though by comparison, for example, with the behavior of As_2O_3 in oleum[19] it seems probable that more sulfated species such as $IO(HSO_4)_3$ and possibly $I(HSO_4)_5$ are likely to be formed.

Experimental

The apparatus for the cryoscopic measurements was a slightly modified form of that described previously.[20] The concentrations of the solutions were varied by dilution of a relatively concentrated solution by addition of successive weighed quantities of the solvent rather than by successive additions of weighed quantities of solute. This experimental procedure was adopted because of the slow rate of solution of iodic acid in sulfuric acid even at 100°. Freezing points were measured as previously described[20] using a calibrated resistance thermometer in conjunction with a Mueller bridge.

The conductivity cell was a slightly modified version of that described by Gillespie, Oubridge, and Solomons[21] (Fig. 2). In order to prepare solutions the bulk of the solvent was transferred to the flask A, which contained a Teflon-covered stirring bar and could be placed on a hot-plate magnetic stirrer to hasten the dissolution of the iodic acid. The resistance of a solution in the conductivity cell was measured by means of a Jones bridge (Leeds and Northrup) used in conjunction with a Hewlett-Packard Model 201C oscillator, operated at 1000 c.p.s., and a General Radio Type 1231-B amplifier and null-detector. Conductivity cells were immersed in an oil thermostat maintained at $25 \pm 0.002°$, the temperature of which was checked periodically with a calibrated resistance thermometer.

Acknowledgment.—We thank the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research and the National Research Council, Canada, for financial assistance. We also thank the National Research Council, Canada, for the award of a studentship (to J. B. S.).

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(20) R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2473 (1950).

(21) R. J. Gillespie, J. V. Oubridge, and C. Solomons, *ibid.*, 1804 (1957).

CONTRIBUTION NO. 838 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
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Chemistry of Boranes. VIII.[1] Salts and Acids of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

BY E. L. MUETTERTIES, J. H. BALTHIS, Y. T. CHIA, W. H. KNOTH, AND H. C. MILLER

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A kinetic stability unique for boranes toward thermolysis, hydrolysis, and oxidation has been found for the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ anions.

We have found the stability of the $B_{10}H_{10}^{-2}$ [2–4] and $B_{12}H_{12}^{-2}$ [2,5,6] anions toward heat, acids and bases, and oxidizing agents to be truly surprising when contrasted with that of other boron hydrides. Since both $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ are thermodynamically[7] unstable with reference to boric oxide or boric acid, much of the observed stability, particularly the hydrolytic and oxidative stability, must be kinetic in nature.

Properties of the Polyhedral Borane Anions in Water.—There is no evidence of reaction between $B_{10}H_{10}^{-2}$ or $B_{12}H_{12}^{-2}$ and strong aqueous sodium hydroxide even at 95°. Since these boranes bear a dinegative charge, this resistance to the thermodynamically favored hydrolysis is at least in part a reflection of a coulombic repulsion effect.

In 3 *N* hydrochloric acid $B_{12}H_{12}^{-2}$ is stable at 95° while $B_{10}H_{10}^{-2}$ reacts only slowly. There is rapid proton exchange between water and the anions under acidic conditions. This latter effect is evidenced by rapid changes in the characteristic B^{11} n.m.r. spectra when solutions of the anions in D_2O are acidified. Thus, the doublet B^{11} spectrum of $B_{12}H_{12}^{-2}$ collapses to a single peak due to conversion to $B_{12}D_{12}^{-2}$, and the two doublets of $B_{10}H_{10}^{-2}$ yield two singlets. By following rates of B^{11} doublet collapse, rough estimates for the rate of deuteration were obtained. With a relative rate of 1 for $B_{12}H_{12}^{-2}$, the values for $B_{10}H_{10}^{-2}$ are 68 for equatorial positions and 330 for apical positions. We find that the greater reactivity of $B_{10}H_{10}^{-2}$ toward an electrophilic reagent is maintained in the derivative chemistry of the polyhedral anions to be detailed in succeeding papers.

With but few exceptions,[8] anionic boron hydrides are rapidly degraded by acids, and the kinetic stability of the $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ anions is unexpected. Passage of salts of these anions through a column of strongly acidic ion-exchange resin yields stable solutions of the acids. The solutions may be concentrated at room temperature to give crystalline hydrates of the acids. Free-flowing but still somewhat wet-looking crystals of the B_{12} acid with as many as 20 moles of water have been obtained. The B_{10} acid, however, becomes crystalline only at much lower degrees of hydration. Both acids are strong, comparable to sulfuric acid, and there

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(1) Paper VII: J. A. Forstner, T. E. Haas, and E. L. Muetterties, *Inorg. Chem.*, **3**, 155 (1964).

(2) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, E. L. Muetterties, and J. C. Sauer, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(3) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **81**, 5519 (1959).

(4) W. N. Lipscomb, M. F. Hawthorne, and A. R. Pitochelli, *ibid.*, **81**, 5833 (1959).

(5) M. F. Hawthorne and A. R. Pitochelli, *ibid.*, **82**, 3228 (1960).

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

(7) Salts of these anions can be ignited in a flame and hydrolysis to boric acid can be effected under strongly acidic conditions at temperatures above 200°.

(8) $B_{10}H_{12}P(C_6H_5)_2^-$ is rather resistant to acid degradation: E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, **1**, 731 (1962).

was no evidence in aqueous systems of gross proton nonequivalence in an acidity function study. Thus, as discussed by Britton,[9] it can be estimated that the first and second ionization constants do not differ by more than a factor of 16. Furthermore, salts of the anions, with certain exceptions as discussed below, function as strong electrolytes; a detailed study of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ ion conductances will be reported separately.[10]

The reactivity of the hydrated acids is a function of both water content and temperature. Reactivity is enhanced with reduction in water content or by increase in temperature. When the hydronium salt of $B_{12}H_{12}^{-2}$ in dilute aqueous solution is heated in a sealed tube at temperatures above 150°, hydrogen is evolved and $B_{12}H_{11}OH^{-2}$ can be isolated. A similar reaction occurs with the hydronium salt of $B_{10}H_{10}^{-2}$ at temperatures above 50°. Substitutions of this nature will be described in detail in a later paper.

Dehydration of the B_{10} acid sometimes yields a non-salt-like volatile species, $B_{10}H_{12}OH_2$, which may be a member of the $B_{10}H_{12}\cdot$base or $B_{10}H_{13}^-$ structural class.[11] This conversion is not always reproducible. Because of some unknown factor, complete degradation to boric acid may prevail upon attempted dehydration.

Thermal Stability.—Salts of both $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with cations which are not readily reduced and are themselves thermally stable have high thermal stability. For example, $Cs_2B_{12}H_{12}$ when heated to 810° in an evacuated sealed quartz tube is recovered unchanged. Under similar conditions, $Cs_2B_{10}H_{10}$ is unchanged at 600°.

Toxicity.—Sodium salts of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, administered orally to rats, were found to have a low order of acute toxicity, with the approximate lethal dose for *rats* being 7.5 g./kg. of body weight and >7.5 g./kg. of body weight for $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$, respectively.[12] On the basis of these tests, the oral toxicity of these polyhedral boranes to *rats* is roughly comparable to sodium chloride. This again demonstrates the unique stability of these polyhedral borane anions since most if not all other boron hydrides are very toxic.

