accentuated to such an extent that we can reasonably conclude that the value of g_{IV} lies between 0 and 0.8.

The best straight line for each set of data in Figure 3 was determined by the method of least squares. The slopes of these lines lie between 0.59 and 0.70. Thus the value of *n* is between 1.8 and 2.1. According to eq 1, *n* must be an integer so the data are quite adequate to distinguish between the best value, 2, and the next best values, 1 and 3. We conclude that the formula of III with respect to bismuth is Bi_8^{2+}. Thus eq 1 can be written as $22Bi + 2Bi^+ = 3Bi_8^{2+}$. With this information we may convert the formal molar absorptivity scale on curve A of Figure 1 to the molar absorptivity of Bi_8^{2+} by multiplying by $^{22}/_3$.

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The Synthesis of Some Compounds Containing Divalent and Trivalent Boron Cations[1]

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Trimethylamine–boron tribromide can be made to react with 4-ethylpyridine, pyridine, 3,5-dimethylpyridine, and 3-chloropyridine to produce water-soluble bromides containing, respectively, trivalent, divalent, and monovalent boron cations. Derivatives of the initial parent compounds have been prepared in the form of hexafluorophosphates and -arsenates. Cationic charge is retained as confirmed by conductivity data. The cations are stable to acidic hydrolysis, but show stability in basic solutions given by trivalent cations > divalent cations > monovalent cations. Work with ten other pyridine derivatives shows that the successful preparation of these cations depends on the basicity of the displacing amine and favorable steric factors.

There are no substantiated references in the literature to boron-containing cations of charge greater than +1. Sowa[3] reports a homologous series of boron-containing cations of charge +1 through +3, but does not offer experimental proof for the existence of these species. Singh[4] recently reports having synthesized a number of compounds of the type $[D_3BCl]Cl_2$, where D is a secondary or tertiary amine. However, no work was done to verify these postulated structures.

In this study, displacement reactions between trimethylamine–boron tribromide, $(CH_3)_3N \cdot BBr_3$, and various substituted pyridines were examined to determine which donor molecules, depending on their basicity and geometry, would displace trimethylamine and more than one bromine atom from $(CH_3)_3N \cdot BBr_3$ to produce stable ionic species containing boron cations of charge greater than +1. The adduct $(CH_3)_3N \cdot BBr_3$ was considered a good starting material since Fetterolf[5] was successful in obtaining compounds of the type $[D_2BCl_2]Cl$ when $(CH_3)_3N \cdot BCl_3$ was similarly studied.

An important aspect of the study was to determine further the hydrolytic stability of any +1, +2, or +3 boronium ions which could be prepared. Stabilities were measured in various media to compare the stabilizing effect of the displacing amine on the positive species produced.

Experimental Section

Materials.—All of the reactants, except $(CH_3)_3N \cdot BBr_3$, were obtained commercially. All amines were dried over calcium hydride and redistilled before use. Potassium hexafluorophosphate (KPF_6) and potassium hexafluoroarsenate ($KAsF_6$) were recrystallized from water solutions prior to using them for conductance measurements.

$(CH_3)_3N \cdot BBr_3$ was prepared by passing trimethylamine gas into a dispersion of boron tribromide (50 ml) in *n*-pentane (500 ml) until no additional formation of the white solid was observed. This product, purified by three recrystallizations from 95% ethanol, melted at 234–235°. *Anal.* Calcd for $C_3H_9NBBr_3$: C, 11.6; H, 2.90; N, 4.50. Found: C, 11.5; H, 3.01; N, 4.50.

Methods of Analysis.—Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn. After hydrolysis of the samples with hot concentrated NaOH, total bromine analyses were performed using Volhard titrations on the acidified hydrosylates. Ionic bromine was determined on acidified aqueous solutions of the respective compounds. Melting points were measured on a Fisher-Johns block apparatus with a range of 20–300°.

