The complex prepared in this work is a new member of the series of cationic metal borane complexes and is the first monomeric copper(I) complex in which the central metal is bound tetrahedrally to four hydrogen atoms. In connection with this, copper atom in polymeric $Cu_2(B_{10}H_{10})$ is bound tetrahedrally to adjacent $B_{10}H_{10}^{2-}$ ions through four vicinal hydrogen atoms.[28]

Although the complex is a 1:1 ionic salt, the packing in the crystal is, interestingly, rather complex as shown in Figure 2. A cation is surrounded by four cations (Cu···Cu = 6.622 (3)–7.701 (2) Å) tetrahedrally and six anions (Cu···I = 7.645 (1)–8.180 (2) Å), four of which surround the cation tetrahedrally and the rest of which lie in capping positions of the hexahedron made of four anions and four cations. An anion is surrounded by six cations and four anions (I···I = 7.644 (1)–7.678 (1) Å), inversely.

**C. NMR Spectra.** $^1$H, $^{11}$B{$^1$H}, and $^{31}$P{$^1$H} NMR spectra of the iodide and the chloride in $CD_2Cl_2$ at room temperature are almost the same, suggesting that these complexes take the same structure in solution.

The $^1$H NMR spectrum (200 MHz) of $[Cu\{B_2H_4{\cdot}2P(CH_3)_3\}_2]^+$ consists of two signals in a 36:8 ratio. The intense low-field one at +1.29 ppm was assigned to the methyl protons of trimethylphosphine groups. This appears as a triplet with a peak separation of 5.3 Hz due to the virtual coupling to $^{31}$P.[29] The high-field signal is a broad doublet ranging from +0.7 to −1.0 ppm with the center at −0.1 ppm and is assigned to the eight hydrogens connected to boron atoms. The signal shows temperature dependence with a 90-MHz instrument. It is featureless at room temperature but appears as a single peak at −90 °C. This phenomenon is due to quadrupole-induced $^{10}$B and $^{11}$B spin relaxation ("thermal" decoupling), which is general among boranes.[30] The area of this peak shows that $B_2H_4{\cdot}2P(CH_3)_3$ ligands are fluxional and the bridging and terminal hydrogens are equivalent on an NMR time scale even at −90 °C.[31] The chemical shift of $^{11}$B for the present complex is smaller than that of free $B_2H_4{\cdot}2P(CH_3)_3$ by about 7.1 ppm,[29] but is comparable with that of $ZnCl_2\{B_2H_4{\cdot}2P(CH_3)_3\}$.[9]

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**Supplementary Material Available:** Tables SI and SII, listing crystallographic and experimental data and thermal parameters for non-hydrogen atoms (3 pages); a table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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(27) The B–B distance in $B_2H_4{\cdot}2PF_3$ was reported to be 1.800 (12) Å by the electron diffraction method: Lory, E. R.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1971**, *10*, 1072–1075.

(28) (a) Dobrott, R. D.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *37*, 1779–1784. (b) Paxson, T. E.; Hawthorne, M. F.; Brown, L. D.; Lipscomb, W. N. *Inorg. Chem.* **1974**, *13*, 2772–2774.

(29) Hertz, R. K.; Denniston, M. L.; Shore, S. G. *Inorg. Chem.* **1978**, *17*, 2673–2674.

(30) (a) Bushweller, C. H.; Beall, H.; Grace, M.; Dewkett, W. J.; Bilofsky, H. S. *J. Am. Chem. Soc.* **1971**, *93*, 2145–2149. (b) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1981**, *19*, 589–593.

(31) Details of the fluxional behavior of the complex will be reported elsewhere.

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# Reaction of Dimethyl Sulfide–Triborane(7) with Dimethyl Sulfide. A Formation Reaction of Pentaborane(9)

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The triborane(7) adduct of dimethyl sulfide was isolated as a liquid at room temperature. The adduct reacted with additional dimethyl sulfide to give pentaborane(9) and dimethyl sulfide–borane(3). This conversion of triborane(7) to pentaborane(9) was interpreted in terms of borane framework expansion involving diborane(4) adducts that had been established in this laboratory.

## Introduction

Some years ago, studies of the reaction chemistry of boron hydride compounds with trimethylphosphine were initiated in our laboratory. The purpose of the studies was to find stable products and definable reactions of these compounds by taking advantage of the strongly basic character of $P(CH_3)_3$. Because of the strong "$(CH_3)_3P \rightarrow$borane" dative bond, secondary reactions, which are often caused by the dissociative instability of borane adducts, were suppressed, and thus definable reactions could be identified in reaction systems that would be intractable otherwise. A summary of the results has been described elsewhere.[1]

Some successful results having been obtained in the above studies, efforts were then directed to borane reactions involving other Lewis bases, including weaker bases. New observations, particularly those involving weaker bases such as $N(CH_3)_3$,[2] were then interpreted in the light of knowledge acquired from the earlier studies. Recently, we extended the same line of study to the reactions between lower borane compounds and alkyl sulfides. In this report, the behavior of $B_3H_7{\cdot}S(CH_3)_2$ toward $S(CH_3)_2$ is described and interpreted.

