

The salt may be purified by recrystallization from hot anhydrous acetonitrile. Ebullioscopic molecular weight determinations in acetonitrile yielded values of 205 and 214 (calcd. 530). Partial, but not complete (theory 177), ionization in acetonitrile is indicated.<sup>12</sup> No e.p.r. signal was observed with a solution of  $[(CH_3)_4N]_2B_9Cl_8H$  in acetonitrile.

The n.m.r. proton spectrum of  $[(CH_3)_4N]_2B_9Cl_8H$  consisted of a sharp singlet of moderate intensity at  $-3.0$  p.p.m. (tetramethylsilane reference) due to the N-methyl protons. The components of the quartet expected for a proton attached to boron were not observed because of the low solubility of the salt. Each component of this quartet would necessarily be of an intensity about one hundredth of that of the N-methyl proton resonance.

$[(C_2H_5)_4N]_2B_9Cl_8H \cdot B_9Cl_8H$  (0.5 g.) was dissolved in 300 ml. of degassed water. Immediately after dissolution 3 ml. of a 10% aqueous solution of  $(C_2H_5)_4NOH$  was added, precipitating  $[(C_2H_5)_4N]_2B_9Cl_8H$ .

*Anal.* Calcd. for  $C_{18}H_{40}B_9Cl_8N_2$ : C, 29.9; H, 6.43; B, 15.1;

(12) Similar behavior was observed in the case of  $[(C_2H_5)_3NH]_2B_{10}Cl_{10}$ . Ebullioscopic molecular weight measurements in acetonitrile yielded 309 and 324 (calcd. for complete ionization, 229).

Cl, 44.1; N, 4.35. Found: C, 30.5; H, 6.44; B, 14.5; Cl, 44.2; N, 4.47, 4.44.

Infrared absorptions, as a Nujol mull, include the following: 2505 (w), 1300 (w), 1180 (m), 1165 (m), 1105 (m), 1060 (m), 1045 (m), 1030 (m), 997 (m), 962 (m), 817 (w), and 785 (m)  $cm^{-1}$ . Ebullioscopic molecular weight determinations in acetonitrile yielded values of 270 and 258 (calcd. 642), indicating partial ionization.

$[(C_2H_5)_4N]_2B_9Cl_8H$  is very soluble in acetonitrile with no appreciable temperature coefficient in the  $0-82^\circ$  range. It may be recrystallized from methanol-acetonitrile, but is insoluble in chloroform and dichloromethane.  $[(C_2H_5)_4N]_2B_9Cl_8H$  neither melts nor changes appearance when heated in a sealed capillary to  $360^\circ$ . When a solution of this salt (0.2 g.) in 200 ml. of water was heated to  $100^\circ$  for 3 hr., quantitative hydrolysis to boric acid occurred.

The  $B^{11}$  resonance spectrum of  $[(C_2H_5)_4N]_2B_9Cl_8H$  in acetonitrile consisted simply of a broad signal with a low-field spike.

**Acknowledgment.**—The mass spectral data were obtained by Mr. R. J. Berndt.

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## Chemistry of Boranes. IX.<sup>1</sup> Halogenation of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

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Halogenated derivatives of  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  have been prepared by reaction of these anions with chlorine, bromine, or iodine and by reaction of  $B_{12}H_{12}^{-2}$  with hydrogen fluoride, hydrogen chloride, or fluorine. These derivatives are exceedingly resistant toward thermal degradation and chemical attack.

This is the second of a series of papers which will describe in detail the chemistry of  $B_{10}H_{10}^{-2}$  <sup>2a</sup> and  $B_{12}H_{12}^{-2}$  <sup>2b</sup> outlined in a recent communication.<sup>3</sup> In the preceding paper,<sup>1</sup> it was shown that salts of  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  are thermally stable and resistant toward degradation by acids, bases, and mild oxidizing agents to a degree unique in boron hydride chemistry or inorganic hydride chemistry generally. In addition, these anions react readily with a variety of reagents to give substitution derivatives,<sup>3</sup> some of which rival or exceed the parent anions in chemical and thermal stability. In this context, the halogenated derivatives are outstanding.

The dianions  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  react smoothly in aqueous or alcoholic solutions with chlorine, bromine, iodine, N-iodosuccinimide, and similar reagents to give derivatives in which from one to all of the hydrogens have been replaced by halogen. Conversion of  $B_{12}H_{12}^{-2}$  to halogenated derivatives can also be effected with hydrogen halides and with elemental fluorine, although in the latter case some degradation of the cage occurs. Halogenated derivatives of  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  which contain other substituents (e.g.,

$B_{12}Br_{11}OH^{-2}$ ,  $B_{10}Cl_9COC_6H_5^{-2}$ ,  $B_{10}H_2Cl_6[S(CH_3)_2]_2$ ) will be described in later papers.

**Halogenation.**—The initial reactions of both  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  with chlorine, bromine, and iodine are extremely rapid. The rates decrease as halogenation is continued,  $B_{12}H_{12}^{-2}$  being significantly more resistant to electrophilic poly- or perhalogenation than  $B_{10}H_{10}^{-2}$ . As would be expected, the order of reactivity of the halogens is  $Cl > Br > I$ . The initial rapid rates lead to difficulties in isolating some species, particularly those with a low degree of halo substitution. For example, kinetic studies<sup>4</sup> have shown that the first three iodine atoms to enter  $B_{10}H_{10}^{-2}$  are kinetically indistinguishable even at  $-40^\circ$ , although the rate of iodination of  $B_{12}H_{12}^{-2}$  is measurable at  $25^\circ$  and is 70-fold greater than the rate of iodination of  $B_{12}H_{11}I^{-2}$ . Thus, pure  $B_{10}H_9I^{-2}$  cannot be made by simply using one equivalent of iodine, although this procedure is satisfactory for the preparation of  $B_{12}H_{11}I^{-2}$ . Salts of  $B_{10}H_9I^{-2}$  and  $B_{10}H_8I_2^{-2}$  have been separated, however, by repeated fractional crystallizations. Kinetic studies have not as yet been completed for the other halogenations, but it is apparent that initial kinetic lack of discrimination between successively entering halogens is even more prevalent with bromine and

(4) Details of these kinetic studies and of related stereochemical work will be published in a later paper.

(1) Paper VIII: *Inorg. Chem.*, in press.

(2) (a) M. F. Hawthorne and A. R. Pitocchi, *J. Am. Chem. Soc.*, **81**, 5519 (1959); (b) *ibid.*, **82**, 3228 (1960).

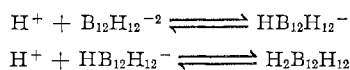
(3) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *ibid.*, **84**, 1056 (1962).

chlorine for both  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$ . In the preparation of most of the partially halogenated species reported here, we have minimized the heterogeneity of the products by adding halogen until there is a noticeable decrease in reaction rate, and characterizing the species thus formed. In this fashion,  $B_{10}H_2Cl_8^{-2}$ ,  $B_{10}H_3Br_7^{-2}$ ,  $B_{10}H_7I_3^{-2}$ ,  $B_{10}H_6I_4^{-2}$ ,  $B_{10}H_4I_6^{-2}$ ,  $B_{12}H_6Br_6^{-2}$ ,  $B_{12}H_2Br_{10}^{-2}$ , and  $B_{12}H_{10}I_2^{-2}$  have been prepared. More forcing conditions have given perchloro, perbromo, and periodo derivatives of both  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$ . In addition,  $B_{12}H_3Br_6Cl_3^{-2}$ ,  $B_{12}Br_8F_4^{-2}$ , and  $B_{12}H_3F_3I^{-2}$  have been prepared by straightforward combinations of reactions as discussed in the Experimental section.

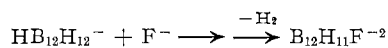
Hydrogen fluoride reacts with  $B_{12}H_{12}^{-2}$  to give  $B_{12}H_3F_4^{-2}$ ,  $B_{12}H_7F_5^{-2}$ , or  $B_{12}H_6F_6^{-2}$ , depending on reaction conditions, while hydrogen chloride gives  $B_{12}H_{11}Cl^{-2}$  at  $85^\circ$ . Fluorination of  $B_{12}H_{12}^{-2}$  and  $B_{12}H_6F_6^{-2}$  in water with elemental fluorine at  $0^\circ$  or room temperature has given  $B_{12}F_{11}OH^{-2}$  and  $BF_4^-$  in about equal yields.

Halogenation of  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  with elemental halogens, iodine monochloride, and N-iodosuccinimide is assumed to be electrophilic. Bromination of  $B_{12}$  species with a mixture of chlorine and bromine is believed to be a radical reaction,<sup>5</sup> and the  $F_2$ - $B_{12}H_{12}^{-2}$  reaction can be nothing but a free radical reaction.

Halogenation of  $B_{12}H_{12}^{-2}$  with hydrogen fluoride and hydrogen chloride cannot be satisfactorily explained as a radical or as an electrophilic process. It can be rationalized as a nucleophilic reaction if the following equilibria are assumed.



These equilibria, which cannot be important in dilute aqueous media because of the strength of the  $B_{12}H_{12}^{-2}$  conjugate acid, could be important in reactions where water content is minimal. The protonated species should contain electrophilic boron atoms which would be susceptible to nucleophilic attack; subsequent loss of hydrogen would give the observed products.



Accordingly, we have tentatively characterized this type of reaction as acid-catalyzed nucleophilic substitution. A number of other reactions have been encountered in  $B_{12}H_{12}^{-2}$  chemistry which are best explained by similar mechanisms, and these will be discussed in a following article of this series.<sup>6</sup>

It is thus apparent that a variety of reaction mechanisms are available to  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$ , and it would be reasonable that the relative availabilities of these mechanisms would be different for the two species.

If this is true then it would not be surprising to find that some reactions give quite different types of products with  $B_{10}H_{10}^{-2}$  than with  $B_{12}H_{12}^{-2}$ . Several examples of this have been found<sup>7</sup> and will be reported subsequently.<sup>6</sup> The important point is that, despite the superficial similarity of these halogenation reactions,  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  should not be considered as completely chemically analogous systems.