Infrared and Ultraviolet Spectra.—Infrared spectra were obtained using a Perkin-Elmer Model 337 spectrophotometer. Solids were pressed into KBr disks; liquids were examined between KBr plates. Ultraviolet spectra were recorded on a Bausch & Lomb Spectronic Model 505 spectrophotometer. Standard quartz cells (1 cm) were used.

Conductance Measurements.—Conductances were measured using an Industrial Instruments Model RC-16B2 conductivity

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(3) F. J. Sowa, U. S. Patent 2,655,524 (1951).

(4) S. P. Singh and N. P. Singh, *J. Proc. Inst. Chemists* (India), **38**, 22 (1966).

(5) R. N. Fetterolf, M.S. Thesis, University of Florida, Gainesville, Fla., 1964; see also H. Noeth, P. Schweizer, and F. Ziegelgaensberger, *Chem. Ber.*, **99**, 1089 (1966).

TABLE I

BORONIUM COMPOUNDS

Compd	Name	Formula	Mp, °C	% bromine				% carbon		% hydrogen		% nitrogen	
				Total		Ionic							
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
I	Tetrakis(4-ethylpyridine)boron(III) bromide[a]	$[(C_7H_9N)_4B]Br_3$	290	35.3	35.8	35.3	35.8	49.3	48.1	5.29	5.60	8.24	8.05
II	Tetrakis(4-ethylpyridine)boron(III) hexafluorophosphate	$[(C_7H_9N)_4B](PF_6)_3$	205[b]	...	...	...	...	38.4	38.3	4.12	4.24	6.42	6.65
III	Tetrakis(4-ethylpyridine)boron(III) hexafluoroarsenate	$[(C_7H_9N)_4B](AsF_6)_3$	258[b]	...	...	...	...	33.6	33.3	3.58	3.65	5.56	5.37
IV	Bromotris(3,5-dimethylpyridine)boron(III) bromide[a]	$[(C_7H_9N)_3BBr]Br_2$	290	42.0	43.0	28.0	30.5	44.2	44.5	4.72	5.20	7.38	7.48
V	Bromotris(3,5-dimethylpyridine)boron(III) hexafluorophosphate	$[(C_7H_9N)_3BBr](PF_6)_2$	130[b]	11.4	10.7	...	...	35.9	36.6	3.85	4.22	5.99	5.95
VI	Bromotris(3,5-dimethylpyridine)boron(III) hexafluoroarsenate	$[(C_7H_9N)_3BBr](AsF_6)_2$	124[b]	10.1	10.0	...	...	31.9	32.3	3.42	3.24	5.32	5.12
VII	Bromotris(pyridine)boron(III) bromide	$[(C_5H_5N)_3BBr]Br_2$	290	49.1	48.7	32.8	32.2	36.7	36.7	3.07	3.22	8.60	8.63
VIII	Bromotris(pyridine)boron(III) hexafluorophosphate	$[(C_5H_5N)_3BBr](PF_6)_2$	218	12.9	13.0	...	...	29.2	29.2	2.45	2.62	6.80	6.78
IX	Bromotris(pyridine)boron(III) hexafluoroarsenate	$[(C_5H_5N)_3BBr](AsF_6)_2$	250	11.3	11.0	...	...	25.5	25.6	2.14	2.26	5.95	5.79
X	Dibromobis(3-chloropyridine)boron(III) bromide	$[(C_5H_4ClN)_2BBr_2]Br$	228	50.3	50.6	16.8	16.3	25.2	25.3	1.67	1.73	5.87	5.74
XI	Dibromobis(3-chloropyridine)boron(III) hexafluorophosphate	$[(C_5H_4ClN)_2BBr_2]PF_6$	201	29.5	30.2	...	...	22.1	22.3	1.47	1.61	5.16	5.00
XII	Dibromobis(3-chloropyridine)boron(III) hexafluoroarsenate	$[(C_5H_4ClN)_2BBr_2]AsF_6$	236	27.4	28.3	...	...	20.5	20.7	1.36	1.47	4.78	4.72

[a] Hygroscopic. [b] Decomposition.

bridge and a cell with a cell constant of 0.10 cm^{-1}. The water used to prepare the solutions was repeatedly deionized using a Crystal Lab Deeminizer until its specific conductance was no greater than 10^{-6} ohm^{-1} cm^2. Molar conductances were determined at 25° and at concentrations of 10^{-3} M.

