemicals were used (Na/Hg, B₂H₆, BH₃, B₄H₁₀ and BF₃O(C₂H₅)₂), which hinder any large scale applications. Other methods were developed by using oxidizing agents as CuCl for instance. Nevertheless, Pylypko *et al.* reported the systematic failure of the procedure [10]. Iodine was also used, but the presence of I⁻ in solution make the isolation of pure B₃H₈⁻ complicated [15]. Weidong *et al.* used Na/NaCl fine powder for their synthesis which can be highly flammable [18]. It can also be seen from the table that for each synthesis involving BH₃, disproportion into NaB₃H₈ and NaBH₄ is observed which lowers the conversion to NaB₃H₈.

Table 1. Non exhaustive list of published NaB₃H₈ synthesis

Reactants	Solvent	Reaction	Ref
Na, B ₂ H ₆	Et ₂ O	2Na/Hg + 2B ₂ H ₆ → NaBH ₄ + NaB ₃ H ₈	[11]
Na, BH ₃	THF	2Na/Hg + 4BH ₃ -THF → NaBH ₄ + NaB ₃ H ₈	[17]
Na, B ₄ H ₁₀	Et ₂ O	2Na/Hg + 2B ₄ H ₁₀ → NaB ₃ H ₈ + 1/2B ₂ H ₆ + (BH) _x	[14]
NaH, B ₄ H ₁₀	Et ₂ O	B ₄ H ₁₀ + NaH → NaB ₃ H ₈ + 1/2B ₂ H ₆	[12]
NaBH ₄ , B ₄ H ₁₀	Et ₂ O	B ₄ H ₁₀ + NaBH ₄ → NaB ₃ H ₈ + B ₂ H ₆	[12]
NaBH ₄ , I ₂	Diglyme	3NaBH ₄ + I ₂ → 2NaI + 2H ₂ + NaB ₃ H ₈	[15]
NaBH ₄ , BF ₃ O(C ₂ H ₅) ₂	Diglyme	3NaBH ₄ + 4BF ₃ O(C ₂ H ₅) ₂ → 3NaBF ₄ + 2NaB ₃ H ₈ + 2H ₂ + 4(C ₂ H ₅) ₂ O	[16]
NaBH ₄ , CuCl	Diglyme	3NaBH ₄ + 2CuCl → NaB ₃ H ₈ + 2Cu + 2NaCl	[19]
NaBH ₄ , TBABr, CH ₂ Cl ₂	DCM	3NaBH ₄ + TBABr + 2CH ₂ Cl ₂ → TBAB ₃ H ₈ + 2CH ₃ Cl + 2NaCl + NaBr + H ₂	[20]
Na/NaCl, NaBH ₄ , CuCl	THF	NaBH ₄ + CuCl → BH ₃ -THF + NaCl + Cu BH ₃ -THF + Na/NaCl → NaB ₃ H ₈ + NaBH ₄	[18]

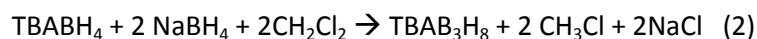
Recently, Hansen *et al.* [21] summarized the different synthetic routes to prepare Na₂B₁₂H₁₂, most of which involve B₂H₆, or B₁₀H₁₄ which are again toxic and overpriced [22, 23]. Another route has been proposed using the thermal decomposition of NaB₃H₈ in diglyme leading to the disproportion of NaB₃H₈ into Na₂B₁₂H₁₂ and NaBH₄ [24]. Furthermore, direct thermal decomposition of NaB₃H₈ in a tubular furnace at 500°C was also reported [18]. However the yield for this reaction is fairly low, about 10%.

Results and discussion

a. Preparation of TBAB₃H₈

The goal of this work was to synthesize Na₂B₁₂H₁₂ starting from NaBH₄. Our strategy was to first synthesize B₃H₈⁻ anion in a reproducible, safe, scalable and cheap way and then use it as a building block to get Na₂B₁₂H₁₂. To reach this purpose, we first tried to reproduce the synthesis proposed by Bürcner *et al.* [20]. The synthesis involves two steps, first a salt metathesis between TBABr and NaBH₄ in dichloromethane (DCM) (Equation 1), and second a reduction of DCM by NaBH₄ (Equation 2). They used ultrasonic bath to improve NaBH₄ solubilization in DCM. Nevertheless with our ultrasonic bath we were never able to obtain TBAB₃H₈. This led us to divide the synthesis in two independent parts, first the salt metathesis and second the reduction of DCM by BH₄⁻.