Properties of the Salts.—In general, large unipositive cations yield relatively water-insoluble salts of $B_{12}H_{12}^{-2}$ and $B_{10}H_{10}^{-2}$. These salts are readily isolated and purified and are useful derivatives for analysis. Examples of the cations commonly employed here are Tl^+, Cs^+, Rb^+, $(CH_3)_4N^+$, and $(CH_3)_3S^+$. In general, the salts of $B_{10}H_{10}^{-2}$ are more water soluble than their $B_{12}H_{12}^{-2}$ counterparts. A striking example is shown by the triethylammonium salts. The $B_{10}H_{10}^{-2}$ salt is highly water soluble whereas the $B_{12}H_{12}^{-2}$ salt is very insoluble. Also noteworthy is the greater solubility in aqueous acid than in aqueous base of quaternary ammonium and sulfonium salts. This behavior bears a formal analogy to the enhanced solubility of insoluble sulfates in strongly acidic solutions and suggests that the second ionization of the acids is repressed by high hydrogen ion concentrations to the point that the dianion concentration is too low to permit precipitation of those salts of borderline insolubility. $Cs_2B_{12}H_{12}$ is only slightly soluble in water, but in the presence of certain other anions, double salts even less soluble in water are isolated. Examples of anions (Y^-) which form these insoluble double salts include Cl^-, CN^-, and BH_4^-. In each case the $Cs_2B_{12}H_{12}\cdot CsY$ ratio has been 1:1.

Small unipositive cations and most dipositive cations, such as Ba^{+2} and Ca^{+2}, form water-soluble salts isolated as hydrates upon evaporation. This is true also for many divalent and trivalent transition and rare earth elements. Their salts are again isolated as

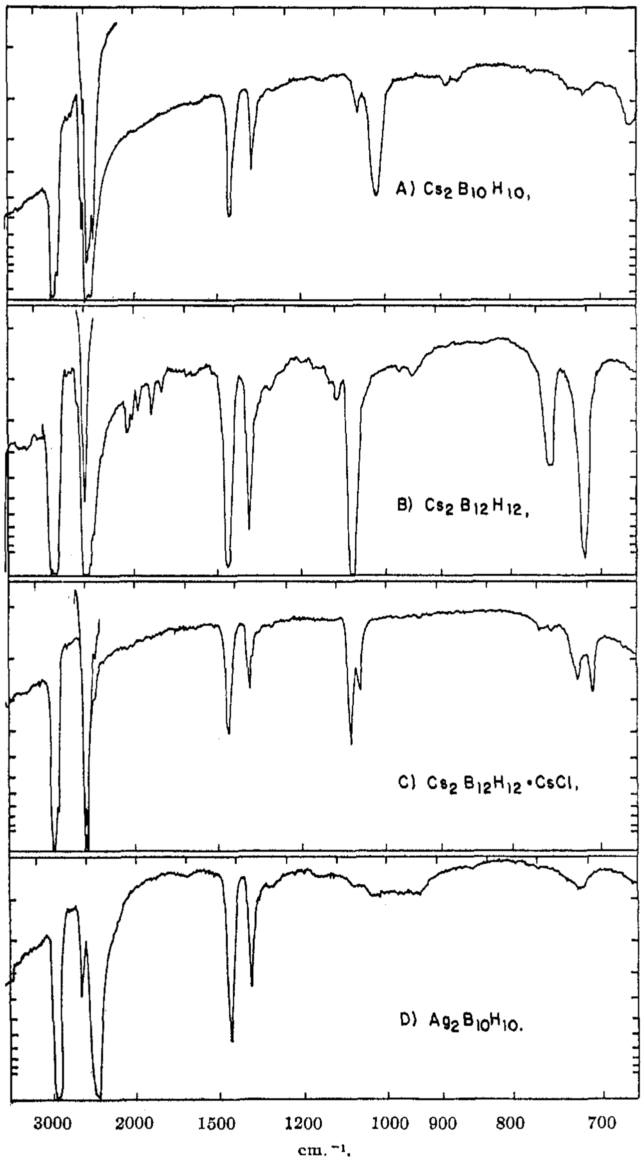

Fig. 1.—Infrared spectra (Nujol mulls) of (A) $Cs_2B_{10}H_{10}$, (B) $Cs_2B_{12}H_{12}$, (C) $Cs_2B_{12}H_{12}\cdot CsCl$, (D) $Ag_2B_{10}H_{10}$.

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(9) H. T. S. Britton, "Hydrogen Ions," Vol. I, Chapman and Hall, Ltd., London, 1955.

(10) Y. T. Chia, to be published.

(11) (a) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961); (b) M. F. Hawthorne, A. R. Pitochelli, R. D. Strahm, and J. J. Miller, *J. Am. Chem. Soc.*, **82**, 1825 (1960).

(12) W. H. Sweet, A. N. Soloway, and R. L. Wright, *J. Pharmacol. Exptl. Therap.*, **137**, 263 (1962), report low toxicity of $Na_2B_{10}H_{10}$ to white Swiss albino mice and to humans.

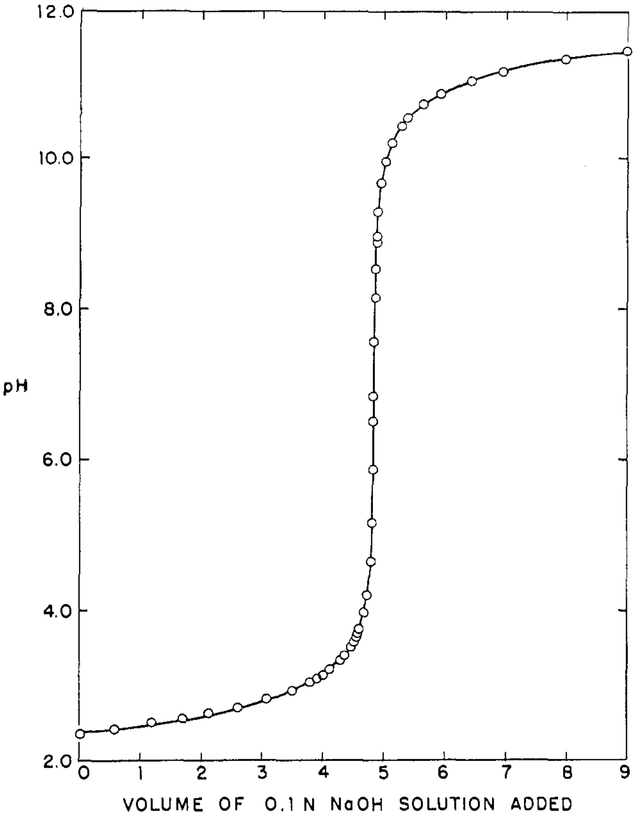

Fig. 2.—The titration curve of aqueous $H_2B_{12}H_{12}$.

hydrates. If the water in the coordination sphere of the metal is replaced by other basic ligands, such as NH_3, then water solubility of the salts decreases significantly.

Cations with strong polarizing properties, such as Ag^+, Cu^+, and Hg^{+2}, form water-insoluble salts which are notable in several respects. First, the salts form without any evidence of metal ion reduction. Reduction of silver ion has in the past been a diagnostic test for BH bonds. This again shows the unique stability of these polyhedral anions. Secondly, spectroscopic data (*vide infra*) suggest a significant and localized (symmetry loss) interaction between cation and anion. This effect is more notable in $B_{10}H_{10}^{-2}$ than in $B_{12}H_{12}^{-2}$ and is consistent with the general finding that $B_{10}H_{10}^{-2}$ is more susceptible to electrophilic attack. No irreversible reactions occur in the formation of these salts since the anions can be regenerated from the salts. The silver salts show some solubility in concentrated silver nitrate solutions and in excess $B_{12}H_{12}^{-2}$ suggesting complex ion formation.

