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2n Framework Electron Compounds: The Thermal Decomposition of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$ Revisited. Evidence for the Formation of the Polyhedral Boron Halides, B_nCl_n , $n = 13-20$

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The thermal decomposition of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$ has been reexamined under dynamic vacuum. The major nine-vertex products are $\text{H}_2\text{B}_9\text{Cl}_7$, HB_9Cl_8 , and B_9Cl_9 . At ambient temperature any differences in the boron NMR chemical shifts of the halogen-substituted boron atoms in HB_9Cl_8 are unresolved at 28.9 MHz. A variety of other products are also formed during the decomposition. Among the species observed are $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$, and $\text{B}_{12}\text{Cl}_{12}$. Mass spectrometric evidence indicates the existence of the boron halides, B_nCl_n , $n = 13-20$.

Introduction

The polyhedral boron halides are a series of molecular cluster compounds of the formula B_nX_n , where $n = 4, 8-12$ for $\text{X} = \text{Cl}$ and $n = 7-10$ for $\text{X} = \text{Br}$. They and their derivatives are of interest since there are only $2n$ framework electrons in the bonding framework molecular orbitals rather than the $2n + 2$ electrons usually associated with main-group or substituted main-group deltahedral clusters ($n > 4$).^{1,2}

The first well-characterized derivative of any of the larger $2n$ framework electron polyboranes was octachlorononaborane, HB_9Cl_8 .³ However, the synthesis and some of the properties that have been attributed to HB_9Cl_8 are singular in several respects when compared to those of B_9Cl_9 and B_9Br_9 .^{4,5}

One unusual feature was the boron NMR of " HB_9Cl_8 ". The proton-decoupled spectrum of " HB_9Cl_8 ", which was recorded at 19.2 MHz, indicated four quite distinct magnetic environments for the boron atoms.^{3,6} In contrast, at ambient temperature the observed spectra of B_9Cl_9 and B_9Br_9 , obtained at 28.9 or 115 MHz, are singlets.^{4,5}

Additionally, the solid-state structures of B_9Cl_9 and B_9Br_9 have been shown to be based upon a tricapped trigonal prism,^{7,8} a geometry that corresponds to a deep minimum in the potential energy surface for the related nine-atom families ML_9 and M_9X_9 .⁹ For HB_9Cl_8 , however, a framework atom structure based upon a tricapped trigonal prism was unambiguously ruled out in solution by the boron NMR data.^{6,10}

Finally, during the preparation of HB_9Cl_8 from the thermal decomposition of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10} \cdot 2\text{H}_2\text{O}$ at 260 °C, no evidence for molecular cluster compounds other than HB_9Cl_8 was reported. Yet in the seemingly analogous preparation of $\text{CH}_3\text{B}_9\text{Br}_8$ from the thermal decomposition of $[(\text{C}_2\text{H}_5)_3\text{N}-\text{H}]_2\text{B}_{10}\text{Br}_{10}$ at 430 °C numerous other $2n$ framework electron clusters were simultaneously formed.¹¹

We have reexamined the thermal decomposition of the aqueous salt of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$. Three aspects of the reaction were of most interest: (1) Was the ¹¹B NMR of HB_9Cl_8

indeed indicative of a static molecule? (2) Did the spectra rule out a tricapped-trigonal-prismatic configuration of boron atoms? (3) Were clusters other than HB_9Cl_8 formed in this reaction?

Experimental Section

General Considerations. All manipulations of air-sensitive material were carried out with either a standard vacuum line equipped with Teflon valves or a nitrogen-atmosphere glovebox. Fourier transform ¹¹B NMR spectra were acquired with Bruker HFX-90 or WP-80 spectrometers, which operate at 28.9 and 25.7 MHz, respectively. Chemical shifts are referenced to external $\text{BF}_3 \cdot \text{OEt}_2$; positive values are deshielded relative to the standard. Infrared spectra are from a PE 521 spectrophotometer. Mass spectra and exact mass data were obtained from an AEI MS30 double-focusing instrument at 70 eV; the ionization chamber was at ambient temperature.