**Isolation and Purification of Products.**—Halogenated  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  derivatives present no handling problems and are amenable to conventional methods of salt formation and purification. Initial isolation was generally accomplished by precipitation as a cesium, tetramethylammonium, or similar salt of a large univalent cation. After suitable recrystallization, these salts were converted to solutions of their conjugate acids by passage through a strongly acidic ion-exchange resin. These solutions were evaporated to obtain the acids as hydrates, or new salts could be formed from the solutions by a number of conventional techniques such as precipitation, neutralization and evaporation, reaction with metal oxides or carbonates, etc. For partially halogenated species the absence of anions of different degrees of halogenation was not rigorously established.

**Stereochemistry.**—Examination of the structures<sup>8,9</sup> of the  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  anions readily reveals that the stereochemistry of their substitution derivatives can be quite complex. Even where all substituents are identical, position isomers are possible for all partially substituted species except those of the types  $B_{12}H_{11}X^{-2}$  and  $B_{12}HX_{11}^{-2}$ . Isomer possibilities are obviously greater for  $B_{10}H_{10}^{-2}$  ( $D_{4d}$ ) than for  $B_{12}H_{12}^{-2}$  ( $I_h$ ). To illustrate, there are only three possible isomers for a disubstituted  $B_{12}$  anion, whereas there are seven for a disubstituted (like substituent)  $B_{10}$  anion if  $d, l$  pairs are ignored.

N.m.r. ( $H^1$  and  $B^{11}$ ) is not a sufficiently sensitive tool to provide a definitive answer to isomer purity. Chromatographic separation and X-ray analysis will be required and we are pursuing this aspect now. The only statements regarding isomers that can be made on the basis of symmetry arguments or analysis of n.m.r. data are as follows<sup>10</sup>:

$B_{10}H_9I^{-2}$	Mixture of the two possible isomers
$B_{12}H_{11}I^{-2}$	Only one isomer possible
$B_{12}H_{10}I_2^{-2}$	Mixture of 1,7- and 1,12 isomers ( <i>vide infra</i> )
$B_{10}H_8I_2^{-2}$	Mixture of isomers
$B_{10}H_7I_3^{-2}$	Mixture of isomers
$B_{10}H_6I_4^{-2}$	Mixture of isomers
$B_{12}Br_6H_6^{-2}$	Possibly a single isomeric species ( <i>vide infra</i> )
$B_{12}Br_{10}H_2^{-2}$	Improbable the 1,2 isomer is present

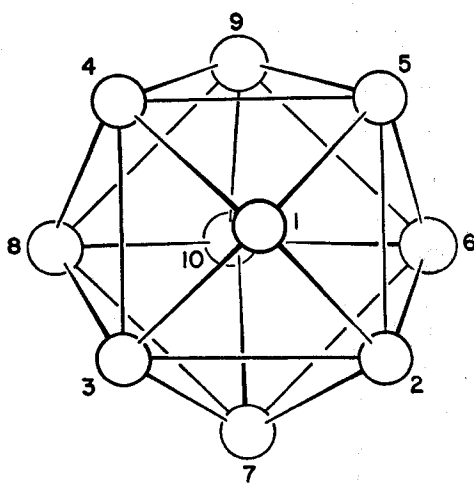
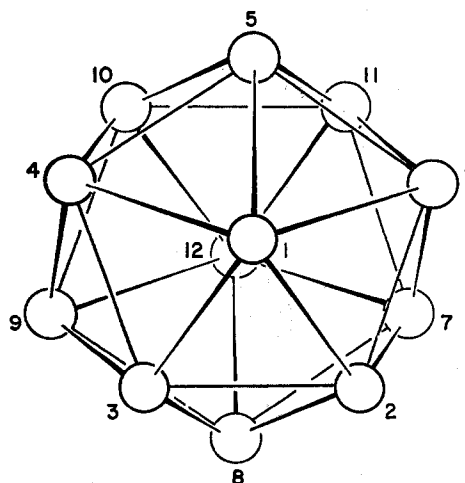
(7) For example, benzoyl chloride converts  $B_{10}H_{10}^{-2}$  cleanly to  $B_{10}H_9CC_6H_5^{-2}$ . In the analogous  $B_{12}$  reaction,  $B_{12}H_{10}(OH)_2^{-2}$  is the major product; only trace amounts of benzoyl derivatives could be detected.

(8) W. N. Lipscomb, M. F. Hawthorne, and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

(9) J. A. Wunderlich and W. N. Lipscomb, *ibid.*, **82**, 4427 (1960).

(5) A mixture of chlorine and bromine has been used (J. L. Speier, *J. Am. Chem. Soc.*, **73**, 826 (1951)), to effect bromination on carbon and this has been rationalized (C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 379) as a radical reaction:  $Cl \cdot + RH \rightarrow R \cdot + HCl$ ,  $R \cdot + Br-Cl \rightarrow RBr + Cl \cdot$ .

(6) W. H. Knoth, D. C. England, W. R. Hertler, J. C. Sauer, and E. L. Muetterties, paper XI, to be published.

Fig. 1.— $B_{10}H_{10}^{-2}$ .Fig. 2.— $B_{12}H_{12}^{-2}$ .

Deuteration studies<sup>1</sup> have shown that the ratio of the deuteration rates of the apical and equatorial positions in  $B_{10}H_{10}^{-2}$  under acidic conditions is 5:1. If the assumption were made that the ratio for the rates of monoiodination in the apical and equatorial positions of  $B_{10}H_{10}^{-2}$  was also 5:1, then one would expect (since there are four times as many equatorial positions as apical ones) that slightly more apically than equatorially substituted species would result from the monoiodination of  $B_{10}H_{10}^{-2}$ . Boron nuclear magnetic resonance studies on  $B_{10}H_9I^{-2}$  show the presence of both apical and equatorial substitution, and the data can be interpreted as suggesting that more equatorial than apical substitution has occurred. This would be expected if the iodination rate is sufficiently fast that the reaction rates approach collision rates, which is a possibility in this particular case.<sup>11</sup> The iodination of  $B_{12}H_{11}I^{-2}$ , however, is sufficiently slow that the directive influence of the first iodine should be important. It has been predicted<sup>12</sup> that a halogen substituent in  $B_{12}H_{12}^{-2}$  should serve as a source of electrons by resonance interaction, in which case a second electrophilic substitution would give the 1,2 isomer. Our kinetic studies<sup>4</sup> have demonstrated, however, that iodine in  $B_{12}H_{11}I^{-2}$  is not serving as an electron source. Proton magnetic resonance data for  $B_{12}H_{10}I_2^{-2}$  suggest the 1,7 isomer is the major product, with a small amount of the 1,12 isomer present. The 1,7 to 1,12 ratio appears to be about 5:1, which agrees with a prediction<sup>12</sup> for the results of electrophilic halogenation of a monosubstituted  $B_{12}H_{12}^{-2}$  derivative where the first substituent withdraws electrons inductively.

Proton resonance studies reveal only one type of

(10) We have adopted the numbering system for  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  shown in Fig. 1 and 2. In  $B_{10}H_{10}^{-2}$ , the numbering starts at an apex and proceeds to the other apex. Designating any particular boron atom as 1 in  $B_{12}H_{12}^{-2}$  is, of course, quite arbitrary. In a  $B_{12}H_{11}X^{-2}$  species, therefore, the substituted boron is numbered 1 and the rest as shown above. In a  $B_{12}H_{10}XY^{-2}$  species, the boron atom would be numbered 1 which would come first in the name of the species following nomenclature rules. In a polysubstituted  $B_{12}$  species, the boron atom to be numbered 1 would be chosen so that the total of the resulting numerical designations would be the lowest possible.

(11) A correlation of stereochemistry and reaction mechanism will be presented in the paper detailing our kinetic studies.<sup>4</sup>

(12) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 520 (1962).

proton in  $B_{12}H_6Cl_6^{-2}$  and  $B_{12}H_6Br_6^{-2}$ . This suggests that this anion consists largely of one isomer in which the bromine atoms are on two sets of three adjacent boron atoms on opposite sides of the  $B_{12}$  cage with a puckered ring of six hydrogen-bearing boron atoms between these two sets, or, alternatively, the anion has the analogous configuration with the hydrogen and bromine positions reversed. The small chemical shifts encountered with these  $B_{12}$  derivatives preclude rigorous conclusions in this particular isomer question.

**Spectral Properties.**—The infrared and Raman spectra of  $B_{12}Cl_{12}^{-2}$ ,  $B_{10}Cl_{10}^{-2}$ , and  $B_{10}Br_{10}^{-2}$  have been reported in an earlier paper.<sup>13</sup> The infrared spectra of  $B_{10}Cl_{10}^{-2}$ ,  $B_{10}Br_{10}^{-2}$ , and  $B_{10}I_{10}^{-2}$  are quite similar, as shown in Table I. The infrared spectra of  $B_{12}Cl_{12}^{-2}$ ,  $B_{12}Br_{12}^{-2}$ , and  $B_{12}I_{12}^{-2}$  (Table I) are also similar to

TABLE I  
INFRARED ABSORPTION FREQUENCIES (CM.<sup>-1</sup>)

$B_{10}Cl_{10}^{-2}$	1150 (m; sh. at 1190), 1010 (s), 870 (m)
$B_{10}Br_{10}^{-2}$	1120 (m; sh. at 1150), 971 (s; sh. at 990), 850 (m)
$B_{10}I_{10}^{-2}$	1080 (m; sh. at 1100), 980 (s; sh. at 990), 820 (m)
$B_{12}Cl_{12}^{-2}$	1030 (s)
$B_{12}Br_{12}^{-2}$	1000 (s), 980 (s)
$B_{12}I_{12}^{-2}$	940 (s), 925 (s)

each other, with one strong broad band for  $B_{12}Cl_{12}^{-2}$  and strong doublets for  $B_{12}Br_{12}^{-2}$  and  $B_{12}I_{12}^{-2}$ .

The  $B^{11}$  n.m.r. spectra of  $B_{12}Cl_{12}^{-2}$ ,  $B_{12}Br_{12}^{-2}$ , and  $B_{12}I_{12}^{-2}$  in acetonitrile each consist of one relatively sharp peak at 31.0, 30.7, and 34.4 p.p.m., respectively, referred to methyl borate. The  $B^{11}$  spectrum of  $B_{10}Cl_{10}^{-2}$  in acetonitrile has a peak at 28.7 p.p.m. with a shoulder at 23.4 p.p.m., while that of  $B_{10}Br_{10}^{-2}$  has the major peak at 33.5 p.p.m. and a smaller one at 21.9 p.p.m.