These observations are not surprising in view of the crystal structure of $Cu_2B_{10}H_{10}$ reported by Dobrott and Lipscomb.[13] These authors find the copper ions to be within bonding distance of the apex-equatorial edges of the B_{10} polyhedron and propose that there is significant localized interaction between the copper ions and the B_{10} cage. In the infrared spectrum of $Cu_2B_{10}H_{10}$, the characteristic "cage" bands at 1015 and 1070 cm.$^{-1}$ are no longer evident, the normally strong B–H stretching around 2500 cm.$^{-1}$ is weak, and a second broad absorption at 2100–2300 cm.$^{-1}$ appears. These changes in the infrared spectrum are attributed to a polarization of the B_{10} cage. On the basis of infrared spectra, $Ag_2B_{10}H_{10}$ and $Ag_2B_{12}H_{12}$ are similar to the copper salt. The infrared spectra of the mercuric salts of both B_{10} and B_{12} anions suggest that these compounds have a character intermediate between the Ag^+ or Cu^+ salts and the ionic salts in that the "cage" bands are no longer observed but the B–H stretching absorption is like that of a cesium salt. The B^{11} n.m.r. data for $B_{10}H_{10}^{-2}$ in the presence of copper (I) ion (Fig. 4) show the chemical shift of the apical boron atoms to be more affected than that of the equatorial boron atoms, suggestive of close approach of the apical boron atoms and the copper atoms. However, such a conclusion is not valid without a more detailed analysis of changes in chemical shifts and relaxation times.

Certain salts of $B_{10}H_{10}^{-2}$ are colored, and the origin of the color is ascribed to a charge-transfer band. The pyridinium and α,α'-dipyridinium salts of $B_{10}H_{10}^{-2}$ are yellow and the quinolium salt deep yellow. Since pyridinium and α,α'-dipyridinium iodides are not colored, $B_{10}H_{10}^{-2}$ would appear to be a better electron donor than is I^-. In contrast, the corresponding salts of $B_{12}H_{12}^{-2}$ are colorless. These data conform with our polarographic finding that $B_{10}H_{10}^{-2}$ is significantly more prone to oxidation, *i.e.*, electron transfer or donation, than is $B_{12}H_{12}^{-2}$.

Spectral Properties of the Salts and Acids.—Neither $B_{10}H_{10}^{-2}$ nor $B_{12}H_{12}^{-2}$ has absorption maxima in the visible region or in the ultraviolet down to 200 mμ, where strong end absorption appears.

The Raman and infrared data for $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ have been discussed in detail in an earlier paper.[14] In general, we find infrared absorption excellent for characterization of $B_{10}H_{10}^{-2}$ or $B_{12}H_{12}^{-2}$ salts. In addition to the B–H stretching absorption at about 2470–2480 cm.$^{-1}$ there is, in $B_{12}H_{12}^{-2}$, a strong cage absorption frequency at 1070 cm.$^{-1}$ and decreasingly weaker absorptions in the regions of 720, 750, and 1115 cm.$^{-1}$, and in $B_{10}H_{10}^{-2}$ a strong cage absorption frequency at 1015 cm.$^{-1}$ and a much weaker absorption at 1070 cm.$^{-1}$.

The B–H stretching frequency is characterized as a single sharp absorption at 2480 cm.$^{-1}$ for solutions of $B_{12}H_{12}^{-2}$. A sharp B–H band at 2470 cm.$^{-1}$ with a more or less well developed secondary band or shoulder at 2532 cm.$^{-1}$ is shown by $B_{10}H_{10}^{-2}$. The shoulder is assignable to the apical B–H stretch. For Nujol mulls or KBr disks of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ salts, the B–H absorption often shows fine structure due to coupling with lattice vibrations. These characteristics are maintained throughout the acids and salts with the exception of (1) the silver, cuprous, and mercuric salts as discussed above and (2) the double salts of

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(13) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962)

(14) E. L. Muetterties, R. E. Merrifield, H. C. Miller, W. H. Knoth, and J. R. Downing, *J. Am. Chem. Soc.*, **84**, 2506 (1962). See also ref. 2 and 3.

$Cs_2B_{12}H_{12}$ with CsCl, CsCN, or $CsBH_4$ in which all of the major absorption bands (at 2475, 1070, 750, and 720 cm.$^{-1}$) become doublets. In Fig. 1 the infrared spectra of $Cs_2B_{12}H_{12}$, $Cs_2B_{12}H_{12}\cdot CsCl$, $Cs_2B_{10}H_{10}$, and $Ag_2B_{10}H_{10}$ are reproduced.

B^{11} Resonance.[15]—As reported by Lipscomb, Hawthorne, and Pitochelli,[4] $B_{10}H_{10}^{-2}$ shows two doublets of intensity ratio of 1:4. We find the small low-field doublet is centered at +23 p.p.m. and the high-field doublet at +53 p.p.m. The coupling constants are 140 and 125 c.p.s., respectively. Upon irradiation at 60 Mc. the B^{11} doublets collapse to singlets of relative intensities 1 and 4 at +23 and +53 p.p.m., respectively.

Similarly, the B^{11} resonance of $B_{12}H_{12}^{-2}$ reported by Hawthorne and Pitochelli[5] was confirmed as a doublet and found to be of 130 c.p.s. separation centered at +35 p.p.m. It collapses into a singlet at +35 p.p.m. upon irradiation at 60 Mc.

H^1 Resonance.[15]—The proton n.m.r. spectra of the anions are unexpected in that the hydrogen atoms of $B_{12}H_{12}^{-2}$ and, to a lesser extent, the nonapical hydrogen atoms of $B_{10}H_{10}^{-2}$ do not give sharp, four-line spectra. The spectrum of $B_{12}H_{12}^{-2}$ consists of a broad plateau with a line width of about 400 c.p.s. (three times the B–H coupling constant) centered at about −2.0 p.p.m. At each end of the plateau is a broad peak somewhat above the level of the center area. Upon irradiation at 19.2 Mc., the 60-Mc. H^1 signal becomes a sharp singlet at −2.0 p.p.m. The H^1 resonance of the equatorial hydrogens of $B_{10}H_{10}^{-2}$ is observed as a broad quartet centered at −0.9 p.p.m. and A_{BH} = 124 c.p.s. The apical hydrogens show a relatively sharp quartet, $\delta = -4.3$ p.p.m. and A_{BH} = 140 c.p.s. Upon irradiation at 19.2 Mc., the $B_{10}H_{10}^{-2}$ proton spectrum reduces to two sharp lines at −4.3 and −0.9 p.p.m. of relative intensity of 1 to 4.