## Results

**A. Isolation of $B_3H_7{\cdot}S(CH_3)_2$.** The reaction of tetraborane(10) with dimethyl sulfide gives dimethyl sulfide adducts of triborane(7) and borane(3).[3] The triborane(7) adduct $B_3H_7{\cdot}S(CH_3)_2$, was separated from its coproduct $BH_3{\cdot}S(CH_3)_2$ by fractional condensation as a stable liquid that could be handled at room temperature without decomposition. A dichloromethane solution of the compound remained unchanged for several hours at room temperature. Similarly, the diethyl sulfide adduct of triborane(7) was isolated. Dimethyl sulfide–triborane(7) could also be prepared by treating $B_3H_7{\cdot}THF$ with $S(CH_3)_2$. This latter method has an advantage over the other of not having $BH_3{\cdot}S(CH_3)_2$ in the products; the time-consuming fractionation can be avoided if the compound has to be separated in a pure form. The $^{11}$B NMR

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(1) Kodama, G. In *Advances in Boron and the Boranes*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Chapter 6.

(2) (a) Kameda, M.; Shimoi, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3705. (b) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 287. (c) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 1116. (d) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 1836.

(3) (a) Edwards, L. J.; Hough, W. V.; Ford, M. D. *Proc. Int. Congr. Pure Appl. Chem.* **1958**, *16*, 475. (b) Kodama, G.; Saturnino, D. J. *Inorg. Chem.* **1975**, *14*, 2243.

0020-1669/90/1329-0817$02.50/0

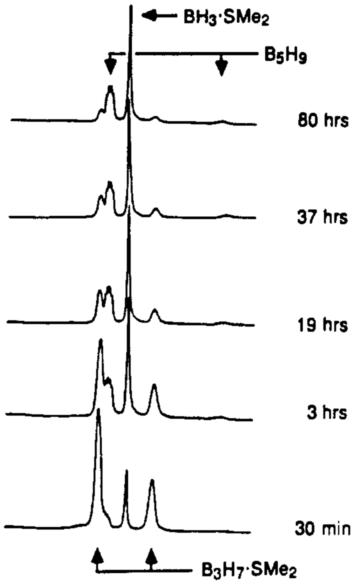

**Figure 1.** $^{11}B\{^1H\}$ NMR spectra (25.5 MHz) of $B_3H_7{\cdot}S(CH_3)_2$ in $S(CH_3)_2$, indicating the formation of $B_5H_9$. The spectra are normalized to the tallest peak.

shift data are as follows: $B_3H_7{\cdot}S(CH_3)_2$, −30.9 ($B_1$) and −11.7 ($B_{2,3}$) ppm; $B_3H_7{\cdot}S(C_2H_5)_2$, −33.7 ($B_1$) and −12.5 ($B_{2,3}$) ppm [$BF_3{\cdot}O(C_2H_5)_2$ as external standard].

**B. Reaction of $B_3H_7{\cdot}S(CH_3)_2$ with Dimethyl Sulfide.** When the adduct, $B_3H_7{\cdot}S(CH_3)_2$, was dissolved in liquid dimethyl sulfide at room temperature, a slow change occurred to form $B_5H_9$ and $BH_3{\cdot}S(CH_3)_2$ in a 1:4 molar ratio, as determined from the $^{11}B$ NMR spectra of the reaction solution. No other compounds were produced; *the solution remained clear and colorless, and no hydrogen gas was found in the reaction tube.* Figure 1 illustrates the process of this reaction as observed in the $^{11}B$ NMR spectra. The following equation is appropriate for the reaction:

$$3B_3H_7{\cdot}S(CH_3)_2 + S(CH_3)_2 \xrightarrow[\text{in } S(CH_3)_2]{\text{room temp}} B_5H_9 + 4BH_3{\cdot}S(CH_3)_2 \quad (1)$$

This reaction proceeded in a dichloromethane solution also, but the reaction was much slower.