In contrast to  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$ , which have no absorption maxima in the ultraviolet, some of the halogenated species do have ultraviolet absorption maxima.

(13) E. L. Muetterties, R. E. Merrifield, H. C. Miller, W. H. Knoth, Jr., and J. R. Downing, *J. Am. Chem. Soc.*, **84**, 2506 (1962).

**Chemical Behavior.**—All of the halogenated species examined are exceedingly stable to both acid and base. The stability to strong acids is shown by the strongly acidic systems in which they are formed; by isolation of crystalline hydrated conjugate acids of  $B_{10}Cl_{10}^{-2}$ ,  $B_{10}I_{10}^{-2}$ ,  $B_{12}Cl_{12}^{-2}$ , and  $B_{12}Br_{12}^{-2}$ ; and by the preparation of solutions of the pure conjugate acids of a number of different species in the process of converting from one salt to another. Acidity function studies have shown that the conjugate acids of  $B_{12}Br_{12}^{-2}$  and  $B_{12}Cl_{12}^{-2}$  are slightly stronger than sulfuric acid; this is about the same acidity as the  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  acids.<sup>1</sup> The other conjugate acids appear to be equally strong, but quantitative measurements have not been made.

The stability of these anions to nucleophilic attack is shown by lack of reaction with aqueous sodium hydroxide; a 91% recovery of  $[(CH_3)_4N]_2B_{10}H_3Br_7$  after being refluxed for 1 hr. in methanolic sodium methoxide; inertness of  $B_{10}H_7I_3^{-2}$  and  $B_{12}H_{10}I_2^{-2}$  to potassium amide-liquid ammonia solutions; lack of reaction between  $B_{10}Cl_{10}^{-2}$  and sodium acetylide in liquid ammonia; and failure of  $B_{12}H_{10}I_2^{-2}$  to react with phenylmagnesium bromide or methylmagnesium bromide in refluxing tetrahydrofuran. Even the  $B_{12}I_{12}^{-2}$  anion, which contains about 93% iodine, has an unusual stability; no degradation occurs on treatment with chlorine or 20% aqueous sodium hydroxide at 85° or sulfuric acid at 150°. There is, of course, a limit to this kinetic stability, and  $Cs_2B_{10}Cl_{10}$  decomposed violently when fused with solid sodium hydroxide over an open flame. In addition,  $B_{10}H_7I_3^{-2}$  was found to react with potassium in liquid ammonia to give  $B_{10}H_{10}^{-2}$ , and  $B_{12}H_{10}I_2^{-2}$  reacted with sodium, lithium, and potassium in liquid ammonia to give  $B_{12}H_{12}^{-2}$ .

In the preceding paper, it was reported that  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  form water-insoluble silver salts (with no reduction to  $Ag^0$ ) which are covalent. The brominated and iodinated derivatives form similar water-insoluble salts which may have some degree of covalent character, but the polychlorinated and fluorinated species form highly crystalline ionic silver salts.  $Ag_2B_{10}Cl_{10}$ , for example, is very soluble in water, alcohol, ethyl acetate, tetrahydrofuran, dimethoxyethane, and similar polar solvents. Refluxing aqueous solutions of these ionic silver salts does not give any elimination of silver chloride, another example of the inertness of the boron-halogen bonds in these species.

**Thermal Stability.**—As is the case with  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$ , the cesium salts of  $B_{10}Cl_{10}^{-2}$  and  $B_{12}Cl_{12}^{-2}$  are quite thermally stable.  $Cs_2B_{10}Cl_{10}$  suffers only a 4% weight loss when heated under vacuum to 600°, and the infrared spectrum is essentially unchanged. Above 600°, the rate of weight loss increases. Above 800°,  $Cs_2B_{10}Cl_{10}$  decomposes rapidly and completely.  $Cs_2B_{12}Cl_{12}$  is even more stable. In a pyrolysis of  $Cs_2B_{12}Cl_{12}$  a temperature of 700° was required to achieve a 3% weight loss; the infrared spectrum of this sample was essentially unchanged. Heating  $Cs_2B_{12}Cl_{12}$  to 900° caused a 50% weight loss with concurrent forma-

tion of boron trichloride. Decomposition of  $(H_3O)_2B_{10}Cl_{10}$  begins at 260° and is described in detail in paper VII<sup>14</sup> of this series.

**Polarographic Studies.**—Polarographic oxidation studies on  $B_{10}H_2Cl_8^{-2}$ ,  $B_{10}Cl_{10}^{-2}$ ,  $B_{10}Br_{10}^{-2}$ , and  $B_{10}I_{10}^{-2}$  demonstrate that halogen substitution in  $B_{10}H_{10}^{-2}$  increases oxidation stability. Thus,  $B_{10}H_{10}^{-2}$  has a half-wave oxidation potential of +0.85 v.<sup>1</sup> (referred to the saturated calomel electrode), while  $B_{10}Cl_{10}^{-2}$  does not oxidize to +1.1 v.,  $B_{10}H_2Cl_8^{-2}$  and  $B_{10}Br_{10}^{-2}$  begin to oxidize just short of +1.1 v., and  $B_{10}I_{10}^{-2}$  has an  $E_{p/2}$  at +1.3 v. In reduction studies,  $B_{10}Cl_{10}^{-2}$ ,  $B_{10}H_2Cl_8^{-2}$ ,  $B_{10}I_{10}^{-2}$ , and  $B_{10}Br_{10}^{-2}$  did not reduce at a dropping mercury electrode.

## Experimental

Preparations of  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$  have been described previously.<sup>1,2,15</sup> The other reagents used are commercially available and were used without purification. The ion-exchange resin used throughout was Amberlite IR-120, which was purchased in the acid form and used directly or converted to salt forms by exhaustion with aqueous solutions of metal salts appropriate for the particular experiment.

**$B_{10}H_2Cl_8^{-2}$ .**— $(NH_4)_2B_{10}H_{10}$  (2.0 g., 0.013 mole) was dissolved in 40 ml. of water and cooled to 0–5° in an ice bath. Chlorine<sup>16</sup> was passed through the solution and the temperature rose to 10–15°. Chlorination was continued until there was no longer any noticeable exothermic reaction. Excess aqueous tetramethylammonium chloride solution was added and the resulting white precipitate was recrystallized from water to obtain 4.6 g., 0.0085 mole (65% yield), of  $[(CH_3)_4N]_2B_{10}H_2Cl_8$ .

*Anal.* Calcd. for  $[(CH_3)_4N]_2B_{10}H_2Cl_8$ : C, 17.7; H, 4.5; N, 5.2; B, 19.9; Cl, 52.3. Found: C, 17.4, 17.1; H, 5.1, 5.1; N, 4.5; B, 19.6; Cl, 52.9, 52.8. Ultraviolet:  $\lambda_{max}^{CH_3CN}$  219 m $\mu$  ( $\epsilon$  8550).

In a similar experiment the anion was precipitated as a cesium salt by the addition of excess aqueous cesium hydroxide. Recrystallization from water gave a hydrate of  $Cs_2B_{10}H_2Cl_8$ .

*Anal.* Calcd. for  $Cs_2B_{10}H_2Cl_8 \cdot H_2O$ : B, 16.0; Cl, 41.8. Found: B, 16.4; Cl, 41.4. Infrared analysis confirmed the presence of water of hydration.

**$B_{10}Cl_{10}^{-2}$ .**—Analyses for the following  $B_{10}Cl_{10}^{-2}$  salts are in Table II. Chlorine was passed into a solution of  $(NH_4)_2B_{10}H_{10}$  (8.0 g., 0.052 mole) in 120 ml. of water at 15–20° until the exothermic phase was over. Chlorination was then continued at ambient temperature until a cesium salt prepared from an aliquot had no infrared absorption in the 2500  $cm^{-1}$  (B–H) region. The addition of excess aqueous tetramethylammonium chloride to  $1/4$  of the reaction solution precipitated  $[(CH_3)_4N]_2B_{10}Cl_{10}$ , which was recrystallized from 50% aqueous ethanol (8.0 g., 0.013 mole, 100%). Similarly, the  $B_{10}Cl_{10}^{-2}$  anion was precipitated as a cesium salt by the addition of excess cesium chloride. The crude  $Cs_2B_{10}Cl_{10}$  recrystallized from water as needles which were dried at 80–100° in a vacuum oven for 15 hr. (79% yield). An aqueous solution of  $Cs_2B_{10}Cl_{10}$  (30 g., 0.041 mole) was passed slowly through an acidic ion-exchange column. The column was rinsed with water until the rinsings were neutral, and the combined effluent and rinse were evaporated to leave a crystalline solid. This was dried for 9 hr. at 80° under vacuum to give  $(H_3O)_2B_{10}Cl_{10} \cdot 3H_2O$  (20.5 g., 0.037 mole, 85% yield). A solution of  $(H_3O)_2B_{10}Cl_{10} \cdot 3H_2O$  (5.0 g., 0.009 mole) in 80 ml. of water was

(14) J. A. Forstner, T. E. Haas, and E. L. Muetterties, *Inorg. Chem.*, **3**, 155 (1964).

(15) H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3886 (1963).

(16) The use of ammonium salts in halogenation reactions, especially at low temperature, can result in the formation of nitrogen trihalides and appropriate precautions should be taken. It is probably best to avoid the use of ammonium salts in these halogenations.

