

A Simple and Efficient Way to Synthesize Unsolvated Sodium Octahydrotriborate

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A simple and efficient way to synthesize unsolvated sodium octahydrotriborate has been developed. This method avoids the use of dangerous starting materials and significantly simplifies the reaction setup, thus enabling convenient large-scale synthesis. The structure of the unsolvated compound has been determined through powder X-ray diffraction.

The octahydrotriborate anion, $B_3H_8^-$, is of interest because of its high hydrogen content ($NH_4B_3H_8$, 20.5 wt % H) and its utility as chemical vapor deposition (CVD) precursors [$Mg(B_3H_8)_2$ and $Cr(B_3H_8)_2$]¹ and as a starting material for other inorganic species ($NH_3B_3H_7$, 17.7 wt % H, a potential hydrogen storage material). Most MB_3H_8 ($M = K, Rb, Cs$) salts are insoluble in ethyl ether and soluble in solvents such as tetrahydrofuran (THF).⁵ The introduction of such solvents can change the nature of compounds from covalent to ionic [e.g., $Mg(B_3H_8)_2$ being covalent² and $[Mg(THF)_6][B_3H_8]_2$ being ionic⁶]. As a result, these two compounds show very different properties, with $Mg(B_3H_8)_2$ being more reactive than $[Mg(THF)_6][B_3H_8]_2$.

NaB_3H_8 has certain advantages over the above-mentioned MB_3H_8 ($M = K, Rb, Cs$) salts. One of them is that NaB_3H_8 has good solubility in ethyl ether. Because ethyl ether usually has a weak coordination ability, it can be easily pumped away. The unsolvated NaB_3H_8 is also essential for the further synthesis of other octahydrotriborate compounds such as unsolvated $Mg(B_3H_8)_2$ and $Cr(B_3H_8)_2$.³ In addition, sodium is cheaper than all of the other alkali metals and thus more cost-effective for a large-scale synthesis.

Unsolvated NaB_3H_8 was conventionally synthesized by the direct reaction between diborane and sodium metal.⁷ Because of the extreme volatility of diborane, its on-site generation and consumption have recently been developed for such a synthesis.⁸ However, a high-quality airtight apparatus is mandatory for the reaction, and the disposal of residual diborane needs to be carried out properly and carefully. A relatively safe way to synthesize unsolvated NaB_3H_8 was reported, but it involves three steps and requires expensive intermediate compounds such as Bu_4NBr and $NaBPh_4$.⁹ It has been demonstrated that the synthesis of NaB_3H_8 in THF,¹⁰ glyme, and tetraglyme¹¹ only led to oily solvates, from which crystalline dioxanate $NaB_3H_8 \cdot 3C_4H_8O_2$ can be isolated. Vacuum–thermal desolvation of $NaB_3H_8 \cdot 3C_4H_8O_2$ resulted in decomposition of NaB_3H_8 .¹²

Shore and co-workers have found that the $B_3H_8^-$ anion can be obtained by reacting certain metal amalgams with THF–borane ($THF \cdot BH_3$).⁵ Here, we adopted this method to obtain the $B_3H_8^-$ anion and, more importantly, developed an efficient way to isolate the desired unsolvated NaB_3H_8 from the oily THF solvate. This synthesis avoids the use of diborane, largely simplifies the reaction setup, and significantly reduces the cost. Although the unsolvated NaB_3H_8 was first prepared almost 7 decades ago, its structure has never been reported. Attempts to obtain unsolvated NaB_3H_8 single crystals have been unsuccessful. In this work, we solved the structure based on powder X-ray diffraction (XRD) data using Topas-Academic.¹³

Na/Hg amalgam was reacted with $THF \cdot BH_3$ in a flask at room temperature for 3 days, during which a fine white precipitate appeared. After removal of the THF solvent and the residual $THF \cdot BH_3$ under dynamic vacuum, a white powder in an oil suspension remained. The white powder is $NaBH_4$, and the oily product is the THF-coordinated NaB_3H_8 . Dry ethyl ether