## Discussion

**Background.** In the 1950s, Edwards and co-workers reported that tetraborane(10), when dissolved in diethyl ether, slowly decomposed at room temperature to form pentaborane(9), diborane(6), and hydrogen according to the following equation:[3a,4]

$$5B_4H_{10} \rightarrow 2B_5H_9 + 5B_2H_6 + H_2 \quad (2)$$

This reaction was considered to proceed by the interaction of $B_4H_{10}$ with $B_3H_7{\cdot}O(C_2H_5)_2$, which was produced by the reaction of $B_4H_{10}$ with the ether:[3a]

$$B_4H_{10} + (C_2H_5)_2O \rightarrow B_3H_7{\cdot}O(C_2H_5)_2 + \tfrac{1}{2}B_2H_6 \quad (3)$$

Actually, because of the weak base strength of diethyl ether, this reaction (eq 3) does not proceed to a measurable extent ($^{11}B$ NMR spectroscopy). (See Experimental Section, part 5.) However, in view of the fact that $B_4H_{10}$ undergoes a reaction analogous to eq 2 in the presence of $B_3H_7{\cdot}THF$, giving $B_5H_9$, $B_2H_6$, and $H_2$,[3a] the above proposed reaction pathway involving $B_3H_7{\cdot}O(C_2H_5)_2$ is plausible; i.e., the $B_3H_7{\cdot}O(C_2H_5)_2$ that is produced in minute quantities may be the first-step intermediate. Furthermore, when excess $B_4H_{10}$ was treated with amine (e.g., $N(CH_3)_3$ or pyridine), $B_4H_{10}$ was converted to $B_5H_9$ according to eq 2 with $H_2$ gas as one of the products. Here again, the stable triborane(7)–amine that was initially formed acted catalytically on $B_4H_{10}$.[3a] These $B_5H_9$ formation reactions involve a base adduct of $B_3H_7$ and the $B_3H_7$ portion of the $B_4H_{10}$ molecule ("$B_3H_7 + BH_3$"). However, the formation of $B_5H_9$ from $B_3H_7{\cdot}S(CH_3)_2$, which is presented in this paper (eq 1), is clearly different in that no hydrogen gas is produced and that excess base, $S(CH_3)_2$, rather than a borane, is a reactant.

In 1974, Miller and Ryschkewitsch reported a reaction for the preparation of pentaborane(9).[5] In this process, solid $[(n\text{-}C_4H_9)_4N][B_3H_7Br]$ was first prepared from $[(n\text{-}C_4H_9)_4N][B_3H_8]$, and then it was pyrolyzed to form pentaborane(9), hydrogen gas, and diborane(6). The following equation was suggested for the formation of $B_5H_9$:[5a]

$$5[(n\text{-}C_4H_9)_4N][B_3H_7Br] \xrightarrow{100\ °C} 3B_5H_9 + 4H_2 + 5[(n\text{-}C_4H_9)_4N]Br \quad (4)$$

In this $B_5H_9$ formation reaction a triborane derivative, $B_3H_7Br^-$, is involved. However, hydrogen gas was produced and the conditions of the reaction, too, are quite different from those employed in the other $B_5H_9$ formation reactions that are described above.

We have observed in recent years that certain diborane(4) adducts served as reagents for borane framework expansion,[6] and we know that diborane(4) adducts are usually produced by the reaction of $B_3H_7$ adducts with relatively strong Lewis bases.[2b,7] It is, therefore, tempting to explain the conversion of $B_3H_7{\cdot}S(CH_3)_2$ to $B_5H_9$ (eq 1) in terms of this expansion scheme in which "bis(dimethyl sulfide)–diborane(4)" is involved.

**The Expansion Reaction.** When bis(trimethylphosphine)–diborane(4), $B_2H_4{\cdot}2P(CH_3)_3$, is allowed to react with $B_3H_7{\cdot}L$ or $B_4H_8{\cdot}L$ (L = relatively *weak* Lewis base), a borane framework expansion occurs to give $B_4H_8{\cdot}P(CH_3)_3$ or $B_5H_9{\cdot}P(CH_3)_3$, respectively. Thus, the following reactions have been established:

$$B_2H_4{\cdot}2P(CH_3)_3 + B_3H_7{\cdot}THF \rightarrow B_4H_8{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + THF^{2a} \quad (5)$$

$$B_2H_4{\cdot}2P(CH_3)_3 + B_4H_8{\cdot}PH_3 \rightarrow B_5H_9{\cdot}P(CH_3)_3 + BH_3{\cdot}P(CH_3)_3 + PH_3^{6} \quad (6)$$

Likewise, $B_2H_4{\cdot}2N(CH_3)_3$ was found in this study to react with $B_3H_7{\cdot}S(CH_3)_2$ according to eq 7. In these reactions (eqs 5–7),

$$B_2H_4{\cdot}2N(CH_3)_3 + B_3H_7{\cdot}S(CH_3)_2 \rightarrow B_4H_8{\cdot}N(CH_3)_3 + BH_3{\cdot}N(CH_3)_3 + S(CH_3)_2 \quad (7)$$

the diborane(4) adducts, $B_2H_4{\cdot}2L$, split into $BH_3{\cdot}L$ and "$BH{\cdot}L$", and the latter combines with the reacting borane compounds to increase the number of framework boron atoms by 1.