Decaborane (Alfa-Ventron) was sublimed immediately prior to use. Triethylamine, bp 89 °C, was dried over KOH and then distilled from a solution containing 2% phenyl isocyanate. *m*-Xylene was distilled before using. Carbon tetrachloride and *n*-pentane were dried over CaH_2 and then filtered. Chlorine (Matheson) was used as received.

Preparation of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10} \cdot n\text{H}_2\text{O}$. Triethylammonium decahydrodecaborate, $(\text{HNEt}_3)_2\text{B}_{10}\text{H}_{10}$, was prepared by the reaction between decaborane (4.76 g) and triethylamine (15 mL); the solvent was *m*-xylene (100 mL). After 3 h at 100 °C followed by 5 h at reflux, the slightly yellow solid formed was removed by filtration, washed with isopropyl alcohol and then ether, and recrystallized from 50% aqueous ethanol. The purity of the white material obtained, 9.7 g (77%), was assessed by ¹¹B NMR; no resonances other than those due to $\text{B}_{10}\text{H}_{10}^{2-}$ were evident. The dicesium salt, 10.6 g (92%), was prepared by cation exchange with CsCl and then dissolved in water (150 mL). Chlorine was passed through the solution until neither the BH stretch near 2480 cm^{-1} in the IR spectrum (KBr pellet) nor any BH resonance near -29 ppm was observed in the boron NMR. Dicesium decachlorodecaborate, $\text{Cs}_2\text{B}_{10}\text{Cl}_{10}$ (18.1 g), was recovered in 90% yield.

Dicesium decachlorodecaborate (4.89 g) was then dissolved in the minimum amount of water, and the temperature of the solution was raised to 80 °C. The solution was slowly passed through an acid-exchange column (Dowex 50W-X4 in the hydrogen form), which was maintained at 60 °C. The portion of the effluent that was strongly acidic (pH < 1) was collected and, under vacuum, water was removed at ambient temperature until a volume of ca. 7 mL was reached.

Thermal Decomposition of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10} \cdot n\text{H}_2\text{O}$. The apparatus employed during the thermal decomposition of the acid salt is depicted in Figure 1. The aqueous solution of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$ prepared above was placed in a 12.5 mm o.d. Pyrex tube and under dynamic vacuum the remaining uncomplexed water was removed at ambient temperature. By means of the external tube furnace the temperature was raised to 150 °C until no further evolution of water occurred. During the last process the originally white sample turned a pale violet color.

After water was no longer observed, the temperature of the sample was slowly raised to 260 °C, where the onset of the reaction was marked by the formation of HCl, H_2O , BCl_3 , and material that was noncondensable at -196 °C. Within 5 min of the attainment of 260 °C, a purple sublimate began to appear on the walls of the tube.

During the course of the decomposition, 4-96 h, several bands of sublimate formed above the furnace as indicated in Figure 1. Nearest

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- (4) N. A. Kutz, and J. A. Morrison, *Inorg. Chem.*, **19**, 3295 (1980).
- (5) T. Davan, Ph.D. Thesis, University of Illinois, Chicago, 1982; T. Davan and J. A. Morrison, submitted for publication in *Inorg. Chem.*
- (6) The original boron NMR data for HB_9Cl_8 indicated four chemical shifts of 68.4, 63.5, 58.7, and 29.8 ppm in the intensities of 1:6:1:1, respectively. The last resonance was split by one proton, $^1J_{\text{B-H}} = 159$ Hz.
- (7) M. B. Hursthouse, J. Kane, and A. G. Massey, *Nature (London)*, **228**, 659 (1970).
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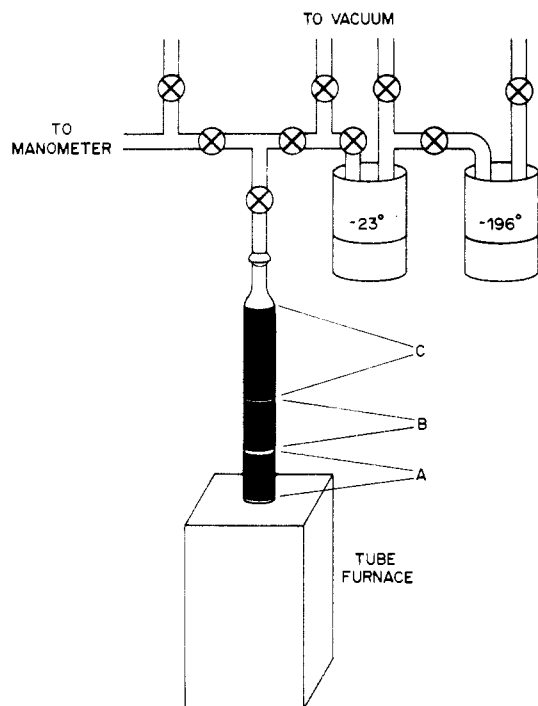