Experimental

Decahydrodecaborate Synthesis.—$(NH_4)_2B_{10}H_{10}$ was prepared from decaborane through the sequence of reactions

$$B_{10}H_{14} + 2(CH_3)_2S \longrightarrow B_{10}H_{12}\cdot 2S(CH_3)_2 + H_2$$

$$B_{10}H_{12}\cdot 2S(CH_3)_2 + 2NH_3 \longrightarrow (NH_4)_2B_{10}H_{10} + 2(CH_3)_2S$$

Decaborane (454 g., 3.7 moles, used as received from Olin Mathieson Co.) was dissolved in dimethyl sulfide (2 l., Crown Zellerbach) with stirring at room temperature over about 10 min. The small amount of insoluble material was removed by rapid filtration through fiber glass filter cloth. The filter was washed with several 250-ml. portions of fresh dimethyl sulfide, and the washings were added to the filtrate. The filtrate and washings, in a 5-l. flask fitted with a water-cooled reflux condenser, were allowed to stand at room temperature for at least 4 days. Hydrogen was evolved and colorless crystals of $B_{10}H_{12}\cdot 2S(CH_3)_2$[11a,16] separated. More dimethyl sulfide was added as necessary to keep the crystals covered. This required several additions over the 4 days. The yellow liquid phase was removed from the crystals by a filter stick, and the crystals were dried by oil pump evacuation at 20–30°. Liquid ammonia was then added to a total volume of about 3 l. Solution was effected with stirring. The stirring was then discontinued and ammonia allowed to evaporate from the open flask. The crude $(NH_4)_2B_{10}H_{10}$ residue was dried *in vacuo* at 25–30°, dissolved in a minimum amount of cold water, and immediately filtered with suction. The filtrate was then evaporated to dryness *in vacuo* in a rotating evaporator, and the resulting solid dried to constant weight at 50° *in vacuo*. The yield was 478 g. (3.1 moles, 83.6% yield). Purification was effected by recrystallization from concentrated water solution. The crude salt was dissolved in water (0.71 ml./g. of salt) at 90°, filtered hot, chilled to 5° overnight, collected, and dried to constant weight (50° *in vacuo*) to give 70–75% recovery in the first crop. More product of good quality could be recovered from the filtrate.

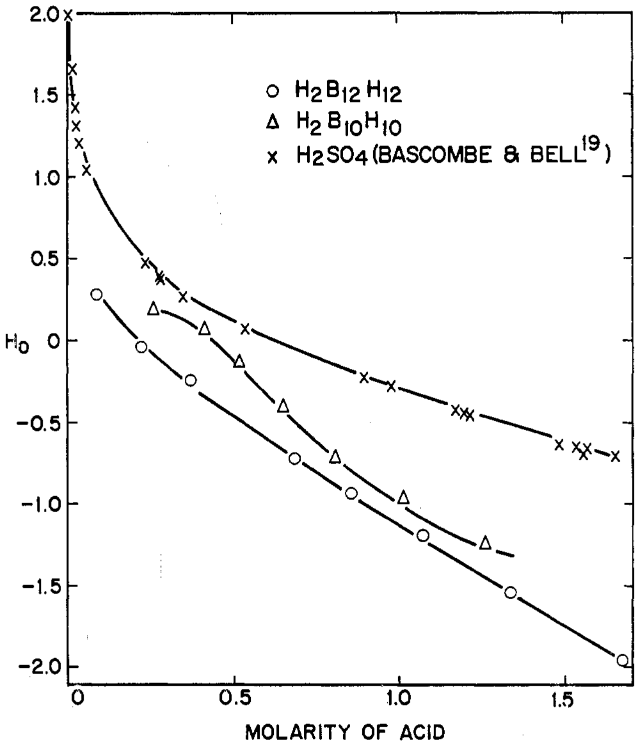

Fig. 3.—Acidity functions of aqueous $H_2B_{10}H_{10}$ and $H_2B_{12}H_{12}$.

Anal. Calcd. for $(NH_4)_2B_{10}H_{10}$: H, 11.7; B, 70.0; NH_3, 22.1. Found: H, 11.6; B, 70.1; NH_3, 22.0.

Dodecahydrododecaborate Synthesis.—The preparation of $B_{12}H_{12}^{-2}$ as its triethylammonium salt is described by Hawthorne and Pitochelli.[5] We employed an alternative synthesis which is described in another paper.[17]

$H_2B_{10}H_{10}\cdot nH_2O$.—A solution of 3.6 g. of $[(CH_3)_3CNH_3]_2B_{10}H_{10}$ in 30 ml. of water was passed through a column containing 30 ml. of a strong acid ion-exchange resin (Amberlite IR 120H). The strongly acidic effluent was collected, and the column was washed with water until all of the acid had been obtained. The water was evaporated at 20–30° under reduced pressure in a rotating evaporator to leave a sirupy tetrahydrate.

Anal. Calcd. for $H_2B_{10}H_{10}\cdot 4H_2O$: H, 10.5; B, 61.9. Found: H, 9.5; B, 61.4.

Further drying at 30° (0.01 mm.) gave a solid which approached a dihydrate in composition. However, hydrogen values were reproducibly low, and the sample was no longer completely water soluble. Thus, some degree of nonreversible reaction had occurred. The infrared spectra showed OH stretch at 3705 cm.$^{-1}$, B–H stretching at 2500 cm.$^{-1}$, and $B_{10}H_{10}^{-2}$ cage absorption at 1085 and 1030 cm.$^{-1}$. Although the residue from acid so dried was not completely water-soluble it was soluble in 5% aqueous potassium hydroxide from which $Cs_2B_{10}H_{10}$ was precipitated by

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(15) Chemical shifts are referred to methyl borate (B^{11}) or tetramethylsilane (H^1).

(16) R. J. Pace, J. Williams, and R. L. Williams, *J. Chem. Soc.*, 2196 (1961).

(17) H. C. Miller, N. E. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **85**, 3885 (1963).

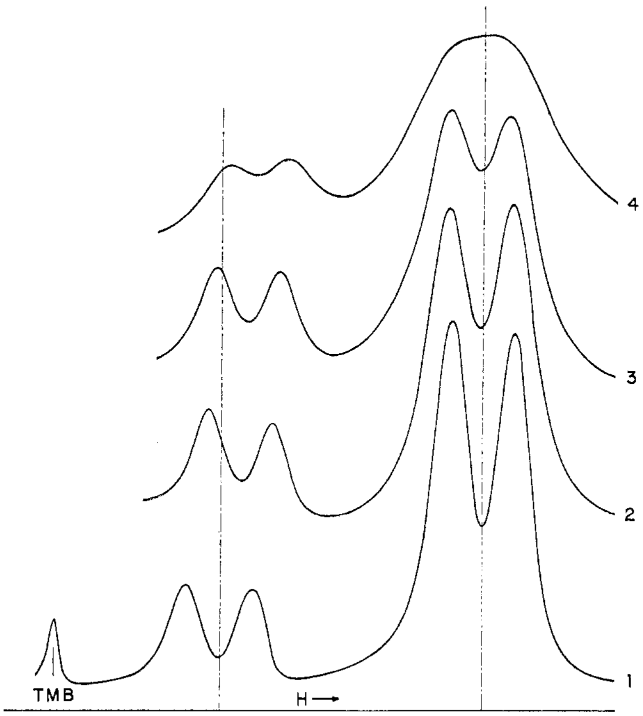

Fig. 4.—B^{11} n.m.r. at 19.25 Mc., trimethyl borate (TMB) reference. Solution 1 contained 0.0171 mole of $(NH_4)_2B_{10}H_{10}$ in 4.5 ml. of water. To this solution was added $Cu_2B_{10}H_{10}$ to give a $Cu_2B_{10}H_{10}$:$(NH_4)_2B_{10}H_{10}$ ratio of 0.25 in (2), 0.4 in (3), and, at $Cu_2B_{10}H_{10}$ saturation, 0.67 in (4).

addition of aqueous cesium fluoride. The residue sublimed with some decomposition at 80° (0.1 mm.). The sublimate melted at 202–206° and its infrared spectrum was not that of $H_2B_{10}H_{10} \cdot nH_2O$. It showed OH stretching absorption at 3570 cm.$^{-1}$ and B–H stretching absorption at 2565 cm.$^{-1}$. The sublimate had absorption at 1430 cm.$^{-1}$ (B–O region) not shown by the hydrated acid. The longer wave length region was suggestive of that of decaborane. In contrast to the free acid, the sublimate was soluble in organic solvents, reduced silver nitrate, and solutions of it in dioxane showed an absorption maximum in the ultraviolet at 2620 Å. with a shoulder at 3250 Å. Elemental analysis was in keeping with $B_{10}H_{14}O$. Solution of the sublimate in 5% KOH gave a clear yellow solution from which $B_{10}H_{10}^{-2}$ could not be isolated. Addition of ammoniacal zinc chloride gave colorless crystals analyzing for a $B_9H_{14}^-$ salt.