**Proposed Scheme.** The triborane(7) adduct of $N(CH_3)_3$ or $P(CH_3)_3$ undergoes a cleavage reaction when treated with $N(CH_3)_3$ or $P(CH_3)_3$, and the adducts of $B_2H_4$ and $BH_3$ are produced.[2b,c,7] On the other hand, a solution of $B_3H_7{\cdot}THF$ in THF remains unchanged for days. The general trend of base strength toward boranes is in the order of $O(C_2H_5)_2 < THF < S(CH_3)_2 < N(CH_3)_3 < P(CH_3)_3$.[8] Therefore, it would not be unreasonable to assume that $B_3H_7{\cdot}S(CH_3)_2$ is cleaved by $S(CH_3)_2$ to produce the short-lived species "$B_2H_4{\cdot}2S(CH_3)_2$", especially when $S(CH_3)_2$ is used as solvent. The diborane(4) adduct would then act as a reagent for framework expansion on $B_3H_7{\cdot}S(CH_3)_2$. The equations for these reactions are

$$B_3H_7{\cdot}S(CH_3)_2 + 2S(CH_3)_2 \rightarrow \text{"}B_2H_4{\cdot}2S(CH_3)_2\text{"} + BH_3{\cdot}S(CH_3)_2 \quad (8)$$

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(4) Hughes, R. L.; Smith, I. C.; Lawless, E. W. *Production of the Boranes and Related Research*; Holzmann, R. T., Ed.; Academic Press: New York, 1967; p 96.

(5) (a) Miller, V. H.; Ryschkewitsch, G. E. *Inorg. Synth.* **1974**, *15*, 118. (b) Ryschkewitsch, G. E.; Miller, V. H. *J. Am. Chem. Soc.* **1975**, *97*, 6258.

(6) Jock, C. P.; Kameda, M.; Kodama, G. K. *Inorg. Chem.* **1990**, *29*, 570.

(7) (a) See, for example: Shore, S. G. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; Chapter 3, p 131. (b) Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302.

(8) Coyle, T. D.; Stone, F. G. A. In *Progress in Boron Chemistry*, Vol. 1; Steinberg, H., McCloskey, A. L., Eds.; MacMillan: New York, 1964; Chapter 2.

and then

$$\text{“}B_2H_4\cdot 2S(CH_3)_2\text{”} + B_3H_7\cdot S(CH_3)_2 \rightarrow B_4H_8\cdot S(CH_3)_2 + BH_3\cdot S(CH_3)_2 + S(CH_3)_2 \tag{9}$$

The tetraborane(8) adduct of $S(CH_3)_2$, which appears in eq 9, should be a stronger borane acid than $B_3H_7\cdot S(CH_3)_2$.[9] Therefore, $B_4H_8\cdot S(CH_3)_2$ is expected to be more reactive toward “$B_2H_4\cdot 2S(CH_3)_2$” than $B_3H_7\cdot S(CH_3)_2$ is; the expansion reaction shown in eq 10 should proceed readily (cf. eq 6). As the observed

$$\text{“}B_2H_4\cdot 2S(CH_3)_2\text{”} + B_4H_8\cdot S(CH_3)_2 \rightarrow \text{“}B_5H_9\cdot S(CH_3)_2\text{”} + BH_3\cdot S(CH_3)_2 + S(CH_3)_2 \tag{10}$$

inertness of $B_5H_9$ toward $S(CH_3)_2$ suggests, “$B_5H_9\cdot S(CH_3)_2$” is expected to be unstable with respect to its dissociation:

$$\text{“}B_5H_9\cdot S(CH_3)_2\text{”} \rightarrow B_5H_9 + S(CH_3)_2 \tag{11}$$

Thus, the overall equation becomes identical with eq 1.