Figure 1. Schematic diagram of the reaction system indicating the location of the sublimed bands obtained during the thermal decomposition of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$.

the hot zone was an orange band, A; slightly higher in the tube was a purple sublimate, B.

These bands consisted of mixtures containing variable amounts of polyhedral boron halides. Four of these halides are readily identifiable: $\text{B}_{12}\text{Cl}_{12}$, $m/e = 555$ ($\delta = 78$); $\text{B}_{11}\text{Cl}_{11}$, $m/e = 509$ ($\delta = 69.9$); $\text{B}_{10}\text{Cl}_{10}$, $m/e = 463$ ($\delta = 63.5$); B_9Cl_9 , $m/e = 416$ ($\delta = 58.5$). In each case the chemical shifts as well as the positions and intensities of the molecular ion envelopes are identical, within experimental error, with those of authentic samples which had been prepared by the thermal decomposition of B_2Cl_4 .⁵ Although the yields of products vary considerably with the conditions utilized in the decomposition (see below) mass spectrometric examination of one "representative" reaction indicated that the approximate ratios of these boron halides in the purple band were 2% $\text{B}_{12}\text{Cl}_{12}$, 15% $\text{B}_{11}\text{Cl}_{11}$, 73% $\text{B}_{10}\text{Cl}_{10}$, and 10% B_9Cl_9 . Attempted separations with standard vacuum sublimation apparatus resulted in only partial separation; complete separation was not effected.

Beginning about 6 in. above the furnace was a broad yellow band, C, which, if the decomposition was completed in ca. 5 h, mass spectrometry and boron NMR indicate contained 11% $\text{B}_{10}\text{Cl}_{10}$, 39% B_9Cl_9 , and 50% HB_9Cl_8 . If longer reaction times were employed, less HB_9Cl_8 and B_9Cl_9 were observed. Although B_9Cl_9 is not sensibly volatile in a standard vacuum line, HB_9Cl_8 and B_9Cl_9 were no longer present in the yellow band if the reaction tube was maintained under dynamic vacuum for prolonged periods, 2–3 weeks. As determined by boron NMR, the yellow-orange material remaining is essentially pure (>95%) $\text{B}_{10}\text{Cl}_{10}$.

In the trap held at -23°C was a yellow to orange mixture of three boron-containing compounds. In agreement with the original report,³ boron NMR spectra of the material contain four distinct, observable resonances at 69.8, 63.2, 58.3, and 29.8 ppm; the last resonance is split by one hydrogen, $^1J_{\text{B-H}} = 165$ Hz. However, typically the intensities of the resonances at 69.8 and 58.3 ppm are not equal (see Figure 2). Further, in spectra obtained from different reactions, the intensity ratios of the absorptions at 69.8, 63.2, and 58.3 ppm varied from 30:65:5 to 4:60:36 as discussed below (see Figure 2). Each time a sample rich in the material that gave the resonance at 58.3 ppm was moved from one portion of the vacuum line to another, a yellow material, later identified as B_9Cl_9 , was left as a residue. In NMR spectra that were then obtained, the resonance at 58.3 ppm was invariably diminished relative to that at 69.8 ppm.