For the salt metathesis (Equation 1), a mechano-chemical synthesis was used (see SI for details). A quantitative conversion was achieved within 1h. **Fig. 1** shows a comparison of infrared spectra of both precursors (NaBH_4 and TBABr) with the final product TBABH_4 . The changes of the B-H stretching modes (around 2300 cm^{-1}) confirm that NaBH_4 has reacted and that the borohydride ion is in a different environment [25]. The different peak intensities around 2300 cm^{-1} are the result of Fermi resonances (interactions of the only IR active stretching mode with combination or sum bands of the deformation modes of the BH_4^- ion). These Fermi resonances have been quantitatively analyzed previously by P. Carbonnière and H. Hagemann [26 a ajouter].

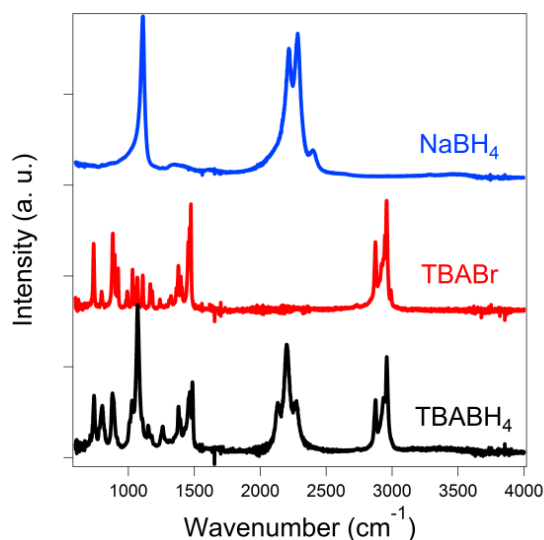


Fig. 1 – Comparison of room temperature ATR-FTIR spectra of NaBH_4 , TBABr and TBABH_4 .

For step (2), a solvothermal technique was used, using a homemade autoclave (**Fig. S1**), in order to:

- i) perform safely the synthesis in a closed and robust system;
- ii) keep all gaseous active species which could be formed inside the reactor (B_2H_6 for instance), hence also to increase the yield if such species are formed;
- iii) and increase the boiling point of DCM hence increase NaBH_4 solubility.

We found that a temperature of 80°C with a reaction time of 16h were optimal for TBAB_3H_8 synthesis. This procedure was found to be highly reproducible with almost quantitative conversion (>80%) (see SI for details).

To gain insight into the reaction mechanism of the formation TBAB_3H_8 , ex-situ sampling of the liquid phase at different reaction time (12, 24, 30, 36 and 48 hours) were performed, for this particular experiment, a reaction temperature of 60°C was chosen in order to slow down the reaction and identify the intermediates. Samples were then analyzed by ^{11}B NMR (**Fig. 2**).

The ex-situ measurements show the complete conversion of BH_4^- ($\delta = -38.8\text{ppm}$, $J_{\text{B-H}} = 82 \text{ Hertz}$) into B_3H_8^- ($\delta = -30\text{ppm}$, $J_{\text{B-H}} = 33.2 \text{ Hertz}$) by increasing the reaction time. Nevertheless, several intermediate compounds are formed. The quartet at -11.4 ppm , was attributed to a BH_3 adduct due to its multiplicity. Another signal centered at -20.5 ppm was recorded, however, by increasing the resolution and using proton decoupled ^{11}B NMR, it can be seen that this signal is a combination of 3 signals at: -19.6 , -21.5 and -22.3 ppm (**Fig. S2**). The proton coupled ^{11}B NMR spectra (**Fig. S2**) reveals

that the signal at -19.6 ppm is a quartet which we assigned to another BH_3 adduct. The other two signals at -21.5 and -22.3 ppm are too much overlapping to establish their multiplicity.