The $^{11}B$ signals for $B_4H_8\cdot S(CH_3)_2$ were absent in the spectra of reaction solutions during the course of the $B_5H_9$ formation. This may suggest an alternative reaction pathway by which the reaction proceeded without forming $B_4H_8\cdot S(CH_3)_2$ as an intermediate. for example, two molecules of $B_2H_4\cdot 2S(CH_3)_2$ might have reacted with each other to form $BH_3\cdot S(CH_3)_2$ and “$B_3H_5\cdot 3S(CH_3)_2$” or “$B_3H_5\cdot 2S(CH_3)_2$”, which then reacted according to the following equation to give $B_5H_9$:

$$\text{“}B_3H_5\cdot 2S(CH_3)_2\text{”} + B_2H_4\cdot 2S(CH_3)_2 \rightarrow B_5H_9 + 4S(CH_3)_2 \tag{12}$$

However, when $B_4H_8\cdot S(CH_3)_2$ was present in a $S(CH_3)_2$ solution containing $B_3H_7\cdot S(CH_3)_2$, the formation of $B_5H_9$ was accelerated and the $B_3H_7$ adduct was rapidly consumed. See Experimental Section, Part 4(iii). This fact suggests direct involvement of $B_4H_8\cdot S(CH_3)_2$. Although $B_4H_8\cdot S(CH_3)_2$ alone undergoes a change in $S(CH_3)_2$ to give $B_5H_9$ at room temperature, the rate is very much slower than that of the $B_5H_9$ formation from $B_3H_7\cdot S(CH_3)_2$.[10] The accelerated rate of $B_5H_9$ formation, therefore, may be interpreted in terms of the reaction of $B_4H_8\cdot S(CH_3)_2$ with $B_3H_7\cdot S(CH_3)_2$. These observations may then support the $B_5H_9$ formation scheme that was expressed by eqs 8–11.

**Conclusion.** Dimethyl sulfide–triborane(7) reacted slowly with dimethyl sulfide to give pentaborane(9) and dimethyl sulfide–borane(3). A two-step framework expansion scheme involving “$B_2H_4\cdot 2S(CH_3)_2$” as an intermediate was proposed for this conversion of triborane(7) to pentaborane(9) species. The proposed scheme is an extrapolation of the borane framework expansion reaction that was established earlier in this laboratory for $B_2H_4\cdot 2P(CH_3)_3$; this represents a test case for the generality and applicability of the results from our earlier studies. The assumption of “$B_2H_4\cdot 2S(CH_3)_2$” involvement will further be exploited for the syntheses of higher borane compounds.

## Experimental Section

**1. Chemicals and Equipment.** Conventional vacuum-line techniques were used throughout for the handling of volatile and air-sensitive compounds. Tetraborane(10) was prepared by the hydrolysis of $B_5H_{11}$[11] or by the treatment of $(CH_3)_4N^+B_3H_8^-$ with $BF_3$.[12] Pentaborane(11) was our laboratory stock.[13] Commercial grade dimethyl and diethyl sulfides were refluxed over calcium hydride, fractionally distilled, and then stored over molecular sieves. These were directly distilled into the vacuum line as needed. The $^{11}B$ NMR spectra were recorded on either a Varian FT-80A, XL-100, or XL-300 spectrometer. The $^{11}B$ chemical shift values for $B_5H_9$,[14a] $B_4H_8\cdot S(CH_3)_2$,[3b] $B_4H_8\cdot N(CH_3)_3$,[13] $BH_3\cdot S(CH_3)_2$,[14b] $BH_3\cdot N(CH_3)_3$,[14c] $B_3H_7\cdot N(CH_3)_3$,[15] $B_3H_7\cdot$THF,[16] $B_3H_7\cdot O(C_2H_5)_2$,[16] $B_3H_8^-$,[14d] and $B_2H_4\cdot 2N(CH_3)_3$[2b] are found in the respective references cited, and these were used to identify the components in the reaction mixtures.

**2. Isolation of $B_3H_7\cdot S(CH_3)_2$. (i) Directly from $B_4H_{10}$.** A solution containing 0.44 mmol of $B_4H_{10}$ in ca. 3 mL of $CH_2Cl_2$ was prepared in a 10 mm o.d. Pyrex tube which was equipped with a Teflon valve, and then a 0.935 mmol sample of $S(CH_3)_2$ was condensed into the tube at −197 °C. The tube was then allowed to warm to −80 °C and shaken to mix the solution. Conversion of $B_4H_{10}$ to $B_3H_7\cdot S(CH_3)_2$ and $BH_3\cdot S(CH_3)_2$ was complete at this temperature. The mixture was allowed to warm to room temperature and was fractionated through −20 and −197 °C traps under dynamic vacuum. The −20 °C trap was Y-shaped and equipped with a Teflon valve on each of the two upper arms and was attached to the vacuum line by ball-socket O-ring joints. After 5 h of continuous pumping, the −20 °C trap was removed from the line and weighed to determine the yield of $B_3H_7\cdot S(CH_3)_2$ collected in it: 36.5 mg (0.36 mmol) or 82% yield. Then, dichloromethane was condensed into the lower arm of the Y-shaped trap to make a solution of the product, and the tube was inserted in the probe of the NMR spectrometer for purity check. No impurity was found in the spectrum. The $B_3H_7$ adduct retained $BH_3\cdot S(CH_3)_2$ strongly; $BH_3\cdot S(CH_3)_2$ was often found as an impurity present in varying amounts depending upon the length of pumping time. The triborane adduct did not decompose when the product was handled at room temperature for weighing and recording of the NMR spectrum. The mixing ratio of $B_4H_{10}$ and $S(CH_3)_2$ should be kept close to the stoichiometric value; the use of $S(CH_3)_2$ in a large excess results in the formation of $B_5H_9$ at the expense of $B_3H_7\cdot S(CH_3)_2$ at room temperature. See part 4(ii) of this section.

