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# Lower Oxidation States of Bismuth. $Bi_8^{2+}$ Formed in $AlCl_3$–NaCl Melts[1]

BY NIELS J. BJERRUM AND G. PEDRO SMITH

*Received May 12, 1967*

The entity $Bi_8^{2+}$ was prepared by reaction between excess bismuth metal and dilute solutions of bismuth trichloride in molten mixtures of $AlCl_3$ and NaCl at 130–250°. The reaction equation was $22Bi(\text{metal}) + 2Bi^{3+}(\text{soln}) = 3Bi_8^{2+}(\text{soln})$. With molten 63 mole % $AlCl_3$–37 mole % NaCl as solvent, spectrophotometric measurements show that this situation is displaced strongly to the right so that the oxidation state of the product can be established as $+^1/_4$ from a measurement of the number of moles of metal that react with a known amount of $BiCl_3$. With molten $NaAlCl_4$ saturated with NaCl as solvent the above reaction leads to an equilibrium with both $Bi^{3+}$ and $Bi_8^{2+}$ present in measurable amounts. Spectrophotometric measurements on such equilibrium mixtures at various $Bi^{3+}$ concentrations permit establishment of the complete reaction stoichiometry and, hence, fix the formula $Bi_8^{2+}$. These measurements give no information on the ligands attached to $Bi_8^{2+}$.

## Introduction

In previous publications[2] it was reported that $Bi^+$ and $Bi_5^{3+}$ are products of the reaction between bismuth metal and dilute solutions of bismuth trichloride in liquid $AlCl_3$–NaCl and $ZnCl_2$–KCl mixtures. It was pointed out that a third reaction product appears when the bismuth trichloride solution in $AlCl_3$–NaCl mixtures reacts with sufficient bismuth metal so that the latter forms a separate phase. We shall present evidence that a molecular unit of this entity contains eight bismuth atoms with an oxidation state per atom of $^1/_4$.[3] We represent this information by the formula $Bi_8^{2+}$. No information was obtained on the number of ligands (chloride ions or chloroaluminate ions) attached to this entity. Thus the charge on the molecular unit consisting of $Bi_8^{2+}$ plus ligands (if any) is unknown.

## Experimental Section

The materials and experimental techniques used in the present work are the same as used in the previous work.[2] Sodium chloride was reagent grade material further purified by treatment in the molten state with HCl gas followed by filtering. The $AlCl_3$ was made from zone-refined aluminum metal and HCl. Bismuth trichloride was made by reaction between bismuth metal and chlorine, and then purified by distillation.

The reaction between bismuth metal and solutions containing bismuth trichloride was measured spectrophotometrically with a Cary Model 14H spectrophotometer equipped with a high-temperature furnace. The optical cells consisted of fused-silica cuvettes with a 1-cm² cross section. The path length of a cell could be reduced by placing in it a fused-silica insert. Completely sealed cells were used in order to avoid volatilization of $AlCl_3$ as well as atmospheric contamination.

The initial amounts of bismuth metal and bismuth trichloride and the amount of unreacted bismuth metal were determined by microbalance weighings.

Two compositions of $AlCl_3$–NaCl mixtures were used as solvents. One mixture was close to the eutectic composition (63 mole % $AlCl_3$). The other mixture was prepared by saturating the $AlCl_3$–NaCl eutectic with NaCl at 250°. The latter melt contained approximately 50.4 mole % NaCl. The densities of these two compositions were obtained from the work of Boston.[4]

## Definitions and Assumptions

The amount of bismuth metal that reacted with bismuth trichloride in solution will be referred to as *excess bismuth* in solution. The total amount of bismuth in solution will be referred to as *total bismuth.* The moles of excess bismuth and total bismuth per liter of reaction mixture will be denoted $M_E$ and $M_T$, respectively.

The absorbance values mentioned here always refer to the absorbance of the bismuth in solution; that is, the absorbance of the cell and solvent have always been subtracted.

The quantity

$$A(\text{prod.}) = A(\text{mix.}) - A(BiCl_3, \text{mix.})$$

will be called the absorbance of the reaction products, where $A(\text{mix.})$ is the absorbance of the reaction mixture and $A(BiCl_3, \text{mix.})$ is the absorbance of a solution of $BiCl_3$ at the same concentration as in the reaction mixture. We shall define the formal molar absorptivity of reaction products, $\epsilon(\text{prod.})$, to be $\epsilon(\text{prod.}) = A(\text{prod.})/M_E l$, where $l$ is the path length in centimeters.