Mass spectra of the mixtures obtained from the trap maintained at -23°C indicated three strong molecular ions, assigned to B_9Cl_9 , HB_9Cl_8 , and $\text{H}_2\text{B}_9\text{Cl}_7$, along with ions in which the molecular ion had

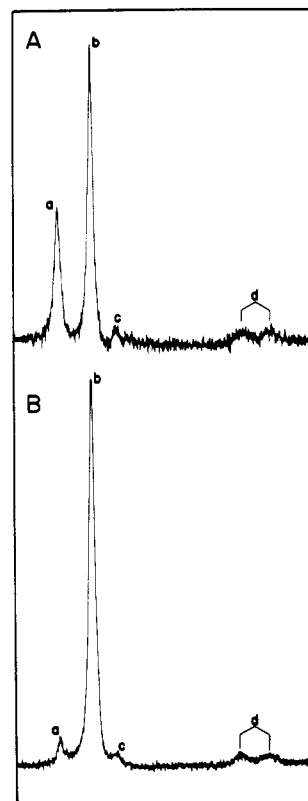


Figure 2. (A) ^{11}B NMR spectrum of the mixture obtained when $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$ decomposes under conditions such that the amount of $\text{H}_2\text{B}_9\text{Cl}_7$ is maximized (see text). The relative amounts of $\text{H}_2\text{B}_9\text{Cl}_7$ (a, $\delta = 69.8$), HB_9Cl_8 (b, d, $\delta = 63.2, 29.8$, $J = 165$ Hz), and B_9Cl_9 (c, $\delta = 58.3$) are 32:64:4. (B) ^{11}B NMR spectrum of octachlorononaborane after separation. The relative amounts of $\text{H}_2\text{B}_9\text{Cl}_7$, HB_9Cl_8 , and B_9Cl_9 are now 3:96:1.

lost BCl_3 . Mass spectrum for B_9Cl_9 : B_9Cl_9^+ , $m/e = 416$ (30%); $\text{B}_9\text{Cl}_9 - \text{BCl}_3^+$, $m/e = 299$ (100%). Mass spectrum for HB_9Cl_8 : HB_9Cl_8^+ , $m/e = 382$ (50%); $\text{HB}_9\text{Cl}_8 - \text{BCl}_3^+$, $m/e = 265$ (100%). Mass spectrum for $\text{H}_2\text{B}_9\text{Cl}_7$: $\text{H}_2\text{B}_9\text{Cl}_7^+$, $m/e = 347$ (60%); $\text{H}_2\text{B}_9\text{Cl}_7 - \text{BCl}_3^+$, $m/e = 230$ (100%). Each ion envelope was found to have the calculated isotopic intensities.

Octachlorononaborane was separated, with difficulty, by utilizing a standard low-temperature column with the head temperature maintained at -8°C . The infrared spectrum of HB_9Cl_8 (CCl_4 solution) contains major absorptions at 1030 (s) and 740 (s) cm^{-1} . The mass spectrum of the compound contains mass envelopes centered at m/e 382 (HB_9Cl_8 (50%)), 299 (B_9Cl_9 (81%)), 265 (HB_8Cl_7 (100%)), 182 (B_7Cl_7 (53%)), and 171 (B_6Cl_6 (62%)), each ion in the envelope having the expected intensity. High-resolution mass measurements at m/e 383 confirmed the elemental composition $^1\text{H}^{10}\text{B}^{11}\text{B}_8^{35}\text{Cl}_6^{37}\text{Cl}_2$ (observed 382.8385, calculated 382.8401; $\Delta m/e = 4.2$ ppm) while those at m/e 265 confirmed the composition $^1\text{H}^{10}\text{B}^{11}\text{B}_7^{35}\text{Cl}_4^{37}\text{Cl}$ (observed 264.9272, calculated 264.9272; $\Delta m/e = 0$). Boron NMR spectra, at 28.9 MHz, indicate only two types of boron environments. One absorption is found at 63.2 ppm (intensity 8) and one is found at 29.8 ppm (intensity 1); $J_{\text{B-H}} = 164$ Hz. The yields and relative yields of the nonaboranes are discussed below.

In addition to the polyboranes, other products of the reaction include a mixture of H_2O , HCl , and BCl_3 , which was found in the trap held at -196°C . Additionally, a white hygroscopic material, 0.2–0.8 g, remained at the bottom of the reaction tube. When dissolved in water, this nonvolatile material gave an NMR spectrum identical with that of boric acid.