TABLE II  
 $B_{10}Cl_{10}^{-2}$  SALTS

Cation	Calcd.					Found				
	B	Cl	C	H	M, S, N	B	Cl	C	H	M, S, N
$2(CH_3)_4N^+a$	17.7	58.0	15.7	4.0	4.6	17.7	57.5	16.1	4.1	4.6
$2Cs^+$	14.8	48.7	...	...	36.5	14.7	48.2	...	...	34.0
$2H_3O^+ \cdot 3H_2O^b$	19.6	64.1	...	...	...	19.4	63.0	...	...	...
$2Tl^+$	12.7	40.7	...	...	46.9	12.4	40.2	...	...	46.4
$2Li^+ \cdot 5H_2O$	19.1	62.6	...	...	2.4	19.1	62.8	...	...	2.3
$2Ag^+$	16.0	52.2	...	...	31.8	15.8	52.0	...	...	31.7
$2H^+ \cdot 4HCON(CH_3)_2$	14.3	...	19.0	4.0	7.4	14.6	...	19.4	4.1	7.3
$2H^+ \cdot 4(CH_3)_2SO$	13.9	45.6	12.4	3.4	16.5	14.7	44.4	12.6	3.6	16.7

<sup>a</sup> Ultraviolet  $\lambda_{max}^{CH_3CN}$  224  $m\mu$  ( $\epsilon$  11,000), shoulder at 270  $m\mu$  ( $\epsilon$  226). <sup>b</sup> Neut. equiv. calcd. 276; found 271.

neutralized with aqueous thallium hydroxide and evaporated to give 8.1 g., 0.0093 mole (102%), of crude  $Tl_2B_{10}Cl_{10}$ . Recrystallization of 5 g. from 5 ml. of water followed by vacuum drying in the presence of phosphorus pentoxide gave 4.1 g. of  $Tl_2B_{10}Cl_{10}$ . An aqueous solution of 7.6 g., 0.14 mole, of  $(H_2O)_2B_{10}Cl_{10} \cdot 3H_2O$  was passed through a lithium-charged ion-exchange column and evaporated. The residual crystals were dried for 6 hr. at 80° under vacuum to give 5.8 g., 0.010 mole (73%), of  $Li_2B_{10}Cl_{10} \cdot 5H_2O$ .  $H_2B_{10}Cl_{10}$  (89.3 ml. of 0.112 M) was stirred overnight with 2.55 g., 0.011 mole, of silver oxide (10% excess). The solution was filtered and evaporated to dryness at 50° in subdued light to yield 6.74 g., 0.0099 mole (99%), of  $Ag_2B_{10}Cl_{10}$ . The addition of a concentrated aqueous solution of  $H_2B_{10}Cl_{10}$  to 50% dimethylformamide-50% concentrated hydrochloric acid gave  $H_2B_{10}Cl_{10} \cdot 4HCON(CH_3)_2$ . This was recrystallized from water (this must be done rapidly because prolonged boiling results in dissociation of the cation). The use of dimethyl sulfoxide in place of dimethylformamide gave  $H_2B_{10}Cl_{10} \cdot 4(CH_3)_2SO$ .

$B_{10}H_3Br_7^{-2}$ .—(*t*- $C_4H_9NH_3$ ) $_2B_{10}H_{10}$  (0.97 g., 0.0036 mole) was dissolved in 30 ml. of water which was cooled in a wet ice bath. Bromine was added slowly with stirring until the bromine color persisted in the solution of 1-2 min. and was not rapidly discharged on warming to room temperature. The addition of tetramethylammonium chloride, 2.8 g., 0.26 mole, in 10 ml. of water precipitated 2.8 g., 0.0034 mole (94%), of  $[(CH_3)_4N]_2B_{10}H_3Br_7$  which was dried at 60° under vacuum overnight.

Anal. Calcd. for  $[(CH_3)_4N]_2B_{10}H_3Br_7$ : C, 11.7; H, 3.3; N, 3.4; B, 13.2; Br, 68.3. Found: C, 11.6, 11.5; H, 3.1; N, 3.6; B, 12.2; Br, 68.9. Ultraviolet:  $\lambda_{max}^{CH_3CN}$  223  $m\mu$  ( $\epsilon$  8170), shoulder at 275  $m\mu$  ( $\epsilon$  323).

$B_{10}Br_{10}^{-2}$ .— $(NH_4)_2B_{10}H_{10}$  (3.0 g., 0.02 mole) was dissolved in 100 ml. of 50% aqueous ethanol. A solution of 60 g., 0.37 mole, of bromine in 200 ml. of ethanol was added slowly with stirring until the color no longer was rapidly discharged. The reaction solution was heated to reflux while the remainder of the bromine solution was added periodically over a 4-hr. period. The volatile materials were removed under vacuum and the residue was dissolved in 10 ml. of water and mixed with excess concentrated cesium chloride solution. The precipitate was recrystallized from water to obtain 12.4 g., 0.01 mole (50%), of  $Cs_2B_{10}Br_{10} \cdot H_2O$ .

Anal. Calcd. for  $Cs_2B_{10}Br_{10} \cdot H_2O$ : Cs, 22.3; B, 9.1; Br, 67.1; neut. equiv., 596. Found: Cs, 21.9; B, 9.0; Br, 66.9; neut. equiv., 596. Infrared analysis confirmed the presence of water of hydration. The neutral equivalent was determined by titration with base of the effluent from passage of aqueous  $Cs_2B_{10}Br_{10} \cdot H_2O$  through an acid ion-exchange column.

In a similar experiment, the  $B_{10}Br_{10}^{-2}$  anion was obtained as a tetramethylammonium salt in 73% yield by the addition of aqueous tetramethylammonium chloride to the reaction solution. The product was recrystallized from water.

Anal. Calcd. for  $[(CH_3)_4N]_2B_{10}Br_{10}$ : B, 10.2; Br, 75.7; N, 2.6. Found: B, 10.4; Br, 74.8; N, 2.7. Ultraviolet:  $\lambda_{max}^{CH_3CN}$  236  $m\mu$  ( $\epsilon$  8450), shoulder at 288  $m\mu$  ( $\epsilon$  210).

$Cs_2B_{10}Br_{10} \cdot H_2O$  (0.20 g., 0.00016 mole) was dissolved in 5 ml. of water and mixed with a solution of 0.065 g., 0.00038 mole, of silver nitrate in 5 ml. of water.  $Ag_2B_{10}Br_{10}$  precipitated and was

washed thoroughly with water and alcohol and dried under vacuum. This salt is white but darkens on prolonged exposure to light.

Anal. Calcd. for  $Ag_2B_{10}Br_{10}$ : Ag, 19.2. Found: Ag, 19.3.

$B_{10}H_9I^{-2}$  and  $B_{10}H_8I_2^{-2}$ .—Potassium iodide (19 g., 0.11 mole) and iodine (20.4 g., 0.08 mole) were mixed with 1 l. of water. Methanol was added to dissolve the iodine and the solution was added to  $(NH_4)_2B_{10}H_{10}$  (12.4 g., 0.08 mole) in 1 l. of water over a 2.5-hr. period with high-speed stirring. The solution was concentrated to 500 ml. and a concentrated solution of cesium fluoride was added followed by neutralization with tetramethylammonium hydroxide. A concentrated solution of tetramethylammonium chloride was added until crystals (25 g.) separated. This product was a mixed tetramethylammonium cesium salt with an I:B ratio of 1.67:10. Further concentration of the reaction solution yielded 2.4 g. of a crystalline cesium tetramethylammonium salt which had an iodine:boron ratio of 0.9 to 10. The first product obtained was fractionally recrystallized from water-acetonitrile-methanol to give 17 fractions. Fractions 11 through 15 had superimposable infrared spectra. These fractions were combined, dissolved in aqueous methanol, and passed through an acid ion-exchange column. The addition of tetramethylammonium chloride to the effluent precipitated  $[(CH_3)_4N]_2B_{10}H_8I_2$ , which was recrystallized several times from hot aqueous methanol.

Anal. Calcd. for  $[(CH_3)_4N]_2B_{10}H_8I_2$ : B, 21.0; I, 49.2. Found: B, 21.2; I, 48.2. The  $B^{11}$  spectrum of solutions of this diiodo fraction showed that a significant amount of unreacted apical BH was still present.

Fractions 7 and 8 of the gross recrystallization were again recrystallized from aqueous methanol to give the monoiodo derivative.

Anal. Calcd. for  $Cs(CH_3)_4NB_{10}H_9I$ : B, 24.0; I, 28.2. Found: fraction 7: B, 23.8; I, 27.4; fraction 8: B, 23.8; I, 28.0. The  $B^{11}$  spectrum of this monoiodo derivative showed that a considerable fraction of apical BH was still present in this compound and the equatorial BH region was significantly more perturbed than that of the apical BH.

$B_{10}H_7I_3^{-2}$  and  $B_{10}H_6I_4^{-2}$ .— $(NH_4)_2B_{10}H_{10}$  (10.0 g., 0.065 mole) was stirred in 150 ml. of ethanol, and sufficient water to dissolve the salt was added. The solution was cooled to 5-10° and iodine (44.0 g., 0.17 mole) was added in small portions with stirring. The solution was then warmed and stirred until colorless and divided into two portions. Excess aqueous cesium fluoride was added to one, forming a gummy precipitate which was recrystallized from water to give 1.9 g., 0.0025 mole (8%), of  $Cs_2B_{10}H_7I_3$ .

Anal. Calcd. for  $Cs_2B_{10}H_7I_3$ : Cs, 34.9; B, 14.2; I, 50.0. Found: Cs, 35.8; B, 14.0; I, 49.3, 49.1. Ultraviolet:  $CH_3CN$ , no max.; shoulder at 270  $m\mu$  ( $\epsilon$  226).

The remaining half of the reaction mixture was refluxed and iodine was added slowly until color persisted for 1 hr. The solution was concentrated until  $NH_4I$  separated. This was filtered and the filtrate was diluted with an equal volume of water, filtered again, and excess 50% aqueous cesium fluoride was added. The precipitate was recrystallized twice from water to obtain 4.1 g., 0.0035 mole (11%), of  $Cs_2B_{10}H_6I_4 \cdot H_2O$ .

Anal. Calcd. for  $Cs_2B_{10}H_6I_4 \cdot H_2O$ : Cs, 23.0; B, 9.3; I,

65.8. Found: Cs, 23.1; B, 9.3; I, 66.9. Ultraviolet:  $\text{CH}_3\text{CN}$ , no max. Infrared analysis confirmed the presence of water.

N-Iodosuccinimide (14.1 g., 0.06 mole) was added to a solution of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  (3.9 g., 0.025 mole) in 100 ml. of water. The addition of aqueous tetramethylammonium chloride gave a precipitate. The mixture was filtered and the filtrate was evaporated. The residue was recrystallized twice from water to obtain 1.1 g. of white solid.

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_7\text{I}_3$ : B, 16.8; I, 59.1. Found: B, 17.7; I, 56.7. The  $\text{B}^{11}$  n.m.r. is essentially the same as that of  $\text{B}_{10}\text{H}_7\text{I}_3^{-2}$  prepared from  $\text{B}_{10}\text{H}_{10}^{-2}$  and iodine. The latter has peaks at 14.6, 22.2, and 44.8 p.p.m. from methyl borate, while the present product has similar peaks at 13.8, 22.2, and 44.3 p.p.m.