Synthetic Methods.—With only slight modifications, the procedure described by Fetterolf[5] was employed in preparing the compounds listed in Table I. $(CH_3)_3N \cdot BBr_3$ (0.01 mole) was combined with pyridine or a substituted pyridine (0.2 mole) in a round-bottomed flask fitted to an Allihn bulb condenser in upright position. A distillation head was used which permitted a stream of dry nitrogen to be swept over the top of the column. The reaction mixture was heated to gentle boiling and refluxed at this temperature for at least 90 min. After cooling to room temperature, crystalline solids were removed by filtration, washed with *n*-pentane, and dried at reduced pressure. Compounds I, IV, VII, and X were obtained in 74, 66, 31, and 73% yields, respectively. Compounds I, VII, and X were purified from mixtures of ethanol and *n*-pentane prior to further investigation. No suitable solvent was found for recrystallizing IV. All bromides (I = yellow, crystalline; VII, X = white, crystalline; IV (impure) = brown) were soluble in water and ethanol and insoluble in nonpolar solvents.

The hexafluorophosphate and -arsenate derivatives of the above boronium compounds were prepared by addition of saturated aqueous solutions of KPF_6 and $KAsF_6$ to water solutions of compounds I, IV, VII, and X, respectively. The resulting white precipitates were removed by filtration, washed free of Br^- with cold water, and dried at reduced pressure.

Results and Discussion

Synthesis.—Four new boron-containing bromides and eight derivatives were obtained reproducibly. Since some of them tend to decompose in solution, purification by recrystallization is not always satisfactory, and some difficulty was encountered in keeping the bromides anhydrous. Nevertheless, most of the bromides and all derivatives form crystalline compounds for which good comparison is found between experimental and theoretical analytical composition.

Properties.—The bromides listed in Table I are all water soluble, indicating ionic character. The dissociation in aqueous solution is suggested to proceed according to

$$(D_1)_4BBr_3 \longrightarrow [(D_1)_4B]^{3+} + 3Br^-$$

$$(D_2)_3BBr_3 \longrightarrow [(D_2)_3BBr]^{3+} + 2Br^-$$

$$(D_3)_2BBr_3 \longrightarrow [(D_3)_2BBr_2]^{+} + Br^-$$

where D_1, D_2, and D_3 are 4-ethylpyridine, 3,5-dimethylpyridine or pyridine, and 3-chloropyridine, respectively. The extracoordinate bromine is precipitated quantitatively from aqueous solutions of the boronium compounds, which is clear evidence of the charge if not the character of the various boronium cationic species. The 1:1 replacement of ionic bromide by PF_6^- and AsF_6^- further substantiates the existence of the boron-containing cations in the parent materials.

The infrared spectra, recorded for all compounds in Table I, were of limiting value in verifying the existence of a B–N dative bond. However, these spectra do show that the cationic species in the bromides are retained in their hexafluorophosphate and -arsenate derivatives, as evidence by identical absorption bands from 2.5 to 11 μ for the bromides and their respective derivatives.

Molar conductance data for the isolated bromides and their hexafluorophosphate and -arsenate derivatives further substantiate the existence of +1, +2, and +3 cations in these boronium compounds.

The data tabulated in Table II were compared with molar conductance values reported by Jones[6] for +1, +2, and +3 complex ions of the transition metal series. For monovalent complex ions these values range from 96 to 115, for divalent complex ions from 225 to 270, and for trivalent complex ions from 380 to 432 ohm^{-1} $mole^{-1}$ cm^2 for 10^{-3} M aqueous solutions. Jones' values were extrapolated back to zero time to compen-

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[6] M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 253.

