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Synthesis and Single Crystal Structure of Sodium Octahydrotriborate, NaB_3H_8

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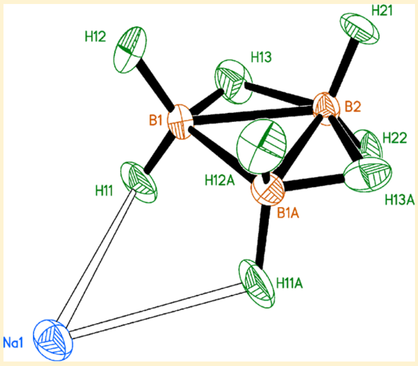
Supporting Information

ABSTRACT: This paper describes a modified synthesis of NaB_3H_8 by the reduction of $BH_3 \cdot THF$ with sodium dispersed on silica gel. Single crystals obtained from CH_2Cl_2 show conclusively that the space group is *Pmn*2_1, in contrast to the *Pmmn* space group previously deduced from powder diffraction data.



■ INTRODUCTION

Molecular complexes of the general stoichiometry MB_xH_y, i.e., that contain only metal, boron, and hydrogen, are of interest owing to their potential as hydrogen storage materials,[1−3] as reductants in both organic and inorganic synthesis,[4,5] as starting materials for the preparation of other boron-containing molecules, and as CVD precursors[6−13] for deposition of metal boride thin films.[14] Most of the compounds in the MB_xH_y class are complexes of the tetrahydroborate (BH_4^-) anion, but also important are metal complexes of the higher hydroborates. Notable among these are compounds of the octahydrotriborate anion, $B_3H_8^-$, which is the third member of the hydroborate series (following BH_4^- and $B_2H_7^-$).[15,16] Typical starting materials for the synthesis of metal $B_3H_8^-$ complexes are the sodium salt (discussed below) or its potassium,[15] rubidium,[15] cesium,[15,17,18] thallium,[19] or tetra(alkyl)ammonium[17,18,20] analogues.

The only structurally characterized examples of homoleptic MB_xH_y complexes that do not contain BH_4 ligands are the octahydrotriborate species $Cs(B_3H_8)$,[21] $Be(B_3H_8)_2$,[22] and $Cr(B_3H_8)_2$.[13] Metal B_3H_8 complexes that bear ancillary ligands are much more common.[22−33] The usual synthetic route to such complexes involves treatment of a metal halide with a $B_3H_8^-$ salt, but the ytterbium species $Yb(B_3H_8)_2(THF)_x$ can be made by treating ytterbium amalgam with $BH_3 \cdot THF$.[15] Structural data for heteroleptic transition-metal complexes containing B_3H_8 ligands[24,26,27,29−33] show that the B_3H_8 group is usually bidentate and occupies two *cis* metal coordination sites.[13]

As a reagent, the sodium salt NaB_3H_8 has certain advantages over other salts of this anion, one of which is that it is soluble in diethyl ether. Stock was the first to prepare NaB_3H_8 by the solventless action of sodium on diborane.[34−37] Later workers discovered that ethers promote this reaction to give a 1:1 mixture of $NaBH_4$ and NaB_3H_8.[38,39] Other methods to make NaB_3H_8 include the reaction of diborane with sodium amalgam,[38] sodium naphthalenide,[40] sodium tetraphenylborate,[40] or sodium borohydride;[40] the reaction of tetraborane with sodium hydride;[41] and the stepwise degradation of decaborane.[20] None of these methods is ideal, however, owing to the reactivity of diborane and the expense or effort required to obtain the higher boron hydrides. Solutions of NaB_3H_8 can also be made by treating $NaBH_4$ with I_2 or $BF_3 \cdot Et_2O$ in diglyme.[17] This procedure has the advantage of avoiding the use of diborane, but removal of the solvent affords an oil of composition $NaB_3H_8(\text{diglyme})_x$. Solvent-free NaB_3H_8 cannot be obtained directly from this oil because diglyme binds firmly to sodium cations.[42] An indirect method to obtain solvent-free NaB_3H_8, ultimately from $NaB_3H_8(\text{diglyme})_x$, has been described,[43] but this method requires several steps and expensive reagents (sodium tetraphenylborate) and is uneconomical on a large scale.[13] Shore has described a significant improvement in the synthesis of solvent-free NaB_3H_8 by the reaction of sodium amalgam with the commercially available reagent $BH_3 \cdot THF$.[2]