$\text{B}_{10}\text{H}_6\text{I}_4^{-2}$ .— $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  (1.0 g., 0.0065 mole) was dissolved in 50 ml. of methanol and iodine (5.6 g., 0.022 mole) was added. The color persisted after stirring 20 min. and tetramethylammonium hydroxide in 20 ml. of methanol was added. A mixture of  $(\text{CH}_3)_4\text{NI}$  and  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_6\text{I}_4$  precipitated. These were separated by recrystallization from water.

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_6\text{I}_4$ : B, 14.1; I, 66.0. Found: B, 13.3; I, 66.5.

$\text{B}_{10}\text{I}_{10}^{-2}$ .—Iodine was added to a refluxing mixture of  $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$  (6 g., 0.039 mole) and 150 ml. of methanol until no further iodine would react. The methanol was removed under vacuum to leave a gummy mass. Iodine monochloride (150 g., 0.092 mole) was added and this mixture was heated to  $80^\circ$  for 3 hr. and then extracted successively with  $\text{CCl}_4$  and  $\text{CS}_2$ . The residue was dissolved in water, filtered, and neutralized with ammonium hydroxide. Excess concentrated aqueous cesium fluoride was added and the resulting precipitate was recrystallized from water to give  $\text{Cs}_2\text{B}_{10}\text{I}_{10} \cdot \text{CsI}$ .

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{10}\text{I}_{10} \cdot \text{CsI}$ : Cs, 20.9; B, 5.7; I, 73.3. Found: Cs, 18.8; B, 6.4; I, 74.0.  $\text{Cs}_2\text{B}_{10}\text{I}_{10} \cdot \text{CsI}$  was dissolved in water and passed through an anion-exchange column. Evaporation of the effluent gave  $(\text{H}_3\text{O})_2\text{B}_{10}\text{I}_{10} \cdot 6\text{H}_2\text{O}$  as a crystalline solid.

*Anal.* Calcd. for  $(\text{H}_3\text{O})_2\text{B}_{10}\text{I}_{10} \cdot 6\text{H}_2\text{O}$ : B, 7.1; I, 83.5; neut. equiv., 761. Found: B, 7.0; I, 83.5; neut. equiv., 751, 754.

$\text{B}_{12}\text{H}_3\text{F}_4^{-2}$ .— $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12} \cdot 5\text{H}_2\text{O}$  (10 g., 0.037 mole) and 40 g., 2.0 moles, of anhydrous hydrogen fluoride were heated in a 400-ml. Hastelloy pressure vessel at  $100^\circ$  for 4 hr. at autogenous pressure. Unreacted hydrogen fluoride was removed in a stream of nitrogen, and the residue was neutralized with cesium hydroxide, cooled, and filtered. The precipitate was recrystallized from water and dried at  $100^\circ$  under vacuum to give  $\text{Cs}_2\text{B}_{12}\text{H}_3\text{F}_4$ , 13.3 g., 0.028 mole (75%).

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_3\text{F}_4$ : B, 27.0; F, 15.7. Found: B, 26.6; F, 15.5.

$\text{B}_{12}\text{H}_7\text{F}_5^{-2}$ .— $\text{K}_2\text{B}_{12}\text{H}_{12}$  (15 g., 0.069 mole) and 40 g., 2.0 moles, of anhydrous hydrogen fluoride were heated in a 400-ml. "Hastelloy C"-lined pressure vessel for 5 hr. at  $150^\circ$  under autogenous pressure. The excess hydrogen fluoride was removed under a stream of nitrogen and aqueous cesium hydroxide was added to the residue until it was basic. The precipitate was recrystallized from water and dried under vacuum at  $100^\circ$  to obtain 17 g., 0.034 mole (49%), of  $\text{Cs}_2\text{B}_{12}\text{H}_7\text{F}_5$ .

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_7\text{F}_5$ : B, 25.9; F, 19.1. Found: B, 25.3; F, 18.6.

$\text{B}_{12}\text{H}_6\text{F}_6^{-2}$ .— $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$  (18.0 g., 0.08 mole) and hydrogen fluoride (90 g., 2.5 moles) were heated to  $200^\circ$  for 5 hr. in a 400-ml. Hastelloy pressure vessel. The volatile materials were vented at  $50^\circ$ , a fresh 90-g., 2.5-mole, charge of hydrogen fluoride was added, and the mixture was reheated to  $200^\circ$  for another 5 hr. It was then cooled and the volatiles were bled off. The residue was concentrated in a platinum dish on a steam bath until a viscous paste formed. This was made alkaline with 9 ml. of 9.5 *N* sodium hydroxide, water (76 ml.) was added, and the solution was filtered. The filtrate was concentrated on a steam bath. The residue was dissolved in 15 ml. of water and 27 g., 0.2 mole, of triethylammonium chloride in 27 ml. of water was added. A white solid precipitated and was recrystallized twice

from water (35 ml. and then 25 ml.) at  $60^\circ$  to give 22.0 g., 0.048 mole (60%), of  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{12}\text{H}_6\text{F}_6$ .

*Anal.* Calcd. for  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{12}\text{H}_6\text{F}_6$ : C, 31.7; H, 8.4; B, 28.6; N, 6.2; F, 25.1. Found: C, 31.4; H, 7.9; B, 27.9; N, 6.0, 5.9; F, 26.3. Ultraviolet:  $\text{H}_2\text{O}$ , no max.

$\text{B}_{12}\text{F}_{11}\text{OH}^{-2}$ -Cs Salt.— $\text{K}_2\text{B}_{12}\text{H}_{12}$  (8.8 g., 0.04 mole) was dissolved in water (200 ml.) in a polytetrafluoroethylene beaker. A 1:5 mixture of fluorine and nitrogen was bubbled into the solution for 50 hr., at a rate of 90 cc./min. with cooling to about  $0^\circ$ .  $\text{KBF}_4$  (6.9 g., 0.055 mole) was removed by filtration; the filtrate was concentrated in a platinum dish on a steam bath to leave a viscous mass that was neutralized with 8 ml. of 7 *N* potassium hydroxide and filtered. The solid obtained from the filtration was washed with 10 ml. of water; the residue remaining was an additional 4.4 g., 0.035 mole, of  $\text{KBF}_4$ . Cesium fluoride, 6 g. in 6 ml. water, was added to the filtrate to precipitate 8.2 g., 0.013 mole (32.5%), of  $\text{Cs}_2\text{B}_{12}\text{F}_{11}\text{OH}$ . Partial concentration of the mother liquor gave another 1.6 g., 0.0025 mole (6.5%), of  $\text{Cs}_2\text{B}_{12}\text{F}_{11}\text{OH}$ . The crude products were combined and recrystallized three times from slightly more than their weight in water and then dried under vacuum at  $100^\circ$ .

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{F}_{11}\text{OH}$ : Cs, 42.8; B, 20.9; F, 33.6. Found: Cs, 42.2; B, 21.3; F, 33.5. Ultraviolet:  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  313  $\mu\text{m}$  ( $\epsilon$  87), 290  $\mu\text{m}$  ( $\epsilon$  100).

The presence of the hydroxyl group was demonstrated by: (1) an infrared band at  $3690\text{--}3660\text{ cm}^{-1}$  (doublet), (2) gross disappearance of this absorption and appearance of bands at  $2710\text{--}2690\text{ cm}^{-1}$  for  $\text{--O--D}$  stretching after recrystallization from deuterium oxide, and (3) gross disappearance of the hydroxyl band and appearance of a strong  $\text{C=O}$  band at  $1720\text{ cm}^{-1}$  after heating the salt with formic acid, presumably due to conversion to  $\text{Cs}_2\text{B}_{12}\text{F}_{11}\text{OCHO}$ . This new infrared pattern persisted after recrystallization from water. Additional evidence was the formation of  $\text{Cs}_2\text{B}_{12}\text{F}_{11}\text{OCOF}$  (infrared analysis only) upon heating  $\text{Cs}_2\text{B}_{12}\text{F}_{11}\text{OH}$  with carbonyl fluoride at  $150^\circ$ . This product hydrolyzed readily in water.

$\text{B}_{12}\text{H}_{11}\text{Cl}^{-2}$ .— $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12} \cdot 5\text{H}_2\text{O}$  (11 g., 0.041 mole) and anhydrous hydrogen chloride (20 g., 0.55 mole) were heated to  $85^\circ$  in a 400-ml. Hastelloy pressure vessel for 4 hr. at autogenous pressure. The hydrogen chloride was removed and the residue was neutralized with aqueous tetramethylammonium hydroxide. The resulting precipitate was recrystallized two times from water to obtain 6 g., 0.018 mole (45%), of  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_{11}\text{Cl}$ .

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_{11}\text{Cl}$ : N, 8.6; Cl, 11.1. Found: N, 8.2; Cl, 11.6. Ultraviolet:  $\text{CH}_3\text{CN}$ , no max.

$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (24.9 g., 0.063 mole) in 100 ml. of water was added slowly with stirring to  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$  (42.4 g., 0.19 mole) in 100 ml. of water. Gold metal precipitated immediately and after 1 hr. of stirring the solution was filtered. The addition of excess aqueous cesium chloride to the filtrate gave  $\text{Cs}_2\text{B}_{12}\text{H}_{11}\text{Cl} \cdot \text{CsCl}$ , which was recrystallized from water.

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_{11}\text{Cl} \cdot \text{CsCl}$ : Cs, 65.3; B, 21.3; Cl, 11.6. Found: Cs, 62.1; B, 21.0; Cl, 11.6.

$\text{B}_{12}\text{H}_6\text{Cl}_6^{-2}$ .— $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12} \cdot 5\text{H}_2\text{O}$  (10 g., 0.037 mole) was dissolved in 100 ml. of water. Chlorine was passed into the solution at  $0^\circ$  until reaction ceased as shown by retention of the chlorine color. The solution was concentrated and neutralized with ammonium hydroxide. The addition of excess aqueous tetramethylammonium chloride solution precipitated  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_6\text{Cl}_6$ .

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_6\text{Cl}_6$ : C, 19.3; H, 6.1; B, 26.1; Cl, 42.7. Found: C, 18.6; H, 5.7; B, 25.7; Cl, 43.2. Ultraviolet:  $\text{CH}_3\text{CN}$ , no max.

From the results of fractionation studies we are fairly certain that there are penta- and heptachloro species present in this material.