Bürchner *et al.* [20] reported the formation of $[\text{Cl-BH}_3]^-$ (quartet at -15.2 ppm) and B_2H_7^- (quartet of doublet at -25.4 ppm) during the synthesis of B_3H_8^- . In our conditions, we found two quartets, then we propose also the formation of tributylamine borane (TBA-BH_3) by losing one butyl chain into butane. To support our assumption we performed ^{11}B NMR on commercial triethylamine borane in the same conditions and we found a quartet at -12.6 ppm which is close to our signal at -11.4 ppm. Hence we suggest, in our conditions, the following attribution: the quartet at -19.6 ppm is due to $[\text{Cl-BH}_3]^-$, the second quartet at -11.4 ppm to TBA-BH_3 and the last two signals at -21.5 and -22.3 ppm correspond to B_2H_7^- formation (bridging and terminal hydrogen).

With these results, we propose the following mechanism. First, TBABH_4 attacks CH_2Cl_2 to form TBA-BH_3 , $\text{TBA}[\text{Cl-BH}_3]$ and CH_3Cl . Then, the anions Cl^- in solution must combine readily with some Na^+ ions from NaBH_4 and precipitate. This precipitation allows to solubilize progressively more of NaBH_4 . Then, the BH_4^- released from the precipitation of NaCl can combine with TBA-BH_3 and/or $\text{TBA}[\text{Cl-BH}_3]$ to form TBAB_2H_7 which reacts with another BH_4^- to form TBAB_3H_8 releasing hydrogen and another Na^+ in solution which must precipitate with Cl^- . Consequently, the releasing of Na^+ and Cl^- in solution followed by their precipitation drive the reaction to the formation of TBAB_3H_8 . The rate limiting step is the solubilization of NaBH_4 in DCM. Our method allows to increase the solubility of NaBH_4 in DCM and speed up the reaction.

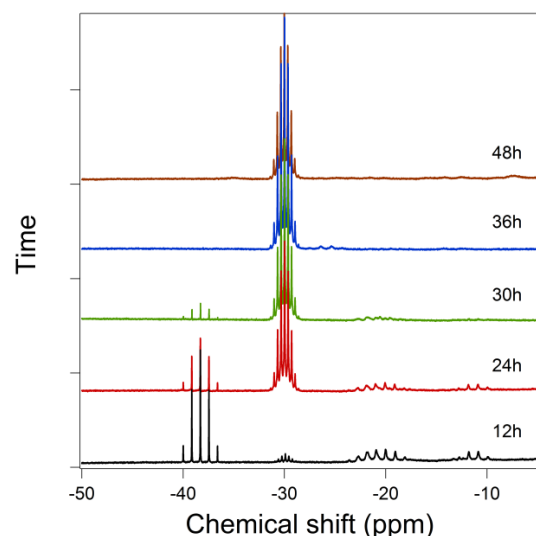


Fig. 2 – ^{11}B NMR of reaction mixtures $\text{TBABH}_4 + 2\text{NaBH}_4$ at 60°C after different reaction times.

b. Formation of NaB_3H_8

It is known from the literature that tetraphenylborate anion in sodium tetraphenylborate (NaBPh_4) precipitates with any kind of ammonium cation in aqueous or alcoholic solution leading to the formation of tetrabutylammonium tetraphenylborate [27]. Hence NaBPh_4 was used to perform the cation exchange (Equation 3). This procedure was found to be quantitative, reproducible and fast leading to unsolvated NaB_3H_8 (**Fig. 3**). The IR spectra of our products NaB_3H_8 and TBAB_3H_8 agree with the literature [10, 20].