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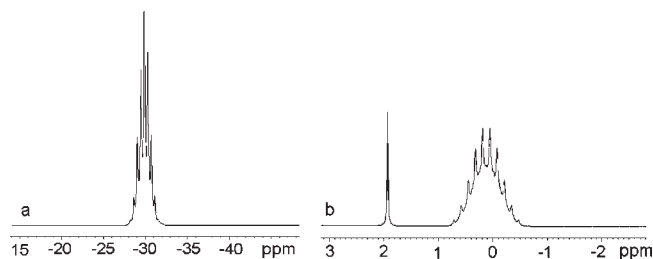


Figure 1. ^{11}B (a) and ^1H NMR (b) spectra of unsolvated NaB_3H_8 in CD_3CN at room temperature.

was distilled onto the crude product, and then the solution was transferred to a vacuum extractor. After NaBH_4 was filtered away, the clear ether solution was pumped via a dynamic vacuum, leaving an oily product. Dry dichloromethane was then distilled onto the oily product, resulting in the formation of a white powder suspended in dichloromethane. The powder was collected through filtration and pumped under dynamic vacuum to remove any residual solvents. Experimental details are included in the Supporting Information.

Isolation of the unsolvated NaB_3H_8 from the oily product is a critical step in the procedure. Dichloromethane can help to break the coordination between THF and the Na cation, leaving a solvent-free NaB_3H_8 powder suspended in dichloromethane. Heating the oily solvate at around 50°C without dichloromethane helped (yet incompletely) to remove the coordinated THF, but the desired NaB_3H_8 decomposed slowly, and the crude product became yellowish overnight. NMR spectra indicate the formation of undesired boron compounds. Only up to now, a simple and efficient method has been successfully developed to synthesize NaB_3H_8 and isolate it from the oily solvate.

Pure NaB_3H_8 exhibits a single nonet ^{11}B NMR spectrum corresponding to the octahydrotriborate anion,⁵ centered at $\delta -30.4$ ppm (Figure 1a). The ^1H NMR spectrum includes a decet centered at $\delta 0.2$ ppm (Figure 1b). Proton peaks associated with THF and Et_2O are absent from the ^1H NMR spectrum, indicating the success of the procedure. The quintet peak at $\delta 1.94$ ppm is from CD_3CN .

The spent mercury can be regenerated by washing with cold water, diluted HCl, and acetone to remove the residual Na, NaBH_4 , and any solvent and impurities. Prior to reuse, the mercury was dried under vacuum with stirring.

Compared with all of the reported methods,^{7–9} this method avoids the use of hazardous starting materials such as diborane and boron trifluoride, thus significantly simplifying the reaction apparatus. Moreover, this method gives a yield higher than 70%. Commercially available $\text{THF}\cdot\text{BH}_3$ enables a safe synthesis in the laboratory. Large-scale synthesis can be realized simply by increasing the quantity of the starting materials. About 4.5 g of unsolvated NaB_3H_8 can be obtained using 400 mL of 1.0 M $\text{THF}\cdot\text{BH}_3$ in a single laboratory reaction.

The structure of unsolvated NaB_3H_8 was solved from powder XRD data (Figure 2). The structure solution is detailed in the Supporting Information. It is worth noting that the elimination of H atoms increases R_{wp} from 4.26 to 7.74, showing a significant contribution from H atoms to XRD intensities. The terminal H atoms were refined to sensible positions without any constraints. The bridging H atom was refined to have an unreasonably short bond distance with B(2) (0.76 Å), so the B(2)–H(1) distance was

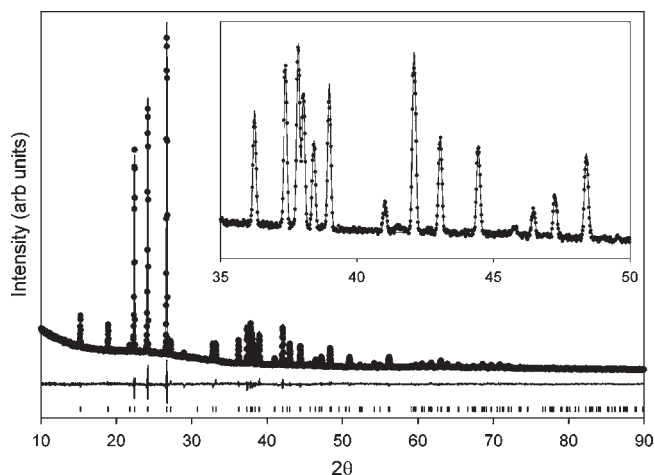


Figure 2. Powder XRD data (dots) of unsolvated NaB_3H_8 , Rietveld refinement results (line), difference trace (observed – calculated), and allowed Bragg reflections (tick marks). The inset shows the expanded scale from $2\theta = 35$ to 50° .