**Chlorination of  $\text{B}_{12}\text{H}_{12}^{-2}$  at  $35$  to  $100^\circ$ .**—Chlorine was passed through a solution of 0.122 mole of  $\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot \text{H}_2\text{O}$  in 500 ml. of water at such a rate that the reaction temperature was maintained at about  $35^\circ$ . After the reaction temperature began to fall, external heat was applied to maintain the temperature at  $35^\circ$  for a period of about 2 hr. The reaction solution was then

TABLE III  
 $B_{12}Cl_{12}^{-2}$  SALTS

Cation	Calcd.						Found					
	B	Cl	C	H	M, S, N	H <sub>2</sub> O <sup>a</sup>	B	Cl	C	H	M, S, N	H <sub>2</sub> O
2Cs	15.5	50.7	...	...	31.7	...	15.6	50.4	...	...	31.2	...
2(CH <sub>3</sub> ) <sub>4</sub> N <sup>b</sup>	18.8	61.2	13.9	3.5	4.0	...	18.1	61.1	13.9	4.0	4.1	...
2(CH <sub>3</sub> ) <sub>4</sub> N·CH <sub>3</sub> O- C <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	16.6	53.6	18.2	4.6	...	...	16.2	52.5	18.0	4.4	...	...
2H <sub>3</sub> O <sup>+</sup> ·4H <sub>2</sub> O	19.6	64.0	...	...	...	16.2	19.9	63.4	...	...	...	16
2H <sub>3</sub> O <sup>+</sup> <sup>c</sup>	21.9	71.7	...	...	...	6.1	22.2	72.3	...	...	...	5.5
2Ag	16.8	55.2	...	...	28.0	...	16.5	54.6	...	...	27.7	...
2Na·2.5H <sub>2</sub> O	20.1	65.8	...	...	7.1	...	19.6	66.0	...	...	7.6	...
Ni·8H <sub>2</sub> O	17.1	56.1	...	...	7.7	...	16.8	58.3	...	...	7.8	...
Ni·4H <sub>2</sub> O	18.9	62.0	...	...	8.5	10.5	18.9	62.8	...	...	8.6	9.7
Ni	...	69.3	...	...	9.6	0.0	...	68.2	...	...	9.4	0.3
Zn·7H <sub>2</sub> O	17.4	57.0	...	...	8.8	...	17.5	57.1	...	...	8.6	...
2(hex) <sub>4</sub> N	10.3	33.7	45.6	8.6	2.2	...	10.0	33.5	45.8	8.6	2.4	...

<sup>a</sup> By the Karl Fischer method, which was found to be applicable to perhalogenated acids and salts. It does not work for  $B_{10}H_{10}^{-2}$  or  $B_{12}H_{12}^{-2}$  acids or salts and has not been attempted with partially halogenated species. <sup>b</sup> Ultraviolet:  $\lambda_{max}^{CH_3CN}$  243 m $\mu$  ( $\epsilon$  110). <sup>c</sup> Neut. equiv. calcd. 298; found 300.

cooled to room temperature and reduced in volume by about 10% by vacuum evaporation. The reaction mixture was divided into three fractions and cesium, trimethylsulfonium, and tetramethylammonium salts were prepared and recrystallized several times from water or water-methanol mixtures. The analytical data showed that in the cesium salt the boron to chlorine ratio was 12:9.5; in the trimethylsulfonium salt, 12:9.5; and in the tetramethylammonium salt, 12:9.1.

Similar procedures were followed with a maximum reaction temperature of 80 and of 97° maintained for periods of 2 hr. Analyses of the various salts established boron to chlorine ratios of 12:10.6 for the 80° reaction and of 12:10.8 for the 97° reaction.

$B_{12}Cl_{12}^{-2}$ .—Analyses for the following  $B_{12}Cl_{12}^{-2}$  salts are in Table III. A solution of  $Na_2B_{12}H_{12} \cdot 2H_2O$  (40 g., 0.18 mole) in 320 ml. of water was chlorinated at ambient temperature for 1.5 hr. and then was split into two portions. Each portion was charged to a 400-ml., silver-lined pressure vessel to which 50 g. of chlorine was then added and the vessels were heated to 150° for 2 hr. under autogenous pressure. The liquids were removed, filtered, and combined. Excess chlorine was removed at reduced pressure and the solution was neutralized with 10 N potassium hydroxide and filtered. Excess concentrated aqueous cesium chloride was added;  $Cs_2B_{12}Cl_{12}$  separated and was recrystallized from 2.8 times its weight of water to obtain 117 g., 0.14 mole (77%), of  $Cs_2B_{12}Cl_{12} \cdot H_2O$ . This salt can be dehydrated over  $P_2O_5$  at 25°. In a similar experiment the  $B_{12}Cl_{12}^{-2}$  anion was precipitated as a tetramethylammonium salt with tetramethylammonium chloride. The  $[(CH_3)_4N]_2B_{12}Cl_{12}$  was recrystallized from water; when recrystallized from aqueous 1,2-dimethoxyethane it was recovered as a monoetherate,  $[(CH_3)_4N]_2B_{12}Cl_{12} \cdot CH_3OCH_2CH_2OCH_3$ .  $Cs_2B_{12}Cl_{12}$  (296 g., 0.36 mole) was dissolved in 2900 ml. of water at 80° and passed through an ion-exchange column containing 755 g. of acidic ion-exchange resin. The effluent was taken to dryness *in vacuo* at less than 50° and the residual crystals were dried over phosphorus pentoxide at 25° under vacuum to obtain a 100% yield of  $(H_3O)_2B_{12}Cl_{12} \cdot 4H_2O$ . Drying of  $(H_3O)_2B_{12}Cl_{12} \cdot 4H_2O$  for 21 hr. at 208° (0.005 mm.) over phosphorus pentoxide gave little change in the infrared spectrum but resulted in formation of  $(H_3O)_2B_{12}Cl_{12}$ . An aqueous solution of  $H_2B_{12}Cl_{12}$  (58 ml., 0.080 M) was stirred with 1.39 g., 0.0056 mole, of silver oxide for 4 hr. and then filtered. Silver oxide, 0.21 g., was recovered and the filtrate was evaporated to leave 3.7 g., 0.0048 mole (103%), of  $Ag_2B_{12}Cl_{12}$  as a white crystalline solid. A 0.086 M solution of  $H_2B_{12}Cl_{12}$  was neutralized with 1 N sodium hydroxide and evaporated to dryness at 25° to obtain crystalline  $Na_2B_{12}Cl_{12} \cdot 2.5H_2O$ . Nickel carbonate, 0.019 mole, was stirred overnight with 200 ml. of 0.086 M aqueous  $H_2B_{12}Cl_{12}$ , filtered, and evaporated under vacuum at room temperature to leave pale green

crystals of  $NiB_{12}Cl_{12} \cdot 8H_2O$  (12 g., 0.015 mole, 85%). Drying 3.6 g., 0.0044 mole, of this salt at 100° under vacuum over phosphorus pentoxide for 3 hr. gave 3.3 g., 0.0044 mole, of  $NiB_{12}Cl_{12} \cdot 4H_2O$ , a yellow crystalline solid. Drying the tetrahydrate at 207° under vacuum for 21 hr. gave  $NiB_{12}Cl_{12}$  as a hygroscopic yellow crystalline solid.  $H_2B_{12}Cl_{12}$  (10.4 ml., 0.2 M) was mixed with zinc oxide (0.75 g., 0.092 mole), diluted to 400 ml., and refluxed for 4 hr. The hot solution was filtered and evaporated. The residue was dried 18 hr. over phosphorus pentoxide and there was obtained 0.84 g., 0.0011 mole, of  $ZnB_{12}Cl_{12} \cdot 7H_2O$ .  $H_2B_{12}Cl_{12}$  (25 ml., 0.3 M) was added with stirring to tetra-*n*-hexylammonium iodide (75 g., 0.9 mole) in 750 ml. of 50% aqueous ethanol at 40°. A white solid precipitated which was filtered, washed with 50% aqueous ethanol, and recrystallized twice from 500 ml. of ethanol.  $[(hex)_4N]_2B_{12}Cl_{12}$ , 9.2 g., 0.0072 mole (96%), was obtained as long colorless needles, m.p. 234–235°. This salt is soluble in methylene chloride, acetone, and methanol, partly soluble in chloroform and dioxane, and insoluble in water, benzene, and hexane.

$B_{12}H_6Br_6^{-2}$ .— $Na_2B_{12}H_{12} \cdot 2H_2O$  (22 g., 0.098 mole) in 200 ml. of 50% aqueous methanol was cooled to 5° and bromine (32.2 ml., 0.62 mole) was added dropwise. The bromine color was completely discharged. The solution was filtered and evaporated at 80° (10 mm.) to leave an oil and a white solid. This residue was made alkaline with aqueous sodium hydroxide and again dried to leave a white solid which was extracted with warm tetrahydrofuran to separate the  $Na_2B_{12}H_6Br_6$  from the insoluble sodium bromide. A dioxanate of the sodium salt can be precipitated in 62% yield from such tetrahydrofuran solutions by the addition of dioxane.

*Anal.* Calcd. for  $Na_2B_{12}H_6Br_6 \cdot 10/3 C_4H_8O_2 \cdot 2H_2O$ : C, 16.2; H, 3.5; B, 13.2; Na, 4.7; Br, 48.6. Found: C, 16.6; H, 3.9; B, 13.4; Na, 4.3; Br, 47.6.

In this run, however, the tetrahydrofuran solution was evaporated, leaving a sirup which was dissolved in 250 ml. of water and again evaporated. A sample of the residual  $Na_2B_{12}H_6Br_6$  (3.3 g., 0.005 mole) was dissolved in 5 ml. of water and a concentrated aqueous solution of 3.3 g., 0.02 mole, of cesium chloride was added. The resulting precipitate was recrystallized twice from water to give 2.5 g., 0.0028 mole, of  $Cs_2B_{12}H_6Br_6 \cdot H_2O$ , m.p. 491–492°.

*Anal.* Calcd. for  $Cs_2B_{12}H_6Br_6 \cdot H_2O$ : H, 0.9; Cs, 29.6; B, 14.4; Br, 53.3. Found: H, 1.1, 1.2; Cs, 29.4; B, 14.5; Br, 52.6. Ultraviolet:  $\lambda_{max}^{IR20}$  220 m $\mu$  ( $\epsilon$  320).