A pure sample of $B_3H_7\cdot S(C_2H_5)_2$ was prepared in a manner similar to that described above for the $B_3H_7\cdot S(CH_3)_2$ preparation. The temperature of $BH_3\cdot S(C_2H_5)_2$ removal had to be considerably higher than that for $BH_3\cdot S(CH_3)_2$. At −20 °C, even after 8 h of pumping, the removal of $BH_3\cdot S(C_2H_5)_2$ was not complete. The product became free of $BH_3\cdot S(C_2H_5)_2$ after an additional 4-h pumping period at room temperature.

**(ii) From $B_3H_7\cdot$THF.** A sample of $B_3H_7\cdot$THF was prepared from 0.55 mmol of $B_4H_{10}$ and excess tetrahydrofuran[17] in a 10 mm o.d. Pyrex tube and was dissolved in ca. 3 mL of $CH_2Cl_2$ at room temperature. Then, the solution was treated with 0.63 mmol of $S(CH_3)_2$ at room temperature. The $^{11}B$ NMR spectrum of the solution showed the product to be $B_3H_7\cdot S(CH_3)_2$ contaminated by a trace of $BH_3\cdot S(CH_3)_2$. The solution was unchanged after standing for 3 h at room temperature.

**3. $B_3H_7\cdot$THF in THF.** A 0.38-mmol sample of $B_3H_7\cdot$THF was prepared from $B_4H_{10}$ and tetrahydrofuran[17] in an 8 mm o.d. Pyrex tube, and then it was dissolved in 1 mL of THF at room temperature. The $^{11}B$ signals of $B_3H_7\cdot$THF at ambient temperature were observed. After the tube had been kept in an ice bath for 10 days, the $^{11}B$ spectrum remained unchanged.

**4. Formation of $B_5H_9$ from $B_3H_7\cdot S(CH_3)_2$ and $S(CH_3)_2$. (i) Mixing Molar Ratio 1.0:3.5 in $CH_2Cl_2$.** A 0.546-mmol sample of $B_3H_7\cdot S(CH_3)_2$ was weighed out in a Y-shaped trap, which was described in part 2(i) of this section, and ca. 3 mL of $CH_2Cl_2$ and 1.920 mmol of $S(CH_3)_2$ were condensed into the tube. The $^{11}B$ NMR spectrum of the solution was recorded at ambient temperature by inserting the lower arm of the Y-tube into the probe of the spectrometer. The spectrum showed only the signals of $B_3H_7\cdot S(CH_3)_2$. Three and a half hours later, the signals of $B_5H_9$ were discerned. At this time, a *faint* signal was seen at −35 ppm ($B_4H_8\cdot S(CH_3)_2$?). Four days later, the −35 ppm signal could not be seen; the $B_5H_9$ signals were stronger than before, but the $B_3H_7\cdot S(CH_3)_2$ signals were still overwhelmingly strong. The solution remained clear (no precipitate) and colorless all the time, and no hydrogen gas was found in the reaction tube.

**(ii) $S(CH_3)_2$ as Solvent.** A 0.781-mmol sample of $B_3H_7\cdot$THF was prepared[17] in a 9 mm o.d. Pyrex tube, and a large excess of $S(CH_3)_2$ (ca. 3 mL) was condensed into the tube. A series of $^{11}B$ NMR spectra of the mixture at room temperature is presented in Figure 1. It is noted that, by the time the first spectrum was recorded, a fair amount of $B_5H_9$ had been produced. The solution remained clear and colorless all the time, and no hydrogen gas was found in the reaction tube.

The initial rapid formation of $B_5H_9$ was consistently observed whenever $B_4H_{10}$ was dissolved in $S(CH_3)_2$ at room temperature. At 0 °C the $B_5H_9$ formation was slow; below −20 °C the reaction did not occur.