To assess the thermal stability of HB_9Cl_8 , a sample of octachlorononaborane (0.1 g) was placed in a 5-mm tube and dissolved in CCl_4 . The mixture was sealed with a torch and then heated to 100°C for 6 h. Later the sample was held at 170°C for 15 h. No change in the boron NMR spectrum was observed.

Although HB_9Cl_8 , B_9Cl_9 , and $\text{B}_{10}\text{Cl}_{10}$ are always the species formed in highest yields, 5–15%, during the thermal decomposition of $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$, the relative amounts of the boranes recovered vary

Table I. Comparison of Experimental and Calculated Mass Spectra for $H_nB_nCl_{9-n}$, $n = 0-2$, and B_nCl_n , $n = 13-20^a$

compd	M ⁺		(M - BCl ₃) ⁺		(M - 2BCl ₃) ⁺		(M - 3BCl ₃) ⁺	
	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
B ₉ Cl ₉	416	416	299	299				
HB ₉ Cl ₈	382	382	265	265				
H ₂ B ₉ Cl ₇	347	347	230	230				
B ₁₃ Cl ₁₃	601	601	484	484	367	...		
B ₁₄ Cl ₁₄	648	648	530	530	413	413		
B ₁₅ Cl ₁₅	694	...	577	577	460	460	342	...
B ₁₆ Cl ₁₆	740	...	623	623	506	506	389	389
B ₁₇ Cl ₁₇	786	...	669	669	552	551	435	434
B ₁₈ Cl ₁₈	833	...	716	...	598	598	481	481
B ₁₉ Cl ₁₉	879	...	762	...	645	645	527	527
B ₂₀ Cl ₂₀	925	...	808	...	691	691	574	574

^a Most intense peaks, calculated from normal isotopic abundances of boron and chlorine.

extensively with the thermal history of the sample. By weight 5–20% of the original material is later recovered as the white, nonvolatile boron oxide (or oxychloride). Approximately 25% by weight of the sample is found as HCl, H₂O, and BCl₃ or lost as H₂. Typically, roughly 50% of the material is found as 2n framework electron clusters.

If the reaction is carried out at 260 °C and the temperature is raised to 300 °C very slowly (over a period of several days), the relative amounts of HB₉Cl₈ and especially H₂B₉Cl₇ isolated are dramatically increased (see Figure 2). When the furnace is rapidly heated, requiring only 3–4 h to reach 300 °C, the amounts of polyhedral boron perchlorides, especially those with more than nine boron atoms, are increased at the expense of the hydrides. A "most typical" yield of HB₉Cl₈ is 10–15%.

As indicated above, an unsuccessful attempt was made to separate the boron halides, B_nCl_n, $n = 9-12$, that were obtained from bands A and B (Figure 1) by means of vacuum sublimation. The samples had been prepared by removing all material volatile at temperatures of 60–150 °C. In the spectra of those mixtures that were of equal or lesser volatility than B₁₂Cl₁₂,¹² especially those originating from the orange band, A, were a very reproducible series of ions at high m/e ratios. The ions observed are collected in Table I along with analogous ions from B₉Cl₉, HB₉Cl₈, and H₂B₉Cl₇.

The ions of highest intensity in this region of the mass spectra were those ascribed to B₁₆Cl₁₆. The ions assigned to B₁₉Cl₁₉ and B₂₀Cl₂₀ were present in lesser amounts. Those due to B₁₃Cl₁₃, B₁₄Cl₁₄, B₁₇Cl₁₇, and B₁₈Cl₁₈ were present in the smallest intensities.

In each case the spectra indicated that the samples were mixtures; for example, all the ions indicated for B_nCl_n, $n = 14-17$, in Table I might be obtained from one sample and those from B₁₈Cl₁₈ through B₂₀Cl₂₀ in a second. Boron NMR of the fractions contained resonances from 48 to 82 ppm deshielded from BF₃·OEt₂.¹³

Results and Discussion

Although the synthesis and isolation of the acid salt of B₁₀Cl₁₀²⁻ proceed essentially as described previously,^{3,14} the thermal decomposition of (H₃O)₂B₁₀Cl₁₀· n H₂O, at least under the conditions described above, yields not one but a great number of 2n framework electron clusters. The most volatile of the polyhedral species detected were H₂B₉Cl₇, HB₉Cl₈, and B₉Cl₉. These compounds are obtained as a mixture that is not easily separated as evidenced by the fact that in the original report "HB₉Cl₈" which had been sublimed three times still consisted of a mixture of 14% H₂B₉Cl₇, 75% HB₉Cl₈, and 11% B₉Cl₉. It was the spectrum of this mixture that incorrectly gave rise to the supposition that the structure of HB₉Cl₈ could not be based upon a tricapped trigonal prism and that the molecule was necessarily static in solution.