Anal. Calcd. for $B_{10}H_{14}O$: H, 10.2; B, 78.2; mol. wt., 138. Found: H, 10.0; B, 78.1; mol. wt., 157 (m.p. of C_6H_6).

Anal. Calcd. for $Zn(NH_3)_4(B_9H_{14})_2$: H, 11.2; B, 54.0; Zn, 18.2; N, 15.6. Found: H, 11.2; B, 53.9; Zn, 18.2; N, 15.6.

The hydrates of $H_2B_{10}H_{10}$ must be handled with some care. The heat of dilution with water or polar organic solvents can bring about a very exothermic decomposition with spontaneous ignition of the evolved gases. Care must also be exercised whenever the borohydride salts or residues containing them are digested with strong oxidants. Analytical procedures involving digestions with concentrated nitric or sulfuric acids have led to violent decompositions.

$H_2B_{12}H_{12} \cdot nH_2O$.—An aqueous solution of 5.7 g. (0.028 mole) $Na_2B_{12}H_{12} \cdot H_2O$ was treated with Amberlite 120H as described above. Concentration of the acid effluent under reduced pressure at room temperature left white crystals. A relatively free-flowing, but still damp-looking, crystalline solid was first obtained. Depending upon the extent of drying, its neutral equivalent weight varied from 158 to 250 (indicating $H_2B_{12}H_{12} \cdot 10H_2O$ to $H_2B_{12}H_{12} \cdot 20H_2O$). A sample dried at 40° (0.05 mm.) for 1 hr. melted at 82° and its infrared spectrum showed, in addition to water bands, BH stretching absorption at 2500 cm.$^{-1}$ and B_{12} cage absorption at 1070 cm.$^{-1}$.

Anal. Calcd. for $H_2B_{12}H_{12} \cdot 4H_2O$: H, 10.3; B, 60.1. Found: H, 10.2; B, 60.7.

Solid $H_2B_{12}H_{12} \cdot 4H_2O$ is *hygroscopic* but remains essentially unchanged upon storage at room temperature in dry air.

The reactivity of the acids toward water depends on both temperature and concentration as shown in Table I from sealed tube experiments with the aqueous acids over a range of concentrations and temperatures. The monohydroxy derivatives will be described in detail in a forthcoming paper.

TABLE I

Acid	Temp., °C.	Molarity	Time, hr.	Moles of H_2/mole of acid	Product recovered
$H_2B_{10}H_{10}$	50	2.8	10	0.4	. . .
	60	2.8	10	1.1	$B_{10}H_9OH^{-2}$
$H_2B_{12}H_{12}$	50	2.8	22	0.006	$B_{12}H_{12}^{-2}$
	60	2.8	22	0.02	$B_{12}H_{12}^{-2}$
	150	0.7	4	Very little	$B_{12}H_{12}^{-2}$
	200	0.2	4	0.8	. . .
		0.8	4	1.8	$B_{12}H_{11}OH^{-2}$

The strength of these two acids was estimated by measuring their acidity functions by the spectrophotometric method.[18-20] Optical densities were measured on either a Model 11 or Model 14R Cary recording spectrophotometer with a 25 ± 0.05° thermostated cell holder. The solutions were studied in the wave length range from 500 to 350 mμ with appropriate length absorption cells. A Beckman Model G pH meter was used for the potentiometric titration.

Conductivity water was used for all experiments. 4-Chloro-2-nitroaniline was used as the indicator.[19] A stock solution of about 5 × 10^{-4} *M* was prepared by direct weighing.

Calculations.—The acidity function was evaluated from the established[19] relation

$$H_0 = \text{p}K + \log\left[\frac{(\text{B})}{(\text{BH}^+)}\right] = \text{p}K + \log\frac{[D - D_{\text{BH}^+}]}{[D_\text{B} - D]} \quad (1)$$

where *K* is the ionization constant of the indicator, (B) and (BH^+) represent the concentration of basic and acidic forms of the indicator, respectively, D_B and D_{BH^+} are the corresponding optical densities, and *D* is the optical density of the acid investigated. In this work the optical density readings at 420 mμ were used for the calculation of H_0. An absorption maximum was observed in the vicinity of that wave length. The values of H_0 for the free acids of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ at different concentrations are reported in Table II. These values are plotted against the concentrations of the acid in Fig. 3. The values of H_0 were also calculated from spectrophotometric results at 400 and 440 mμ. They were found to be in good agreement with those from 420 mμ.

TABLE II

ACIDITY FUNCTIONS OF THE FREE ACIDS OF $B_{12}H_{12}^{-2}$ AND $B_{10}H_{10}^{-2}$

$H_2B_{12}H_{12}$		$H_2B_{10}H_{10}$	
C, M	H_0	*C, M*	H_0
0.0888	0.281	0.262	0.1863
0.222	−0.038	0.415	0.0585
0.371	−0.240	0.519	−0.135
0.685	−0.716	0.648	−0.411
0.857	−0.931	0.810	−0.722
1.071	−1.193	1.012	−0.971
1.338	−1.534	1.265	−1.255
1.671	−1.957		

In order to compare the acid strengths of $H_2B_{10}H_{10}$ and $H_2B_{12}H_{12}$ with a known divalent acid, the values of the acidity functions of

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sulfuric acid reported by Bascombe and Bell[19] are also plotted in Fig. 3 along with a few measurements for sulfuric acid made in the present investigation using 4-chloro-2-nitroaniline as indicator. Our results agree very well with those of Bascombe and Bell.[19] The acidity function of the borane acids was found to be independent of the indicator employed; the same results were obtained with *p*-nitroaniline as indicator.

Salts of B_{10} and B_{12}.—Sparingly water-soluble salts of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ include Ag^+, Tl^+, Hg^{+2}, Cs^+, R_4N^+, R_3NH^+, R_4P^+, R_3S^+, $Ni(NH_3)_6^{+2}$, and the ammine complexes of other divalent transition metals. These salts are readily obtained by metathetical reactions and may be recrystallized. The cesium, thallium, trimethylsulfonium, tetra-*n*-alkylammonium, and quaternary phosphonium salts of both anions recrystallize readily from water. The insoluble ammonia complexes of the Ag^+, Co^{+2}, Ni^{+2}, Cu^{+2}, and Zn^{+2}, etc., salts must be recrystallized from aqueous ammonia to avoid separation of the hydrous oxides of the metals. The ammonia complexes of Co^{+3} and Cr^{+3} are highly water soluble and recrystallize from water only from concentrated solutions with poor recovery. Frequently such salts as the tetramethylammonium salt of $B_{10}H_{10}^{-2}$, which are too water soluble for good recovery, are best recrystallized from aqueous methanol, in which they are less soluble. Salts of large organic cations, such as tetra-*n*-hexylammonium, are best recrystallized from chloroform–petroleum ether or similar solvent mixtures. Examples of salts so prepared and purified are included in Table III.