$Na_2B_{12}H_6Br_6$  (1.5 g., 0.0023 mole) in 50 ml. of water was mixed with excess aqueous trimethylsulfonium iodide, and the resulting precipitate was recrystallized from water to give 1.2 g., 0.0016 mole (68%), of  $[(CH_3)_3S]_2B_{12}H_6Br_6$ , dec. pt. 290°.

*Anal.* Calcd. for  $[(CH_3)_3S]_2B_{12}H_6Br_6$ : C, 9.4; H, 3.1; B,

16.9; Br, 62.3; S, 8.3. Found: C, 10.1, 10.2; H, 3.3, 3.1; B, 16.7; Br, 62.2; S, 8.4.

Adding ammoniacal cupric chloride solution to aqueous  $\text{Na}_2\text{B}_{12}\text{H}_6\text{Br}_6$  precipitated  $\text{Cu}(\text{NH}_3)_4\text{B}_{12}\text{H}_6\text{Br}_6$  (dec. pt. 256–260°) as a dark blue solid which was recrystallized twice from dilute ammonium hydroxide.

*Anal.* Calcd. for  $\text{Cu}(\text{NH}_3)_4\text{B}_{12}\text{H}_6\text{Br}_6$ : H, 2.4; Cu, 8.5; B, 17.4; Br, 64.2; N, 7.5. Found: H, 3.1; Cu, 8.5; B, 17.1; Br, 63.3; N, 7.5.

$\text{B}_{12}\text{H}_2\text{Br}_{10}^{-2}$ .—Bromine was added dropwise with stirring to 10 g., 0.031 mole, of  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_{12}\cdot 8\text{H}_2\text{O}$ , in 150 ml. of water. The temperature rose rapidly to 90–100° and remained there during the addition of 59 g., 0.37 mole, of bromine. The reaction rate fell sharply at this point; an additional 20 g. of bromine was added and the mixture was heated to 80–90° for 1 hr. It was then partially concentrated and separated into two portions. In one, the  $\text{B}_{12}\text{H}_2\text{Br}_{10}^{-2}$  anion was precipitated as a cesium salt by the addition of cesium fluoride and in the other it was precipitated as a tetramethylammonium salt with tetramethylammonium chloride. Both salts were recrystallized from water; the cesium salt was obtained as a tetrahydrate.

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_2\text{Br}_{10}\cdot 4\text{H}_2\text{O}$ : Cs, 21.0; B, 10.2; Br, 63.1. Found: Cs, 22.1; B, 10.3; Br, 62.5.

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_2\text{Br}_{10}$ : C, 8.9; H, 2.2; B, 12.0; Br, 74.1. Found: C, 8.9; H, 2.2; B, 11.6; Br, 74.4. Ultraviolet:  $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$  207 m $\mu$  ( $\epsilon$  4300), shoulder at 255 m $\mu$  ( $\epsilon$  147).

The cesium salt of  $\text{B}_{12}\text{H}_2\text{Br}_{10}^{-2}$  was converted to the acid form by passage through an ion-exchange column. The solution was evaporated to obtain crystalline  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_2\text{Br}_{10}\cdot 6\text{H}_2\text{O}$ .

*Anal.* Calcd. for  $(\text{H}_3\text{O})_2\text{B}_{12}\text{H}_2\text{Br}_{10}\cdot 6\text{H}_2\text{O}$ : B, 12.1; Br, 74.2; neut. equiv., 538. Found: B, 11.5; Br, 74.8; neut. equiv., 539.

The addition of silver nitrate to aqueous  $\text{H}_2\text{B}_{12}\text{H}_2\text{Br}_{10}$  precipitated the silver salt.

*Anal.* Calcd. for  $\text{Ag}_2\text{B}_{12}\text{Br}_{10}\text{H}_2$ : Ag, 18.8; B, 11.3; Br, 69.7. Found: Ag, 18.5; B, 12.0; Br, 68.4.

$\text{B}_{12}\text{Br}_{12}^{-2}$ .—A solution of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  (20 g., 0.09 mole) in 200 ml. of 50% aqueous methanol was cooled to 5–15° and bromine was added dropwise with stirring. After the first 30 ml., 0.58 mole, had been added, the rate of reaction decreased markedly; the cooling was stopped, an additional 30 g. of bromine was added in one portion, and a fast stream of chlorine was passed into the solution. The temperature rose to 50°. After reaction was complete the excess halogens were removed under vacuum and the solution was neutralized with ammonium hydroxide. It was then divided into two portions. In one the  $\text{B}_{12}\text{Br}_{12}^{-2}$  anion was precipitated as a cesium salt with cesium fluoride and in the other it was precipitated as a tetramethylammonium salt with tetramethylammonium bromide. Both salts were recrystallized from water.

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{Br}_{12}$ : Cs, 19.6; B, 9.6; Br, 70.8. Found: Cs, 18.1; B, 9.6; Br, 71.3. Ultraviolet:  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  260 m $\mu$  ( $\epsilon$  100).

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{Br}_{12}$ : C, 7.8; H, 1.9; B, 10.5; Br, 77.6. Found: C, 8.3; H, 2.7; B, 10.6; Br, 77.7.

In a similar run in which all of the product was isolated as a cesium salt, an 80% yield was obtained. Chlorine was shown by analysis to be completely absent. Passage of an aqueous solution of  $\text{Cs}_2\text{B}_{12}\text{Br}_{12}$  through an acid ion-exchange column and evaporation of the effluent gave  $(\text{H}_3\text{O})_2\text{B}_{12}\text{Br}_{12}\cdot 6\text{H}_2\text{O}$  as a white crystalline solid.

*Anal.* Calcd. for  $(\text{H}_3\text{O})_2\text{B}_{12}\text{Br}_{12}\cdot 6\text{H}_2\text{O}$ : B, 10.5; Br, 77.6; neut. equiv., 618. Found: B, 10.3; Br, 77.9; neut. equiv., 613.

$\text{Ag}_2\text{B}_{12}\text{Br}_{12}$  was precipitated in virtually quantitative yield by adding a solution of silver nitrate (0.008 mole) in 25 ml. of water to a stirred solution of  $\text{Cs}_2\text{B}_{12}\text{Br}_{12}$  (0.008 mole) in 200 ml. of water in the dark.

*Anal.* Calcd. for  $\text{Ag}_2\text{B}_{12}\text{Br}_{12}$ : B, 10.0. Found: B, 9.9.

$\text{B}_{12}\text{H}_{11}\text{I}^{-2}$ .—Iodine (25.4 g., 0.10 mole) in 200 ml. of methanol was added gradually to a solution of  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  (22.4 g., 0.10 mole) in 50 ml. of water and 150 ml. of methanol. The iodine color disappeared immediately. The solution was neutral-

ized with ammonium hydroxide and excess aqueous tetramethylammonium chloride was added. The precipitate was recrystallized several times from water.

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_{11}\text{I}$ : C, 23.1; H, 8.4; B, 31.2; I, 30.5. Found: C, 23.6; H, 8.7; B, 30.8; I, 30.4. Ultraviolet:  $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$  224 m $\mu$  ( $\epsilon$  3760).

$\text{B}_{12}\text{H}_{10}\text{I}_2^{-2}$ .—The procedure used to prepared  $\text{B}_{12}\text{H}_{11}\text{I}^{-2}$  was repeated except that 50.8 g., 0.20 mole, of iodine was used and the product was precipitated with cesium fluoride. A  $\text{CsI}-\text{Cs}_2\text{B}_{12}\text{H}_{10}\text{I}_2$  double salt was obtained and recrystallized from water.

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_{10}\text{I}_2\cdot \text{CsI}$ : Cs, 43.7; B, 14.1; I, 41.4. Found: Cs, 42.9; B, 14.0; I, 41.8.

In a separate experiment, hydrogen iodide was removed by evaporating the reaction mixture to dryness. Dissolution of the residue in water followed by addition of cesium fluoride and recrystallization from water gave  $\text{Cs}_2\text{B}_{12}\text{H}_{10}\text{I}_2$ .

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_{10}\text{I}_2$ : B, 19.7; I, 38.5. Found: B, 19.3; I, 39.0. Ultraviolet:  $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$  220 m $\mu$  ( $\epsilon$  6860).

The proton magnetic resonance spectrum of  $\text{Na}_2\text{B}_{12}\text{H}_{10}\text{I}_2$  in  $\text{D}_2\text{O}$  with boron decoupled indicates three types of hydrogen in a 1:3.3:0.88 ratio. 1,7-Substitution would require relative intensities of 1:3:1. The center peak is assigned to protons on borons adjacent to only one iodinated boron and its somewhat greater than theoretical intensity would be explained by the presence of a small amount of 1,12-substituted isomer.

$\text{B}_{12}\text{I}_{12}^{-2}$ .—Iodine (111 g., 0.44 mole) was added to  $\text{Na}_2\text{B}_{12}\text{H}_{12}\cdot 2\text{H}_2\text{O}$  (45 g., 0.20 mole) in 850 ml. of 1,1,2,2-tetrachloroethane, and the mixture was stirred 10 min. Iodine monochloride (450 g., 2.8 moles) in 250 ml. of 1,1,2,2-tetrachloroethane was added and the mixture was refluxed 43 hr., cooled, and the supernatant liquid was decanted. The residue was stirred in 700 ml. of 10% sodium hydroxide and filtered. The filtrate was added to a solution of 75 g., 0.69 mole, of tetramethylammonium chloride in 225 ml. of water to precipitate  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{I}_{12}\cdot (\text{CH}_3)_4\text{NI}$  (288 g., 0.14 mole, 70%). Recrystallization from 6.4 l. of 50% aqueous acetonitrile gave 226 g., 0.11 mole (55%), of this double salt.

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{I}_{12}\cdot (\text{CH}_3)_4\text{NI}$ : C, 7.2; H, 1.8; B, 6.5; I, 82.4; N, 2.1. Found: C, 7.1; H, 1.8; B, 7.0; I, 80.1; N, 2.2.

In a similar experiment run in carbon tetrachloride, the addition of aqueous cesium chloride to the water extract gave a cesium salt which was recrystallized twice from water.

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{I}_{12}$ : Cs, 13.8; B, 6.8; I, 79.4. Found: Cs, 13.2; B, 6.7; I, 78.7.