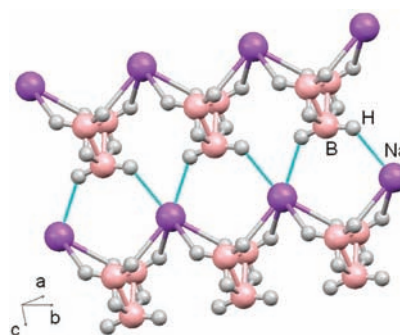


Figure 3. Crystal structure of unsolvated NaB_3H_8 . Color code: Na, violet; B, pink; H, gray.

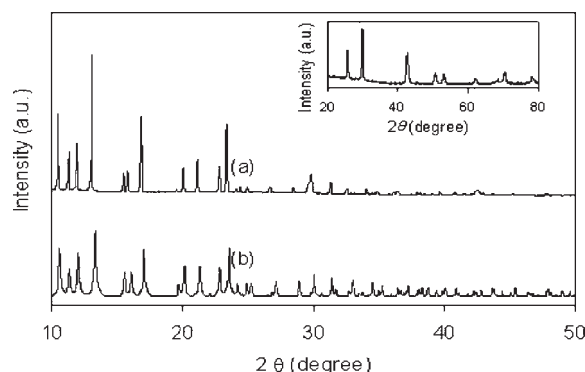


Figure 4. Powder XRD patterns: (a) obtained $\text{Mg}(\text{B}_3\text{H}_8)_2\cdot 2\text{Et}_2\text{O}$ powder; (b) calculation based on single-crystal XRD data² and NaBr (inset).

fixed at 1.08 Å, with the H(1) atom still allowed an angle of rotation in the xz plane.^{2,14}

The compound crystallizes in space group $Pnmm$. The compound has double-stranded chains that are linked through a H bridge between Na and B (Figure 3). The three B atoms form a triangle, with the two B–B distances being 1.794(4) and 1.820(5) Å, similar to the single-crystal XRD data of other B_3H_8 compounds.^{2,14} Because the B_3H_8 anion is

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sterically larger than the BH_4 anion, the observed Na–B distances [3.1302(8) and 3.370(4) Å] are longer than those observed in NaBH_4 (2.80–3.00 Å, depending on the phases^{15,16}). All of the terminal H atoms on the boron triangle unit form short contacts with the Na cations. There are four short Na–H contacts at 2.38(1) Å and two longer contacts at 2.48(2) Å.

The good solubility of NaB_3H_8 in ethyl ether enables a high-yield synthesis of $\text{Mg}(\text{B}_3\text{H}_8)_2 \cdot 2\text{Et}_2\text{O}$, which is considered to be an interesting precursor for the MgB_2 thin film.² A metathesis reaction between NaB_3H_8 and $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ (2:1 molar ratio) in ethyl ether proceeds rapidly because NaBr is insoluble in ether. After removal of NaBr through filtering and slow pumping off of the ether, a colorless $\text{Mg}(\text{B}_3\text{H}_8)_2 \cdot 2\text{Et}_2\text{O}$ powder was obtained. A powder XRD pattern of obtained $\text{Mg}(\text{B}_3\text{H}_8)_2 \cdot 2\text{Et}_2\text{O}$ matches the simulated pattern based on single-crystal XRD data (Figure 4).² The yield of this

synthesis is close to 100%, much higher than that for the reported synthesis (41% yield).²

In summary, we have reported a new route to unsolvated NaB_3H_8 . This route is safer than previously reported methods and can be easily scaled up. The structure of NaB_3H_8 has been solved from powder XRD data and is reported for the first time. Because of its high hydrogen content, the unsolvated NaB_3H_8 could help to develop novel hydrogen storage materials. The solvent-free NaB_3H_8 will facilitate the exploration of various volatile metal–boron–hydrogen-containing precursors for metal diboride thin film deposition.

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Supporting Information Available: Experimental details, refinement details, and structural information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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