Water-soluble $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ salts are most conveniently prepared from the corresponding aqueous free acids either by (1) exact neutralization with aqueous base (LiOH or $Ba(OH)_2$, for example), (2) treatment of the aqueous acid with an insoluble metal oxide or carbonate ($NiCO_3$, for example), or (3) reaction of the aqueous acid with a free metal (Fe or Al, for example). Evaporation of the resulting solution to dryness then gives the desired salt, usually as a hydrate. Examples are given in Table III.

In several instances, double salts of $B_{12}H_{12}^{-2}$ were encountered. For example, when $Cs_2B_{12}H_{12}$ was precipitated in the presence of Cl^-, the first material to separate from solution had the composition $Cs_2B_{12}H_{12}\cdot CsCl$, and this is the only product isolated if sufficient Cl^- is present. Aqueous CsF, Cs_2SO_4, or CsOH precipitates $Cs_2B_{12}H_{12}$, which is recrystallizable from water. Recrystallization from aqueous chloride solution then gives the less soluble CsCl double salt. Other examples of $Cs_2B_{12}H_{12}$ double salts are those with CsCN and $CsBH_4$. In these salts the infrared absorptions at about 2475, 1070, 750, and 725 cm.$^{-1}$ of $Cs_2B_{12}H_{12}$ become doublets at 2500/2470, 1090/1060, 765/750, and 725/710 cm.$^{-1}$, for example, for $Cs_2B_{12}H_{12}\cdot CsCl$.

Anal. Calcd. for $Cs_2B_{12}H_{12}$: H, 3.0; B, 31.8; Cs, 65.2; formula wt., 407.8. Found: H, 3.1; B, 31.6; Cs, 65.4; formula wt., 409.8 (by X-ray: face centered cubic, a = 11.28 Å., d (found) = 1.896; Z = 4); m.p. (sealed capillary) 658–662°.

Anal. Calcd. for $Cs_2B_{12}H_{12}\cdot CsCl$: H, 2.1; B, 22.5; Cs, 69.2; Cl, 6.2; formula wt., 576. Found: H, 2.2; B, 22.1; Cs, 66.2; Cl, 6.3; formula wt., 569 (by X-ray: orthorhombic, a = 14.27 Å., b = 9.85 Å., c = 10.36 Å., d (found) = 2.52, Z = 4); m.p. (sealed capillary) >730°.

Anal. Calcd. for $CsBH_4\cdot Cs_2B_{12}H_{12}\cdot H_2O$: H, 3.2; B, 24.5; Cs, 69.5. Found: H, 3.0; B, 24.3; Cs, 69.5.

Anal. Calcd. for $CsCN\cdot Cs_2B_{12}H_{12}$: C, 2.1; H, 2.1; N, 2.5. Found: C, 2.3; H, 1.9; N, 2.4.

In contrast to the $B_{12}H_{12}^{-2}$ anion, $B_{10}H_{10}^{-2}$ gives highly colored salts with certain aromatic bases. These products were made from aqueous $(NH_4)_2B_{10}H_{10}$ and an acidified aqueous solution of the base.

(Pyridinium)$_2$B$_{10}$H$_{10}$, yellow plates from water, m.p. 221–222° dec. In acetonitrile, the absorption spectrum over the range of 200 to 500 mμ was that of pyridinium (ϵ_{262} 2890, ϵ_{256} 5750, and ϵ_{250} 5030) plus a weak peak at 355 mμ (ϵ 183) which tailed into the visible region.

Anal. Calcd. for $C_{10}H_{12}N_2B_{10}H_{10}$: C, 43.1; H, 8.0; B, 38.9; N, 10.1. Found: C, 42.7; H, 8.0; B, 38.5; N, 9.5.

(Quinolinium)$_2$B$_{10}$H$_{10}$, yellow needles from water, m.p. 202–203° dec. In acetonitrile, the absorption spectrum over 200–500 mμ was that of the quinolinium ion (ϵ_{313} 6700, ϵ_{306} 6050, ϵ_{233} 36,800) plus a weak peak at 412 mμ (ϵ 129).

Anal. Calcd. for $C_{18}H_{16}N_2B_{10}H_{10}$: C, 57.1; H, 6.9; B, 28.6; N, 7.4. Found: C, 56.5; H, 6.9; B, 28.9; N, 7.3, 7.2.

(2,2′-Bipyridinium)$_2$B$_{10}$H$_{10}$, deep yellow crystals from water, m.p. 209–210° dec. In acetonitrile, the absorption over the range 200–500 mμ was that of the bipyridinium cation (ϵ_{302} 15,900, ϵ_{239} 9400).

Anal. Calcd. for $C_{20}H_{20}N_4B_{10}H_{10}$: C, 55.5; H, 6.7; B, 25.0; N, 13.0. Found C, 55.7; H, 6.8; B, 25.2; N, 13.0.

Hydrolytic Stability.—Solutions 0.5 M in $B_{12}H_{12}^{-2}$ and in $B_{10}H_{10}^{-2}$ in 3 N HCl and 3 N NaOH were heated 16 hr. at 95°. Recovery of $B_{12}H_{12}^{-2}$ as its CsCl double salt from both the acidic and basic solution and of $B_{10}H_{10}^{-2}$ as its tetra-*n*-propylammonium salt from the basic solution was quantitative. Recovery of $B_{10}H_{10}^{-2}$ as its tetra-*n*-propylammonium salt from 3 N HCl was 73% before heating and 60% after heating, suggesting a loss of perhaps 10–15% of $B_{10}H_{10}^{-2}$ in 16 hr. at 95° in 3 N HCl.

Thermal Stability.—In a typical experiment, a sample of salt (about 3 g.) was sealed under vacuum in a 14 mm. o.d. × 60 mm. Vycor ampoule equipped with an axial thermocouple well. A matched chromel–alumel thermocouple was placed in a similar sample of an inert material and temperature differences between the salt sample and the control were measured as the samples were heated at a constant rate of 5–6°/min.

$Cs_2B_{12}H_{12}$ showed a large endotherm beginning at 652°, which peaked at 666°. Other small endotherms of undetermined origin with peaks at 157, 569, and 721° were noted up to 811°. The recovered sample appeared to have been molten, was not darkened, and its infrared spectrum was unchanged. The large endotherm reflects a fusion process. Visual observations indicated a sealed tube melting point of 658–662°.

Under similar conditions, $Cs_2B_{10}H_{10}$ showed small endotherms peaking at 143 and 268° and a large endotherm at 606°. The latter absorptions might be attributed to fusion, but this does not check well with the visual sealed tube melting point of 641–642°.

Deuteration.—The rate of H–D exchange of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ has been found to be pH dependent. The exchange is promoted by acid and inhibited by base. Products having no observable infrared B–D stretching absorption at 1870 cm.$^{-1}$ were obtained when $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ were recrystallized from boiling D_2O at a pH of 8–9 (sodium acetate), a pH of 7, or even at a pH of 4–5 (acetic acid–sodium acetate). However, recrystallization from D_2O about 0.02 N in HCl gave a B_{10} salt in which the B–D intensity was twice that of the B–H intensity. Under the same conditions of recrystallization, much less deuterium was introduced into $Cs_2B_{12}H_{12}$. The intensity of B–D absorption was only about one-fifth that of the B–H absorption.