Sodium absorbed into silica gel has recently been employed as a safer and easier to handle synthetic alternative to other forms of sodium.[44] Since its discovery, this reagent has been used in a variety of organic transformations such as Birch[45] and Bouveault-Blanc[46] reductions. Here, we describe a modification of Shore's synthesis of NaB_3H_8 that involves the action of Na/

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SiO_2 on $BH_3{\cdot}THF$. This new method affords pure samples of NaB_3H_8 in high yield and avoids the health and safety concerns associated with the use of elemental mercury. We also report the single crystal structure of NaB_3H_8.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of NaB_3H_8. Reduction of commercially available $BH_3{\cdot}THF$ at 50 °C with 1 equiv of sodium adsorbed on silica gel affords solutions of NaB_3H_8 in excellent yield after 15 h. The workup involves removal of the THF, extraction of the residue into diethyl ether (which leaves behind the insoluble $NaBH_4$), and then removal of the diethyl ether. The resulting oil is then treated with CH_2Cl_2 (an innovation introduced by Shore)[2] to produce the product as an off-white solid, which is collected by filtration. By cooling the CH_2Cl_2 supernatant to −20 °C, a crop of X-ray quality crystals can be obtained. The overall yield is 62%, and the reaction can easily be scaled up to obtain tens of grams of product. The idealized reaction stoichiometry is as follows:

$$2Na + 4BH_3{\cdot}THF \rightarrow NaB_3H_8 + NaBH_4 + 4THF$$

NaB_3H_8 is soluble in diethyl ether, tetrahydrofuran, and acetonitrile, and slightly soluble in dichloromethane. The ^1H and ^{11}B NMR spectra are consistent with the literature values.[2] The IR spectrum contains a broad terminal B−H stretch at 2418 cm^{-1} and a bridging B−H−B stretch at 2118 cm^{-1}. Similar frequencies are observed for other metal $B_3H_8^-$ complexes.[13,15,24,47−50]

Crystal Structure of NaB_3H_8. A previous powder X-ray diffraction study suggested that NaB_3H_8 crystallizes in the centrosymmetric space group *Pmmn*.[2] We have been able to obtain single crystals of this material and find that this is not the correct space group: NaB_3H_8 actually crystallizes in the closely related non-centrosymmetric space group $Pmn2_1$ (the cell parameters and atomic coordinates clearly show that our data crystal is the same crystal form as that investigated by Shore). This choice of space group eliminates the mild disorder in the *Pmmn* refinement that resulted from taking a pseudosymmetry as a true symmetry (see below); the new refinement gives more reasonable B−H distances and more reasonable thermal parameters. The single crystal X-ray diffraction data were of high enough quality that the hydrogen atoms could be refined anisotropically without constraints. Final bond distances and angles are collected in Table 2.

The B_3H_8 anion (Figure 1) straddles a crystallographic mirror plane that is perpendicular to the *a*-axis; the sodium atom and boron atom B2 (and the H atoms attached to B2) reside in this plane. As seen for other B_3H_8 compounds,[13,27,48−51] the three boron atoms form almost a perfect equilateral triangle with B(1)−B(2) = 1.790(1) Å and B(1)−B(1A) = 1.798(2) Å. Each boron bears two terminal hydrogen atoms with B(1)−H(11) = 1.08(2) Å, B(1)−H(12) = 1.10(1) Å, and B(2)−H(21) = 1.06(2) Å. The B(1)−B(2) edge (and its B(1A)−B(2) symmetry related partner) is bridged by a hydrogen atom in an unsymmetric fashion, with B(1)−H(13) = 1.18(1) Å and B(2)−H(13) = 1.40(1) Å. Again, these features are typical for B_3H_8 compounds.