$[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{I}_{12}\cdot (\text{CH}_3)_4\text{NI}$  (47.8 g., 0.024 mole) was dissolved in 1400 ml. of 67% aqueous acetonitrile at 55° and passed through an acid ion-exchange column. The effluent was evaporated to dryness to remove HI and then dissolved in water. A small aliquot was mixed with aqueous tetramethylammonium chloride to precipitate  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{I}_{12}$ .

*Anal.* Calcd. for  $[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{I}_{12}$ : C, 5.3; H, 1.3; B, 7.2; I, 84.5. Found: C, 5.4; H, 1.6; B, 7.1; I, 82.5.

The remainder of the solution was neutralized with sodium hydroxide, evaporated, and dried under vacuum at 40° to obtain 37.2 g., 0.021 mole (89%), of  $\text{Na}_2\text{B}_{12}\text{I}_{12}\cdot 2\text{H}_2\text{O}$ .

*Anal.* Calcd. for  $\text{Na}_2\text{B}_{12}\text{I}_{12}\cdot 2\text{H}_2\text{O}$ : H, 0.27; Na, 2.6; B, 7.5; I, 87.8. Found: H, 0.8; Na, 2.8; B, 7.6; I, 87.7. Ultraviolet:  $\lambda_{\text{max}}^{\text{H}_2\text{O}}$  267 m $\mu$  ( $\epsilon$  4600).

$\text{Na}_2\text{B}_{12}\text{I}_{12}\cdot 2\text{H}_2\text{O}$  (3.6 g., 0.0021 mole) was dissolved in 100 ml. of water. Silver nitrate (0.7 g., 0.004 mole) in 20 ml. of water was added in the dark and the resulting precipitate was filtered and washed with water to give 3.6 g., 0.0019 mole (92%), of  $\text{Ag}_2\text{B}_{12}\text{I}_{12}$ .

*Anal.* Calcd. for  $\text{Ag}_2\text{B}_{12}\text{I}_{12}$ : B, 7.0. Found: B, 7.0.

$\text{B}_{12}\text{H}_3\text{Br}_9\text{Cl}_3^{-2}$ .— $\text{Na}_2\text{B}_{12}\text{H}_6\text{Br}_6$  (6 g., 0.009 mole) in 50 ml. of water was chlorinated with cooling at about 30° until chlorine was no longer absorbed. The solution was neutralized with ammonium hydroxide, and excess concentrated cesium chloride solution was added to precipitate  $\text{Cs}_2\text{B}_{12}\text{H}_3\text{Br}_9\text{Cl}_3\cdot 2\text{H}_2\text{O}$ , which was recrystallized from water.

*Anal.* Calcd. for  $\text{Cs}_2\text{B}_{12}\text{H}_3\text{Br}_9\text{Cl}_3\cdot 2\text{H}_2\text{O}$ : B, 12.7; Br, 47.9; Cl, 10.4. Found: B, 12.7; Br, 46.7; Cl, 10.1.



$B_{12}Br_3F_4^{-2}$ .— $Cs_2B_{12}H_3F_4$  (10 g., 0.021 mole) in 30 ml. of water was heated almost to reflux and 8 ml., 0.016 mole, of bromine was added slowly with stirring. The solution was heated to reflux and chlorine was passed into the mixture. To ensure an excess of bromine, four 2-ml. portions of bromine were added during the chlorination. The solution was cooled and the precipitated solid was filtered and recrystallized from aqueous cesium hydroxide and then from water.

Anal. Calcd. for  $Cs_2B_{12}Br_3F_4$ : B, 11.8; F, 6.8; Br, 57.0. Found: B, 12.9; F, 6.7; Br, 57.1.

$B_{12}H_3F_3I^{-2}$ .—Hydrated  $(H_2O)_2B_{12}H_{11}I$  (14 g., 0.04 mole) and 30 g., 1.5 moles, of anhydrous hydrogen fluoride were heated in a 400-ml. Hastelloy pressure vessel for 4 hr. at 90°. The HF was removed in a stream of nitrogen and the residue was neutralized with aqueous cesium hydroxide. The precipitate was recrystallized twice from water to give  $Cs_2B_{12}H_3F_3I$ .

Anal. Calcd. for  $Cs_2B_{12}H_3F_3I$ : F, 9.7; I, 21.5. Found: F, 10.0, 10.6; I, 20.4, 20.8. Ultraviolet:  $H_2O$ , no max.

**Reaction of Alkali Metals with Iodo Derivatives.**— $[(CH_3)_4N]_2B_{10}H_7I_3$  slurried into 200 ml. of ammonia at  $-33^\circ$  was slowly treated with excess potassium in the form of small pellets. Rapid fading of the blue alkali metal-ammonia color was noted after the first few additions. Reaction times, however, increased as more potassium was added until the blue color lasted more than 2 hr. when all of the metal had been added. The solution was stirred for 6 hr., after which the ammonia was allowed to boil off. The white product was treated with *t*-butyl alcohol followed by ethanol and water. Infrared analysis showed that the only boron-containing species present was  $[(CH_3)_4N]_2B_{10}H_{10}$ . Following the same procedure, three samples of  $Cs_2B_{12}H_{10}I_2$  were treated with excess lithium, sodium, and potassium, respectively. Subsequent work-up yielded  $Cs_2B_{12}H_{12}$  as shown by infrared analysis.

In an effort to isolate intermediates, 4.55 g., 0.0073 mole, of  $Cs_2B_{12}H_{10}I_2$  in 50 ml. ammonia was treated with 1.203 g., 0.030 g.-atom, of potassium. The blue solution was filtered, leaving pinkish white solid. This solid was washed three times with 25-ml. portions of fresh ammonia and then deammoniated by flushing with nitrogen at reduced pressure at room temperature. An infrared spectrum of the product was identical with that of  $Cs_2B_{12}H_{12}$  with the exception of an unknown peak at  $1010\text{ cm.}^{-1}$ , which disappeared upon recrystallization from water.

**Acidity Function Studies.**—The acid strengths of  $H_2B_{12}Cl_{12}$  and  $H_2B_{12}Br_{12}$  were studied by measuring their acidity functions by the spectrophotometric method.<sup>17-19</sup> The apparatus and experimental procedures used were the same as reported previously<sup>1</sup> for similar studies on  $H_2B_{10}H_{10}$  and  $H_2B_{12}H_{12}$ . 4-Chloro-2-nitroaniline was used as the indicator. The acidity functions of  $H_2B_{12}Cl_{12}$  and  $H_2B_{12}Br_{12}$  were found to be independent of the indicator employed; *p*-nitroaniline gave the same results. The acidity functions reported in Table IV were calculated from the optical density readings at  $420\text{ m}\mu$ .

Comparison of these  $H_0$  values with the values presented by

(17) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(18) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(19) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

TABLE IV  
ACIDITY FUNCTIONS OF  $H_2B_{12}Cl_{12}$  AND  $H_2B_{12}Br_{12}$

$H_2B_{12}Cl_{12}$		$H_2B_{12}Br_{12}$	
Concn., <i>M</i>	$H_0$	Concn., <i>M</i>	$H_0$
1.105	-1.073	1.106	-1.103
0.883	-0.828	0.884	-0.850
0.706	-0.647	0.706	-0.672
0.564	-0.494	0.565	-0.504
0.451	-0.380	0.451	-0.390
0.361	-0.251	0.361	-9.276
0.216	+0.009	0.216	-0.060
0.1296	+0.172	0.115	+0.211

Bascombe and Bell<sup>18</sup> for sulfuric acid shows that  $H_2B_{12}Cl_{12}$  and  $H_2B_{12}Br_{12}$  are slightly stronger acids in these concentration regions than is sulfuric acid and they have about the same  $H_0$  values as  $H_2B_{10}H_{10}$  and  $H_2B_{12}H_{12}$ .<sup>1</sup>

**Spectral Characterization.**—Infrared spectra were obtained with a Model 21 Perkin-Elmer spectrophotometer. Ultraviolet and visible spectra were examined on a Cary Model 14 spectrometer. Nuclear magnetic resonance was observed on a Varian spectrometer, Model V4300. Double irradiation was effected with an NMR Specialties Model SF 60 spin decoupler ( $B^{11}$  saturation by 19.2-Mc. irradiation while observing  $H^1$  at 60 Mc. and  $H^1$  saturation by 60-Mc. irradiation while examining  $B^{11}$  at 19.2 Mc.).

**Polarographic Studies.**—All potentials are referred to the saturated calomel electrode (s.c.e.). A graphite-Nujol paste electrode (c.e./Nj) was used for oxidation studies and a dropping mercury electrode (d.m.e.) for reduction.  $Cs_2B_{10}Br_{10}$ ,  $Cs_2B_{10}Cl_{10}$ , and  $Cs_2B_{10}H_2Cl_8$  were run in 0.1 *M*  $LiClO_4$  as electrolyte,  $Cs_2B_{10}I_{10}$  was run in Britton-Robinson pH 4, 7, and 10 buffers and in 0.1 *M*  $KH_2PO_4$  (pH 4.5), which has a more positive available potential range (about 0.3 or 0.4 v.) than the other buffers or  $LiClO_4$ .

**Oxidation: C.e./Nj vs. S.c.e.**— $Cs_2B_{10}Cl_{10}$ —not oxidized out to +1.1 v. (limit of potential range of aqueous 0.1 *M*  $LiClO_4$ ).  $Cs_2B_{10}H_2Cl_8$  and  $Cs_2B_{10}Br_{10}$ —oxidation begins just prior to +1.1 v., the magnitude and  $E_{p/2}$  being masked by the oxidation of solvent-electrolyte (aqueous  $LiClO_4$ ).  $Cs_2B_{10}I_{10}$ —oxidized at  $E_{p/2} + 1.3$  v. in 0.1 *M*  $KH_2PO_4$  electrolyte (pH about 4.5). Oxidation currents are large, as might be expected if total oxidation of B and I were to occur, but they are not proportional to concentration ( $i_p/C$  increases with dilution).

**Reduction: D.m.e. vs. S.c.e.**— $B_{10}Cl_{10}^{-2}$ ,  $B_{10}H_2Cl_8^{-2}$ , and  $B_{10}Br_{10}^{-2}$  were not reduced in 0.1 *M* aqueous  $LiClO_4$  (+0.3 to -1.9 v.).  $B_{10}I_{10}^{-2}$  was not reduced at the d.m.e. in Britton-Robinson buffers at pH 4, 7, and 10 (+0.05 to -1.85 v.).

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