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[9] (a) Parry, R. W.; Edwards, L. J. *J. Am. Chem. Soc.* **1950**, *81*, 3554. (b) Jock, C. P. Master's Thesis, University of Utah, Salt Lake City, UT, 1987.

[10] Ishii, M.; Kodama, G. Unpublished observation; manuscript in preparation.

[11] Norman, A. D.; Schaeffer, R. *Inorg. Chem.* **1965**, *4*, 1225.

[12] Toft, M. A.; Leach, J. B.; Himpsl, F. L.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1952.

[13] Dodds, A. R.; Kodama, G. *Inorg. Chem.* **1979**, *18*, 1465.

[14] Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; W. A. Benjamin: New York, 1969: (a) p 100; (b) p 454; (c) p 459; (d) p 58.

[15] Dodds, A. R.; Kodama, G. *Inorg. Chem.* **1976**, *15*, 741.

[16] Kodama, G. *Inorg. Chem.* **1975**, *14*, 452.

[17] Kodama, G.; Parry, R. W.; Carter, J. C. *J. Am. Chem. Soc.* **1959**, *81*, 3534.

**(iii) $B_4H_{10}$ and $B_5H_{11}$ in $S(CH_3)_2$.** A 0.542-mmol sample of $B_4H_{10}$ and a 0.534-mmol sample of $B_5H_{11}$ were placed in a 10 mm o.d. Pyrex tube and were dissolved in 1.5 mL of $S(CH_3)_2$ at -80 °C. At this temperature the solution gave the signals of $B_3H_7{\cdot}S(CH_3)_2$, $B_4H_8{\cdot}S(CH_3)_2$, and $BH_3{\cdot}S(CH_3)_2$. As the tube was allowed to warm to +20 °C, the $B_5H_9$ and $BH_3{\cdot}S(CH_3)_2$ signals grew rapidly at the expense of the $B_3H_7{\cdot}S(CH_3)_2$ and $B_4H_8{\cdot}S(CH_3)_2$ signals. Seventeen hours later, the signals of $B_3H_7{\cdot}S(CH_3)_2$ were not detectable and weak signals of $B_4H_8{\cdot}S(CH_3)_2$ were seen. The solution remained clear and colorless all the time, and no hydrogen gas was found in the reaction tube. Eleven days later, the spectrum consisted of the signals of $B_5H_9$ (strong), $BH_3{\cdot}S(CH_3)_2$ (strong), $B_4H_8{\cdot}S(CH_3)_2$ (very weak), and others (faint and unidentified). The solution was clear and colorless.

**5. $B_4H_{10}$ in Diethyl Ether.** A mixture of $B_4H_{10}$ and diethyl ether in a 1:3.5 molar ratio was prepared at -80 °C in a 5 mm o.d. NMR sample tube, and its $^{11}B$ NMR spectra were recorded. Below -10 °C, the spectra contained only the signals of $B_4H_{10}$. At -10 °C, the $B_2H_6$ signal began to appear slowly. As the temperature was raised to 15 °C, weak signals of $B_5H_9$ became discernible. No signals of $B_3H_7{\cdot}O(C_2H_5)_2$ could be detected. The solution was clear and colorless.

**6. Reaction of $B_3H_7{\cdot}S(CH_3)_2$ with $B_2H_4{\cdot}2N(CH_3)_3$.** A sample of $B_3H_7{\cdot}S(CH_3)_2$ was prepared from 0.481 mmol of $B_4H_{10}$ in a 10 mm o.d. Pyrex tube that was equipped with a Teflon valve. The sample was dissolved in ca. 2 mL of $CH_2Cl_2$ in the tube, and the solution was frozen at -197 °C. Then, a 0.291-mmol sample of $B_2H_4{\cdot}2N(CH_3)_3$ was introduced into the tube under an atmosphere of nitrogen gas. The tube was allowed to warm to 0 °C, the contents were mixed well, and the $^{11}B$ spectra of the resulting solution were recorded. At 0 °C, the signals of $B_4H_8{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ were seen in addition to those of the initial reactants. The change, however, was very slow. As the temperature was raised to +20 °C, $B_2H_4{\cdot}2N(CH_3)_3$ disappeared in 10 min, the signals of $B_3H_7{\cdot}S(CH_3)_2$ became weaker, and those of $B_4H_8{\cdot}N(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ became stronger. Weak signals of $B_3H_7{\cdot}N(CH_3)_3$ and $B_3H_8^-$ were detectable. The solution was clear and colorless.