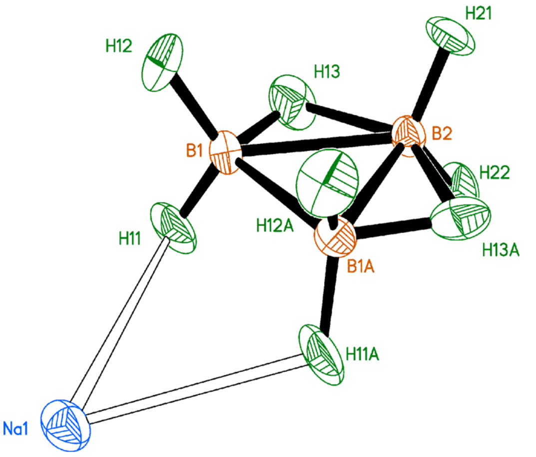

Figure 1. Structure of one NaB_3H_8 formula unit within the polymeric structure. Ellipsoids are drawn at the 30% probability level.

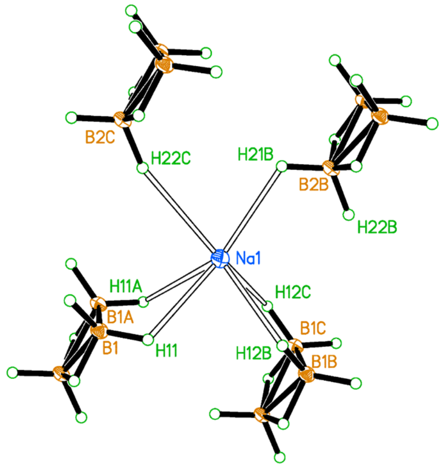

Figure 2. Local environment of the Na cations in NaB_3H_8. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms are depicted as arbitrarily sized spheres.

The cations and anions are linked into two-dimensional sheets (perpendicular to the *a*-axis) by means of Na···H−B bridges involving the terminal hydrogen atoms: four anions surround each cation and four cations surround each anion in a checkerboard pattern (Figure 2). For each sodium cation, the closest neighbors are six terminal hydrogen atoms in a distorted trigonal prismatic arrangement; each terminal hydrogen atom in the $B_3H_8^-$ anion interacts with one neighboring sodium cation. Five of these six Na···H distances lie between 2.37(2) and 2.47(1) Å; the exception is the Na···H(22) distance of 2.63(2) Å.

Five of the six Na···B distances lie between 3.057(1) and 3.115(1) Å; and the boron atom associated with the long Na···H contact is again much longer. The shorter distances are consistent with Na···B distances in other sodium salts of hydridoborate anions: 3.065(1) Å in $NaBH_4$,[52] 2.963(1)−3.010(1) Å in $NaBH_4(H_2O)_2$,[52] 2.912(3)−3.238(3) Å in $NaBHEt_3(tmeda)$,[53] 2.865(2)−2.986(3) Å in $NaBH_4[HC(pz)_3](THF)$,[54] and 2.745(7)−3.133(9) Å in $NaHBEt_3{\cdot}{}^1/_2C_6H_3Me_3$.[55]

The structure as deduced from the single crystal study is similar to that obtained by powder diffraction.[2] The unit cells are identical except for the definition of which axis is *b* and which is *c*. In the *Pmmn* space group chosen for the powder diffraction refinement, there are crystallographic mirror planes perpendicular to the 4.75 Å axis, whereas in $Pmn2_1$ these symmetry elements are not present. In the *Pmmn* refinement, the sodium and boron atoms are restricted to lie in these mirror planes (as well as in the mirror planes perpendicular to the 7.85 Å axis), but this restriction places these atoms in incorrect locations by several tenths of an angstrom. Therefore, the actual packing arrangement of cations and anions is somewhat less symmetrical than in the *Pmmn* refinement, but otherwise, the major conclusions about the structure remain unchanged.