In the present study, samples of HB₉Cl₈ were exposed to temperatures of 170 °C for times up to 15 h, in part to determine if the original mixtures of H₂B₉Cl₇, HB₉Cl₈, and B₉Cl₉ could have risen from the disproportionation of HB₉Cl₈. No reaction was observed. This experiment does indicate that HB₉Cl₈ possesses a reasonable thermal stability.

The demonstration that the previously obtained "HB₉Cl₈" was a mixture resolves many of the questions raised by the earlier report. In particular, at 28.9 MHz the boron NMR of authentic HB₉Cl₈ indicates an identical chemical shift for all of the halogen-substituted boron atoms at ambient temperature as has been observed for the perchlorides B₉Cl₉ and B₉Br₉.^{4,5} The mass spectrum of HB₉Cl₈ contains no ions at m/e values greater than that of the molecular ion.¹⁵ Other inconsistencies such as the variation in molecular weights originally noted can be explained most easily by a variation in the composition of the mixture.

As described in the Experimental Section, the relative amounts of the various cage compounds produced during the decomposition can be influenced by the conditions under which the reaction is carried out. The relative yield of H₂B₉Cl₇, for example, can be enhanced by decomposing the substrate very slowly, keeping the temperature only slightly above that required for the reaction to proceed. Alternatively, the relative amount of B₉Cl₉ present can be increased by decomposing the mixture at temperatures substantially above the minimum. A similar variation in product yield was observed during the thermal decomposition of (Et₃NH)₂B₁₀Br₁₀, where relatively large amounts of the disubstituted (CH₃)₂B₉Br₇ were formed only if the temperature was carefully regulated.¹¹

That macroscopic amounts of hydride-substituted derivatives of only one sized cluster, the nine-vertex cluster, are isolated from this reaction is presumably a reflection of the inherent stability of the nine-atom polyhedron when 2n framework electrons are present. The nine-atom framework compounds, B₉Cl₉ and B₉Br₉, are known to be the most thermally stable of the perchlorinated clusters B_nX_n, $n \leq 12$,^{4,5} and the larger clusters B₁₀Cl₁₀, B₁₁Cl₁₁, and B₁₂Cl₁₂ have been shown to thermally decompose to yield B₉Cl₉.⁴ Nonachlorononaborane and B₉Br₉ are also the most resistant to attack by reagents such as Lewis bases.^{4,5} Thus it appears quite reasonable that the hydride-containing compounds actually isolated in this study would be derivatives of the most stable cluster, the nine-atom cage. It seems likely that hydride-containing derivatives of other sized clusters may well form during the reaction, but these would be expected to be less robust and less likely to survive exposure to the conditions (260–300 °C in the presence of HCl and H₂O) that occur during the decomposition.

The formation of the larger clusters B₁₀Cl₁₀, B₁₁Cl₁₁, and B₁₂Cl₁₂ is one of the more interesting aspects of this reaction since only nine-vertex cages had previously been isolated from the thermal decomposition of salts of either of the halogenated borane anions B₁₀Cl₁₀²⁻ or B₁₀Br₁₀²⁻.^{3,11,16} Even though the yields of B₁₀Cl₁₀, ca. 5%, are less attractive than those from the alternative preparation, the thermal decomposition of B₂Cl₄, this reaction may still prove to be an effective source of B₁₀Cl₁₀ since purification merely required prolonged pumping upon the appropriate sample (band C).