TABLE II

MOLAR CONDUCTANCE[a] OF AQUEOUS SOLUTIONS (10^{-3} *M*) AT 25°

Cation containing	Charge type	Anions: Br^-	PF_6^-	AsF_6^-
3-Chloropyridine	+1	101 ± 0.5	...[b]	...[b]
Pyridine	+2	230	200	171
3,5-Dimethylpyridine	+2	230	194[c]	180[c]
4-Ethylpyridine	+3	305	270	284[c]

[a] All values in ohm^{-1} mole^{-1} cm^2. [b] Insufficiently soluble in water. [c] 0.5×10^{-3} *M* solution.

sate for changes occurring in the conductance of some solutions as they stand. The values in Table II were not corrected for time, which might account for somewhat lower values. Furthermore, since electrical conductance is inversely proportional to the radius of the ions involved and the cations investigated in this study contained ligand molecules which in general were larger than those cited in the above reference, larger ionic radii and consequently lower conductance values would be expected. The decrease in going from bromides to hexafluoroarsenates, as shown in Table II, demonstrates similar effects as the radius of the anions in solution is increased.

TABLE III

HYDROLYSIS OF BORONIUM COMPOUNDS IN BASIC SOLUTION

Boron cation containing	Charge type	Maximum time required for complete hydrolysis — Concentration of NaOH, *M*: 0.1	0.001	0.00025	0.0001
4-Ethylpyridine	+3	1 min	1 hr	...	...
3,5-Dimethylpyridine	+2	1 min	1 min	1 hr	1 week
Pyridine	+2	1 min	1 min	1 min	1 hr[a]
3-Chloropyridine	+1	1 min	1 min	1 min	1 min[a]

[a] Estimate >90% complete.

Stability Studies.—A semiquantitative study was made on the hydrolysis rates of the bromides and their derivatives. Hydrolysis was followed by using ultraviolet-absorption spectral data. The maximum time required for the boronium ions to be hydrolyzed to the respective parent amines, as evidenced by shifts in the absorption peaks of the adducts to those of the parent amines, was recorded in various media. In all cases the boron-containing cationic species were stable (>1 week) in acid solution (0.10 *M* HCl) and moderately stable (24 hr) in neutral solution (water). However, attack of a nucleophilic agent, such as hydroxide ion in sufficient concentration, produces rapid hydrolysis to the parent amines. The data in Table III show a hydrolytic stability order given by: trivalent > divalent > monovalent cations. This is consistent with the results obtained[7] for chloroamine complexes of the transition metal series. Complexes with higher positive charge were found to be more stable than those with lower charges, because separation of a negative charge in the form of halide ions becomes more difficult, the greater the remaining charge on the complex. Weaker bases forming relatively labile bonds with electron-deficient boron should be more easily replaced by hydroxide ions. Considering steric, resonance, and inductive effects, the base strength of the parent amines (column 1, Table III) is given by: 4-ethylpyridine > 3,5-dimethylpyridine > pyridine > 3-chloropyridine. The rate of hydrolysis was found to be inversely proportional to the relative base strength.

Reactions with Other Substituted Pyridines.—As expected from the hydrolytic stability studies above, the relative ease of synthesizing boronium compounds containing +1, +2, and +3 cations depends principally on the basicity and favorable steric factors. Work with ten other substituted pyridines (3-methyl-, 2-methyl-, 2-ethyl-, 4-*n*-propyl-, 2,6-dimethyl-, 2,4,6-trimethyl-, 4-acetyl-, 2-chloro-, 3,5-dichloro-, and 4-cyanopyridine) further confirms that unless both these requirements are met, attempts at displacement reaction result in the production of water-soluble oils due to decomposition of products in the reaction mixture, hydrobromides of trimethylamine and/or of the substituted pyridine, or recovery of starting material.

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(7) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 124–132.