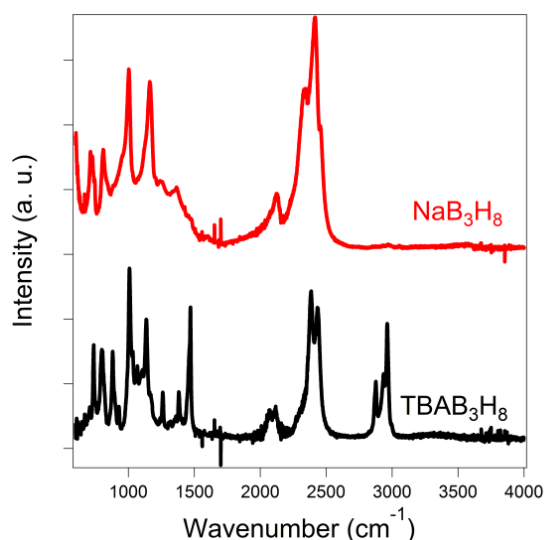


Fig. 3 – IR spectra of solid NaB_3H_8 and TBAB_3H_8 .

c. Synthesis of $\text{Na}_2\text{B}_{12}\text{H}_{12}$

At first, we attempted to prepare $\text{TBA}_2\text{B}_{12}\text{H}_{12}$ from a mixture of TBAB_3H_8 and NaBH_4 (1:3 molar ratio) in diglyme using the solvothermal technique. At the end of the reaction the solid residue was filtered out. The liquid phase was analyzed by ^{11}B NMR (**Fig. S3**). The proton decoupled ^{11}B NMR spectra shows the presence of 5 signals, the 3 main signals are assigned to: tributylamine borane (TBA-BH_3) at -11.7 ppm, $\text{B}_{12}\text{H}_{12}$ at -15.4 ppm and unreacted TBAB_3H_8 at -30 ppm. The two minor signals at -17.1 and -29.3 ppm could be due to $\text{B}_{11}\text{H}_{11}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ respectively [28-30]. The solid was allowed to self-precipitate in diglyme and analyzed ^{11}B (**Fig. S4**) and ^1H NMR (**Fig. S5**) revealing the presence of pure $\text{B}_{12}\text{H}_{12}^{2-}$. Moreover, **Fig. S5** only shows the presence of diglyme, but no tetrabutylammonium, consequently, the solid is $\text{Na}_2\text{B}_{12}\text{H}_{12}$ complexed with diglyme. Thus this route does not allow the formation of $\text{TBA}_2\text{B}_{12}\text{H}_{12}$. Our results suggest a complex mechanism involving first a metathesis between TBAB_3H_8 and NaBH_4 to give NaB_3H_8 and TBABH_4 , then the decomposition of NaB_3H_8 into $\text{Na}_2\text{B}_{12}\text{H}_{12}$ by dehydrocoupling. The lower solubility of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ in diglyme compare to the other boranes eases its separation.

The second route for $\text{Na}_2\text{B}_{12}\text{H}_{12}$ synthesis is similar, however, NaB_3H_8 was used as starting material. The solid residue was filtered off and the liquid analyzed by ^{11}B NMR (**Fig. S6**). The spectrum, display 3 signals at -15.4, -17.1 and -29.3 ppm corresponding to $\text{Na}_2\text{B}_{12}\text{H}_{12}$, $\text{Na}_2\text{B}_{11}\text{H}_{11}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$ respectively. After self-precipitation of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ at room temperature, the solid was separated and dried, the ^{11}B NMR spectrum reveals pure $\text{Na}_2\text{B}_{12}\text{H}_{12}$ but IR spectra shows the presence of diglyme which is coordinated to the sodium (**Fig. S7**). This route provides an efficient way to obtain in a fairly good yield solvated sodium dodecahydro-*closo*-dodecaborate. The yield cannot be calculated accurately due to the presence of an unknown number of diglyme molecules per formula unit.

Conclusion

In this work we have shown that TBAB_3H_8 , NaB_3H_8 and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ can be obtained in a quantitative, safe and reproducible way. The use of mechano-chemistry combined with solvothermal synthesis have proved to be efficient approach to obtain this boranes. For all three synthesis the boron containing precursor was the cheapest borohydride on the market which makes this process attractive. Furthermore, the strategy of converting NaBH_4 into TBAB_3H_8 in order to synthesize higher borane was shown to be interesting, due to the stability of TBAB_3H_8 in ambient conditions without requiring special handling procedures. This precursor could also be used to synthesize other alkaline

or alkaline earth octahydrotriborate or dodecahydro-*closo*-dodecaborate compounds. Work in this direction is under way in our laboratory.

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