Because of the large numbers of boron and halogen atoms that are present, mass spectrometry is the single most reliable tool for identifying the neutral boron halides.¹⁷ In all cases yet known, these compounds exhibit a definite molecular ion, along with a series of ions in which the molecular ion has lost

(12) Dodecachlorododecaborane, B₁₂Cl₁₂, sublimes at 80 °C.⁵

(13) The chemical shifts of B₁₁Cl₁₁ and B₁₂Cl₁₂ are 69.5 and 77.7 ppm, respectively.

(14) W. H. Knoch, H. C. Miller, J. C. Sauer, J. H. Balthus, Y. T. Chia, and E. L. Muettterties, *Inorg. Chem.*, **3**, 159 (1964); M. F. Hawthorne and R. L. Pilling, *Inorg. Synth.*, **9**, 16 (1967).

(15) Originally, ions with m/e ratios as high as m/e 460–470 (B₁₀Cl₁₀) were detected in the mass spectrum of HB₉Cl₈.

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(17) A. G. Massey, *Chem. Br.*, **16**, 588 (1980).

an integral number of BCl_3 groups. For example, for all of the polyhedral boron chlorides, B_nCl_n , $n = 8-12$, the base peak of the mass spectrum is the appropriate molecular ion less BCl_3 .⁴ As shown in Table I, for each of the nine-atom clusters discussed above the molecular ion and the molecular ion less BCl_3 is clearly evident.

Within this context the mass spectral data shown in the remainder of Table I are extremely provocative. Given the mass range of the spectrometer employed (AEI MS30), these ions are precisely those that would be predicted from the polyhedral boron halides B_nCl_n , $n = 13-20$. Of these ions, those ascribed to $\text{B}_{16}\text{Cl}_{16}$ and $\text{B}_{19}\text{Cl}_{19}$, along with $\text{B}_{20}\text{Cl}_{20}$, are found in highest abundance. This result appears to be in agreement with Lipscomb's calculations, which have indicated that the closo boron hydrides $\text{B}_{16}\text{H}_{16}$ and $\text{B}_{19}\text{H}_{19}$ (along with $\text{B}_{22}\text{H}_{22}$) alone would be more stable as the neutral compounds, B_nH_n ($2n$ framework electrons), than as their reduced dianionic analogues, $\text{B}_n\text{H}_n^{2-}$ ($2n + 2$ framework electrons).¹⁸

As yet, partially because of the small amounts of material available, it has not proven possible to separate these boron halides nor even to reliably associate the very deshielded resonances observed in the boron NMR, e.g., 81.7 ppm, with

particular compounds. It is, however, readily apparent that further effort to isolate these species is justified.

Summary

Under dynamic vacuum the thermal decomposition of the acid salt of $\text{B}_{10}\text{Cl}_{10}^{2-}$ has been reexamined and shown to yield numerous polyhedral boron halides. The products isolated include three members of the nine-atom family, $\text{H}_2\text{B}_9\text{Cl}_7$, HB_9Cl_8 , and B_9Cl_9 . The boron NMR previously reported for HB_9Cl_8 is suggested to have arisen from a mixture of these three species. In addition, a number of larger boron mono-halides are also formed during the reaction. The compounds $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$, and $\text{B}_{12}\text{Cl}_{12}$ have been conclusively identified by boron NMR and mass spectrometry. Mass spectra also indicate the existence of the transicosahedral species B_nCl_n , $n = 13-20$.

Acknowledgment. We gratefully acknowledge the financial assistance of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation.

Registry No. $(\text{H}_3\text{O})_2\text{B}_{10}\text{Cl}_{10}$, 85680-78-0; $(\text{HNEt}_3)_2\text{B}_{10}\text{Cl}_{10}$, 85680-80-4; $\text{Cs}_2\text{B}_{10}\text{H}_{10}$, 12008-58-1; $\text{Cs}_2\text{B}_{10}\text{Cl}_{10}$, 12360-16-6; $\text{B}_{12}\text{Cl}_{12}$, 84879-96-9; $\text{B}_{11}\text{Cl}_{11}$, 12230-26-1; $\text{B}_{10}\text{Cl}_{10}$, 61674-49-5; B_9Cl_9 , 31304-34-4; HB_9Cl_8 , 72275-11-7; $\text{H}_2\text{B}_9\text{Cl}_7$, 83525-56-8; decaborane, 17702-41-9.

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