$B_{12}D_{12}^{-2}$.—An almost completely deuterated sample of $B_{12}H_{12}^{-2}$ was prepared as follows: 2.0 g. of $Na_2B_{12}H_{12}\cdot H_2O$ in 16 ml. of D_2O containing a catalytic amount of DCl was allowed to stand for 7 days and then evaporated. The residue was treated with 10 ml. of D_2O containing 2 drops of 38% DCl in D_2O for 5 days at room temperature. This operation was repeated four times and then finally was carried out at reflux. The final residue was dissolved in dilute sodium acetate solution and treated with $(CH_3)_4NCl$ to give an insoluble $(CH_3)_4N^+$ salt in which I_{B-H}/I_{B-D} was only 0.08.

Upon complete deuteration, the B_{12} cage band (at 1070 cm.$^{-1}$ in $B_{12}H_{12}^{-2}$) shifts to 925 cm.$^{-1}$ with much weaker absorption at 960 and 990 cm.$^{-1}$. The strong band at 715 cm.$^{-1}$ and the weaker band at 750 cm.$^{-1}$ (in $Cs_2B_{12}H_{12}$) both disappear upon deuteration.

$B_{10}D_{10}^{-2}$.—In the same manner as described above for deuteration of $B_{12}H_{12}^{-2}$, $B_{10}H_{10}^{-2}$ was converted to $B_{10}D_{10}^{-2}$. The resulting tetramethylammonium salt in which $I_{B-H}/I_{B-D} = 0.136$ had no major infrared absorptions from 1665 to 715 cm.$^{-1}$ other than those attributable to the cation. The apical B–D showed as a shoulder at about 1887 cm.$^{-1}$ on the stronger, equatorial B–D at about 1850 cm.$^{-1}$.

TABLE III: $B_{10}H_{10}^{2-}$ AND $B_{12}H_{12}^{-2}$ SALTS

Salt	Method[a]	Elemental analysis									Remarks[e]
		B		C		H					
		Calcd.	Found	Calcd.	Found	Calcd.	Found		Calcd.	Found	
$Li_2B_{10}H_{10}\cdot H_2O$	c	72.1	72.1					NE[c]	75.1	71.2	Dried under vac. at 100°
$Na_2B_{10}H_{10}\cdot 2H_2O$	c	54.0	55.0	0	0.3	7.0	6.7	Na	23.0	22.8	Dried under vac., r.t., P_2O_5
$Na_2B_{12}H_{12}\cdot H_2O$		63.1	63.5			6.9	7.1	Na	22.3	21.6	
$Cs_2B_{10}H_{10}$	a	28.2	28.1			2.6	2.8				
$Cu_2B_{12}H_{12}$	f	48.3	47.7			4.5	4.8	Cu	47.2	47.2	Begins to darken at 200°, still solid at 585°
$Ag_2B_{10}H_{10}$	a	32.4	32.4			3.0	3.0	Ag	64.6	64.5	Pptd., ex. H_2O. Washed with alcohol. Begins to darken at 270°, still solid at 360°
$Ag_2B_{12}H_{12}$	a	36.4	36.2	0.0	0.5	3.4	4.2	Ag	60.3	58.9	Begins to darken at 320°, still solid at 360°
$Tl_2B_{10}H_{10}$	a	20.5	20.3					Tl	77.6	77.7	Darkens at 400°, still solid at 575°
$Tl_2B_{12}H_{12}$	c	23.5	23.4	0	0.3	2.2	2.4	Tl	74.2	71.9	Darkens at 500°, still solid at 665°
$Mn(H_2O)_6B_{12}H_{12}$	b ($MnCO_3$)	42.6	42.7	0	0.4	7.9	8.0	Mn	18.0	17.6	Dried under vac., 20–30°. Still solid and white at 630°
$MnB_{12}H_{12}\cdot 0.07H_2O$	b ($MnCO_3$)	65.5	65.6	0	0.3	6.2	6.4	Mn	27.7	27.6	Dried under vac., P_2O_5, 111°
$Co(H_2O)_6B_{10}H_{10}$	b ($CoCO_3$)	37.9	37.3	0	0.1	7.8	7.9	Co	20.7	21.2	Pink, dried under vac., r.t., dec. *ca.* 166°
$CoB_{10}H_{10}\cdot 0.06H_2O$	b ($CoCO_3$)	57.5	58.0	0	0.33	6.0	6.2	Co	31.4	30.9	Dried under vac. over P_2O_5, r.t.
$Co(H_2O)_6B_{12}H_{12}\cdot 1.6H_2O$	b ($CoCO_3$)	40.4	40.5	0	0.3	8.0	7.9	Co	18.3	18.3	Pink, dried under vac., r.t., dec. *ca.* 150°
$Ni(H_2O)_6B_{10}H_{10}\cdot 3H_2O$	b ($NiCO_3$)	31.9	32.1	0	0.5	8.3	8.5	Ni	17.3	17.5	Dried under vac., r.t., green, dec. *ca.* 93°. On further drying, turns gray with decn.
$Ni(H_2O)_6B_{12}H_{12}\cdot 0.25H_2O$	b ($NiCO_3$)	41.5	41.4	0	0.6	7.9	8.0	Ni	18.7	18.7	Dried under vac., r.t., pale green
$NiB_{12}H_{12}\cdot 0.8H_2O$	b ($NiCO_3$)	60.3	60.3	0	0.4	6.4	6.2	Ni	27.3	27.2	Dried under vac., P_2O_5 to 100°. Yellow, hygroscopic
$BaB_{12}H_{12}$	b ($BaCO_3$)	46.5	46.8					Ba	49.2	49.1	Dried under vac., 100°. Still white and solid at 650°
$[Al(H_2O)_6]_2(B_{12}H_{12})_3\cdot 16H_2O$	a[b]	39.6	39.4	0	1.1	9.4	9.1	Al	5.5	5.5	Dried under vac., r.t., deliq., dec. *ca.* 150°
$Eu_2(B_{12}H_{12})_3\cdot 11H_2O$	b (Eu_2O_3)	42.0	42.4					Eu	32.8	32.9	Dried under vac., r.t., P_2O_5. Brown
$[Cr(NH_3)_6]_2(B_{12}H_{12})_3\cdot 7H_2O$	c	45.3	45.6	(N = 19.5	19.4)	10.1	9.7	Cr	12.1	11.8	Orange
$[Co(NH_3)_6]_2(B_{12}H_{12})_3\cdot 6H_2O$	c	45.5	44.6	(N = 19.6	20.1)	9.9	9.6	Co	12.8	14.1	Orange. Purple at 190°. Black at 360°
$Ni(NH_3)_6B_{12}H_{12}\cdot 0.5H_2O$	a	41.6	41.6	(N = 26.9	26.9)	10.0	9.8	Ni	18.6	18.8	Lavender. Blackens about 320°
$[(CH_3)_4N]_2B_{10}H_{10}$	a	40.6	39.9	36.1	35.5	12.9	13.0	N	10.5		Dec. *ca.* 330°
$[(CH_3)_4N]_2B_{12}H_{12}$	a	44.7	44.6	33.1	33.7	12.5	13.0	N	9.7	9.8	Dec. *ca.* 340–342°
$(t\text{-}C_4H_9NH_3)_2B_{10}H_{10}$	e	40.6	39.7	36.1	36.6	12.9	12.4	N	10.5	10.5	Dec. *ca.* 270–271°
$[(C_2H_5)_3NH]_2B_{12}H_{12}$	a			41.7	41.6	12.7	12.7	N	8.1	8.0	Dec. *ca.* 298–300°
$[C_6H_{11}NH(CH_3)_2]_2B_{12}H_{12}\cdot 2H_2O$	a	29.9	29.9	44.2	44.4	12.1	12.1	N	6.5	6.3	
$[(C_6H_{13})_4N^{d}]_2B_{12}H_{12}$	a	15.3	15.1	67.8	68.2	13.7	13.8	N	3.3	3.3	M.p. 83–84°
$(CH_3)_3PCH_2CH_2P(CH_3)_3B_{12}H_{12}$	a	40.3	39.9	29.8	29.9	10.6	10.9	P	19.2	19.3	Still white and solid at 600°
$[(CH_3)_3S]_2B_{10}H_{10}$	a	39.7	39.8	26.4	26.7	10.4	9.8	S	23.5	23.5	Dec. *ca.* 202°
$[(CH_3)_3S]_2B_{12}H_{12}$	a	43.8	43.4	24.3	24.4	10.2	10.2	S	21.6	21.7	Dec. *ca.* 254–255°