■ EXPERIMENTAL PROCEDURE

All procedures and manipulations were carried out under argon by using standard Schlenk and drybox techniques. Solvents were distilled from sodium/benzophenone (thf, Et_2O) or calcium hydride (CH_2Cl_2) before use. $BH_3{\cdot}THF$ (Aldrich) and silica gel (Merck, 0.05−0.20 mm grade) were used as received. Elemental analyses were carried out by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Perkin-Elmer Spectrum One infrared spectrometer as Nujol mulls between KBr plates. The NMR data were collected on a Varian Unity 400 instrument at 9.4 T (^1H and ^{11}B). Chemical shifts are reported in δ units (positive shifts to high frequency) relative to $SiMe_4$ (^1H) or $BF_3{\cdot}Et_2O$ (^{11}B) and were referenced internally to residual solvent signals (^1H) or externally to $BF_3{\cdot}Et_2O$ (^{11}B). Melting points were determined in closed capillaries under argon on a Thomas-Hoover Unimelt apparatus.

Table 1. Crystallographic Data for NaB_3H_8 (1) at 193 K

FW (g mol^{-1})	63.48
λ (Å)	1.54178
crystal system	orthorhombic
space group	$Pmn2_1$
a (Å)	7.85
b (Å)	5.81
c (Å)	4.58
V (Å^3)	208.691(14)
Z	2
ρ_{calc} (g cm^{-3})	1.010
μ (mm^{-1})	1.217
R(int)	0.0523
abs corr method	integration
max, min transm factors	0.860/0.708
data/restraints/params	398/1/63
GOF on F^2	1.107
R_1 [$I > 2\sigma(I)$]^a	0.0220
wR_2 (all data)^b	0.0502
max, min $\Delta\rho_{electron}$ (e·Å^{-3})	0.200/−0.108

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

Sodium Dispersion on Silica Gel. A 250 mL Schlenk round-bottom flask was charged with dry silica gel (6.0 g). The silica gel was heated to 160 °C under a vacuum for 1 h to remove traces of water. The flask was filled with Ar, and to the silica gel at 160 °C was added sodium (2.3 g, 0.10 mol) in small pieces (ca. 0.3 g) accompanied by physical agitation in order to disperse the sodium on the silica gel. After complete addition of the sodium metal, the fine black solid was cooled to room temperature.

Sodium Octahydroborate, NaB_3H_8. ***Caution: NaB_3H_8 is pyrophoric and should be handled with care under an inert atmosphere.*** The above dispersion of sodium on silica gel was cooled to −10 °C and treated with $BH_3{\cdot}THF$ (100 mL of a 1.0 M solution in tetrahydrofuran, 0.10 mol). The mixture was warmed to room temperature and subsequently heated to 50 °C for 15 h with stirring. The mixture was cooled to room temperature and allowed to settle, and the supernatant was filtered. The residue was washed with THF (50 mL), and the wash solution was filtered and added to the supernatant. The combined filtrates were taken to dryness in a vacuum. The resulting dark brown solid was extracted with Et_2O (3 × 25 mL), and the extracts were filtered, combined, taken to dryness, and dried overnight at 50 °C in a vacuum. The resulting oily brown residue was stirred with CH_2Cl_2 (50 mL) for 24 h. The desired product, which floats on the solvent, was isolated by filtration as an off-white powder. Yield: 980 mg (62%). Additional material can be obtained as small colorless needles by cooling the CH_2Cl_2 filtrate to −20 °C for 24 h. mp 91−94 °C (dec). Anal. Calcd for B_3H_8Na: B, 51.1; Na, 36.2. Found: B, 48.7; Na, 34.7. ^1H NMR (CD_3CN, 20 °C): δ 0.14 (decet, J_{BH} = 33 Hz). ^1H NMR (THF-d_8, 20 °C): δ 0.05 (decet, J_{BH} = 33 Hz). ^{11}B NMR (CD_3CN, 20 °C): δ −29.5 (nonet, J_{BH} = 33 Hz). ^{11}B NMR (THF-d_8, 20 °C): δ −30.9 (nonet, J_{BH} = 33 Hz). IR (cm^{-1}): 2457 sh, 2418 s, 2332 sh, 2118 m, 1305 m, 1201 sh, 1166 sh, 1156 s, 1005 s, 975 m, 891 w, 807 w.