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# Single-Crystal Polarized Spectra in the Near-Infrared Region: A Local-Mode Analysis of the Spectra of $BaCl_2{\cdot}2H_2O$

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The near-infrared (near-IR) spectra of single crystals of $BaCl_2{\cdot}2H_2O$ and its partially deuterated analogue have been recorded at 10 K in polarized light. Two crystallographically independent water molecules are present in these crystals. Each water gives rise to numerous, often well-resolved overtone and combination features. The bands in the first and second stretch overtone regions were analyzed by using local-mode theory. The local-mode anharmonicity, $X$, and harmonic frequency, $\omega$, were evaluated for each of the oscillators on the two water molecules, as well as the two local-mode coupling constants, $\lambda$. The local-mode parameters so obtained are substantially altered from the values reported for gas-phase water. This is a consequence of hydrogen-bond formation in the crystal.

## Introduction

In several recent articles we have shown that the near-infrared (near-IR) spectra of water in crystals are distinctive and that they are strongly influenced by the chemical environment in which the water is located.[1-3] In some of the cases that we have considered up to now the water molecules are highly oriented with respect to the crystal axes. The bands are strongly polarized in such circumstances, and from the polarization and energy of the bands we were able to clarify the nature of some librational modes that could not be assigned on the basis of the fundamental spectra.[2]

Crystals in which the water molecules are less well oriented with respect to the crystal axes are more common. In this article we examine the polarized near-IR spectra of $BaCl_2{\cdot}2H_2O$ at 10 K. This solid belongs to space group $P2_1/c$ ($C_{2h}^5$, $Z = 4$).[4] Sheets of $BaCl_2{\cdot}2H_2O$ units form a layered arrangement overlying each other along the crystal $b$ axis. The positions of all atoms have been determined by neutron diffraction.[5] The two water molecules, which we shall henceforth call water(I) and water(II), are on $C_1$ sites and are not related by crystal symmetry. The angles and distances characterizing the hydrogen bonds in this substance have been codified by Brink[6] and are shown in Figure 1; we use his numbering system in this paper. Both O–H bonds of water(I) engage in normal hydrogen bonds to chloride ions. One O–H bond of water(II) forms a normal hydrogen bond, while the other engages in relatively weak, bifurcated hydrogen bonds to two neighboring chloride ions at different distances. There are thus four different O-H oscillators in $BaCl_2{\cdot}2H_2O$, and each has distinctive hydrogen-bond properties.

It has been amply shown over the last decade that local-mode theory is most convenient for describing the higher energy vibrational spectra of gas-phase water. In this article we extend the local-mode theory developed for $C_{2v}$ symmetry[7-9] to cases such as $BaCl_2{\cdot}2H_2O$, in which the local oscillators are not related to one another by symmetry. We also show that the local-mode theory can give a good account of the fundamental spectra of water in low-symmetry sites.

## Experimental Section

Reagent grade $BaCl_2{\cdot}2H_2O$ was slowly recrystallized from water to yield crystals suitable for optical spectroscopy. Partially deuterated crystals were prepared by slow evaporation of an $H_2O/D_2O$ solution of $BaCl_2{\cdot}2H_2O$ over concentrated $H_2SO_4$ in a desiccator. The crystals form as large rectangular plates showing the [010] face.[10]

The crystals were mounted in a Displex cryogenic refrigerator, and near-IR spectra were recorded on a Varian 2300 spectrophotometer at 290 and 10 K. Light in both sample and reference beams was polarized by using a pair of Glan–Thompson prisms. The light beam was parallel to the crystal $b$ axis ($C_2$) and was polarized with its electric vector along

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(1) McCarthy, P. J.; Walker, I. M. *Spectrochim. Acta* **1983**, *39A*, 827.
(2) Walker, I. M.; McCarthy, P. J. *Can. J. Chem.* **1986**, *64*, 1012.
(3) Walker, I. M.; McCarthy, P. J. *J. Phys. Chem.* **1989**, *93*, 2230.
(4) Jensen, A. T. *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **1945**, *22*, 22. See also: Wyckoff, R. W. G. *Crystal Structures*; Interscience: New York, 1965; Vol. 3, p 594.
(5) Padmanabhan, V. M.; Busing, W. R.; Levy, H. A. *Acta Crystallogr., Sect. A* **1963**, *A26*, 16.
(6) Brink, G. *Spectrochim. Acta* **1972**, *28A*, 1151.
(7) Child, M. S.; Halonen, L. *Adv. Chem. Phys.* **1984**, *57*, 1.
(8) Mills, I. M.; Robiette, A. G. *Mol. Phys.* **1985**, *56*, 743.
(9) Child, M. S. *Acc. Chem. Res.* **1985**, *18*, 45.
(10) Groth, P. *Chemische Krystallographie*; Wilhelm Engelmann Verlag: Leipzig, Germany 1906; Vol. 1, pp 239 f.

0020-1669/90/1329-0820$02.50/0