[a] Methods: (a) metathesis; (b) aqueous free acid plus insoluble metal compound indicated; (c) aqueous free acid neutralized with aqueous soluble base; (d) aqueous free acid plus free metal; (e) by reaction of $B_{10}H_{12}[S(CH_3)_2]_2$ with $t\text{-}C_4H_9NH_2$ (this salt is highly soluble in water); (f) the Cu^{+2} of aqueous $CuB_{12}H_{12}$ was reduced to Cu^+ by addition of aqueous Na_2SO_3 to precipitate the water-insoluble $Cu_2B_{12}H_{12}$, which was collected, washed, and dried. [b] From aqueous $BaB_{12}H_{12}$ and aqueous $Al_2(SO_4)_3$. [c] Neutral equivalent weight. A weighed sample in water was put through Amberlite 120H column. Acid effluent titrated to pH 7 with standard base. [d] Tetra-*n*-hexylammonium. [e] Melting points detd. in sealed capillaries. Dec. = decomposition without melting.

Relative H–D Exchange Rates.—The B^{11} resonance of a solution of 1.7 mmoles of $Na_2B_{12}H_{12}\cdot H_2O$ in 3 ml. of 3.8% DCl in D_2O was followed with time. As H–D exchange occurred, the initial B–H doublet became less intense as the singlet resonance of B–D began to appear midway between the two B–H peaks. In 19.25 hr., the B–D peak height was approximately equal to the height of the B–H doublet, and the signal had become an essentially flat topped plateau. At the same DCl and anion molarity, the low-field doublet of $B_{10}H_{10}^{-2}$ (apical BH) had disappeared before a measurement could be made, and it required only 17 min. for the high-field doublet to reach the end point. For comparison of the relative exchange rates of apical to equatorial BH in $B_{10}H_{10}^{-2}$, a solution of 600 mg. of $(NH_4)_2B_{10}H_{10}$ in 4 ml. of D_2O containing 1 drop of 38% DCl in D_2O was examined. The high-field doublet became flat in 3.25 hr., and the low-field doublet in 40 min. Thus, the relative rates of deuteration are $B_{12}H_{12}^{-2} = 1$, equatorial $B_{10}H_{10}^{-2} = 68$, apical $B_{10}H_{10}^{-2} = 330$.

Spectral Characterization.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet and visible spectra were examined with a Cary Model 14 spectrometer. Nuclear magnetic resonance was observed on a Varian Model V4300 spectrometer. Double irradiation was effected with an NMR Specialities Model SD 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.).

Polarography.—$Na_2B_{12}H_{12}$ and $[(CH_3)_4N]_2B_{10}H_{10}$ were examined with a dropping Hg electrode *vs.* a saturated calomel electrode over the maximum usable potential range in the following aqueous media: (1) 0.1 *M* $LiClO_4$ (+0.3 to −1.8 v.); (2) 0.1 *M* $LiClO_4$ and 0.002 *M* $HClO_4$ (+0.4 to −1.3 v.); and (3) 0.05 *M* NaOH (−0.1 to −1.8 v.). There was no evidence of either reduction or oxidation of the anions within these potential limits.

To extend the study beyond the oxidation potential of mercury (+0.4 v. in acid solution) the oxidation of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ was examined using a graphite–Nujol paste electrode *vs.* a saturated calomel electrode by which a potential up to about +1.4 v. can be attained.

$B_{12}H_{12}^{-2}$ (3.3×10^{-4} and 10^{-5} *M* $Na_2B_{12}H_{12}$) was not oxidized in 0.1 *M* aqueous KH_2PO_4 up to +1.4 v. $B_{10}H_{10}^{-2}$ (4.6×10^{-5} *M* $[(CH_3)_4N]_2B_{10}H_{10}$) oxidized at a potential of +0.85 v., in Britton–Robinson standard buffer solutions ranging in pH from 2.4 to 9.7. The peak current was a linear function of concentration within the reproducibility of the measurement. The temperature coefficient of the peak current was about 1.5% deg.$^{-1}$, indicating the process to be diffusion controlled. The peak current was insensitive to pH over the range 2.4 to 8.0, indicating that the compound is relatively stable to hydrolysis over this pH region. The peak current divided by concentration gave a value of 329 compared to 10.7 for $K_4Fe(CN)_6$, establishing a multi-electron change, probably due to gross degradation.

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Notes

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Vapor Pressures of Zirconium Tetrachloride above Sodium Chloride and Sodium Hexachlorozirconate(IV)

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The system NaCl–$ZrCl_4$ has been studied by a number of investigators. Morozov and Korshunov[2] and Korshunov, Reznik, and Morozov[3] have published phase information which demonstrates the existence of the compound Na_2ZrCl_6. Cooling curve stops at 377 and 341° led them to suggest that Na_2ZrCl_6 may undergo polymorphic transitions. Howell, Sommer, and Kellogg[4] have confirmed the general features of the phase diagram but observe stops at 381, 373, and 362° and suggest that other intermediate compounds may exist in the system. A simple eutectic behavior between NaCl and Na_2ZrCl_6 with no evidence of solid solution was observed by both groups of workers.

We have made a study of decomposition pressures of $ZrCl_4$ above solid mixtures of NaCl and Na_2ZrCl_6 between 300 and 525°, which includes the range in which transitions were reported. Similar data between 425 and 660° have been reported earlier by Morozov and Sun.[5]

Experimental

A transpiration method was used with (1) argon flowing over mixtures of NaCl and Na_2ZrCl_6 and (2) argon with $ZrCl_4$ flowing over initially pure NaCl. The apparatus was essentially the same as described in previous work from this laboratory.[6] For (1) solid samples of 50–50 mole % NaCl and Na_2ZrCl_6 were prepared by melting together in a Pyrex ampoule weighed amounts of NaCl (Mallinckrodt, analytical grade) and $ZrCl_4$ (Fairmount Chemical, analysis provided: Al, 330 p.p.m.; Fe, 860 p.p.m.; Si, 110 p.p.m.; Ti, 50 p.p.m.; oxychloride, 1.7%, insolubles, <0.1%; Hf, 2–3%. This material was resublimed in a current of chlorine). All samples were handled under high vacuum or in a drybox. The solidified melt was ground, and fresh samples of 4–5 g. were used for each series (*ca.* five runs) of transpiration experiments.

The transported chloride condensate, a white film collected at the edge of the reaction furnace, was washed out with water and the zirconium content determined colorimetrically (with a Beckman DU spectrophotometer) as a zirconium alizarin sulfonate lake.[7]

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