Crystallographic Studies.[56] Single crystals of NaB_3H_8 were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and least-squares refinement using 2980 reflections yielded the cell dimensions given in Table 1.

The orthorhombic lattice and the systematic absences $h0l$ ($h + l \neq 2n$) were consistent with the space groups $Pmn2_1$ and $Pmmn$. The noncentrosymmetric alternative $Pmn2_1$ was chosen, and this choice was confirmed by successful refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, and Lorentz and polarization effects. No corrections for crystal decay were necessary, but a face-indexed absorption correction was applied, with the minimum and maximum transmission factors being 0.708 and 0.860. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. All 398 unique data were used in the least-squares refinement.

The structure was solved by direct methods. Correct positions for all atoms were deduced from an E-map and subsequent least-squares refinement and difference Fourier calculations. The quantity

Table 2. Selected Bond Distances and Angles for NaB_3H_8^{a}

bond distances (Å)			
B(1)−B(2)	1.790(1)	Na(1)···B(1)	3.057(1)
B(1)−B(1)#1	1.798(2)	Na(1)···B(1)#3	3.115(1)
B(1)−H(11)	1.08(2)	Na(1)···B(2)#2	3.078(2)
B(1)−H(12)	1.10(1)	Na(1)···B(2)#4	3.706(2)
B(1)−H(13)	1.18(1)	Na(1)···H(11)	2.47(1)
B(2)−H(13)	1.40(1)	Na(1)···H(12)#3	2.37(2)
B(2)−H(21)	1.06(2)	Na(1)···H(21)#2	2.41(2)
B(2)−H(22)	1.11(2)	Na(1)···H(22)#4	2.63(2)
bond angle (deg)			
B(2)−B(1)−B(1)#1	59.85(3)	H(11)−B(1)−H(13)	103.8(10)
B(1)−B(2)−B(1)#1	60.30(7)	H(12)−B(1)−H(13)	101.9(12)
H(11)−B(1)−H(12)	116.0(11)	H(21)−B(2)−H(22)	115.2(16)

^{a}Symmetry transformations used to generate equivalent atoms: #1 ($-x + 2, y, z$); #2 ($x, y + 1, z + 1$); #3 ($-x + 2, y, z + 1$), #4 ($x, y + 1, z$).

minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0418P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least-squares, independent anisotropic displacement factors were refined for all of the atoms. An isotropic extinction parameter was refined to a final value of $x = 5(1) \times 10^{-5}$, where F_c is multiplied by the factor $k[1 + F_c^2 x\lambda^3/\sin 2\theta]^{-1/4}$, with k being the overall scale factor. Analysis of the diffraction intensities suggested slight inversion twinning; therefore, the intensities were calculated from the equation $I = xI_a + (1 - x)I_b$, where x is a scale factor that relates the volumes of the inversion-related twin components. The scale factor refined to a value of 0.25(6). Successful convergence was indicated by the maximum shift/error of 0.000 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (0.20 e·Å^{-3}) was located 0.90 Å from B(1). A final analysis of variance between observed and calculated structure factors showed no apparent errors.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data (CIF format) for NaB_3H_8. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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