Several assumptions commonly valid for dilute solutions are used in the interpretation of the results. The first of these is the law of additive absorbances, the second is the Bouguer–Beer law, and the third is Henry's law with respect to the activities of bismuth-containing species. Among the reasons for supposing those laws to hold are the fact that the total bismuth concentration never exceeded 1 mole % and the fact that the ionic strengths of the solvents used were very high and not expected to change much upon addition of small amounts of solute ions.

## Results and Discussion

**Determination of Oxidation State.**—Previous studies[2] show that when small amounts of bismuth metal are added to a dilute solution of $BiCl_3$ in the 63 mole %

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[1] Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corp. Paper presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967.

[2] (a) N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *Inorg. Nucl. Chem. Letters*, **1**, 141 (1965); (b) N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

[3] A preliminary report of this result was presented by N. J. Bjerrum and G. P. Smith, *Inorg. Nucl. Chem. Letters*, **3**, 165 (1967).

[4] C. R. Boston, *J. Chem. Eng. Data*, **11**, 262 (1966).

$AlCl_3$–37 mole % NaCl eutectic the primary reaction products are $Bi^+$ and $Bi_5^{3+}$ so long as all of the bismuth metal is consumed. These products may be identified by their distinctive spectra. However, when sufficient bismuth metal is added to form a separate phase, the absorption spectrum of the reaction mixture is quite different from that of either $Bi^+$ or $Bi_5^{3+}$.

The spectrum of the reaction mixture in equilibrium with a bismuth metal phase at 250° is shown in Figure 1, curve A. At wavelengths of 370–1100 mμ this spectrum obeys the Bouguer–Beer law in the sense that $A(\text{mix.})/l$ is proportional to $M_T$. This result is illustrated for a selection of wavelengths in Figure 2. Near 350 mμ a small deviation from Bouguer–Beer law behavior occurs as exemplified by the 350-mμ line in Figure 2. The dashed line near the 350-mμ line is an extrapolation of the slope of the 350-mμ line at low total bismuth concentrations.

Deviations from the Bouguer–Beer law at wavelengths shorter than 350 mμ are plausibly attributed to the presence of very small amounts of unreacted $BiCl_3$. This substance in $AlCl_3$–NaCl melts is transparent in the near-infrared and visible regions of the spectrum, and at low concentrations begins to absorb appreciably near 350 mμ. It has an intense ultraviolet band at 297 mμ with a molar absorptivity of 5400.[2] We observed a shoulder at this wavelength on the reaction product spectrum. This portion of the spectrum, which is very intense, is not shown in Figure 1.

The Bouguer–Beer law behavior in the near-infrared and visible regions indicates that either a single reaction product is formed, or else, if there are two or more products, their concentrations are in constant proportions at all concentration levels studied. Further investigations showed that when the temperature is lowered from 250 to 130°, there are only minor changes in the spectrum of reaction products on a molar absorptivity scale. The bands sharpened somewhat but the band areas did not change significantly. This temperature insensitivity of the spectrum suggests that only a single reaction product was present. If there had been more than one product, the change in temperature should have shifted the concentration ratios of these products and thereby produced much larger changes in the spectrum. As a matter of convenience we label this reaction product III. (Previously,[2] the labels I and II were used to denote $Bi^+$ and $Bi_5^{3+}$, respectively.)

Measurements of the amounts of bismuth trichloride and bismuth metal consumed by reaction showed that the oxidation state of III is $^1/_4$. The data are summarized in Table I. These data show that, to within an uncertainty of less than 2%, each mole of $BiCl_3$ reacted with 11 moles of bismuth metal to form a product containing 12 moles of bismuth. Thus the formula of III with respect to bismuth can be written $Bi_{4n}^{n+}$, where $n$ has an integral value. This reaction may be formulated as

$$\frac{11n}{3}\text{Bi(s)} + \frac{n}{3}\text{Bi}^{3+}\text{(soln)} = \text{Bi}_{4n}{}^{n+}\text{(soln)} \qquad (1)$$

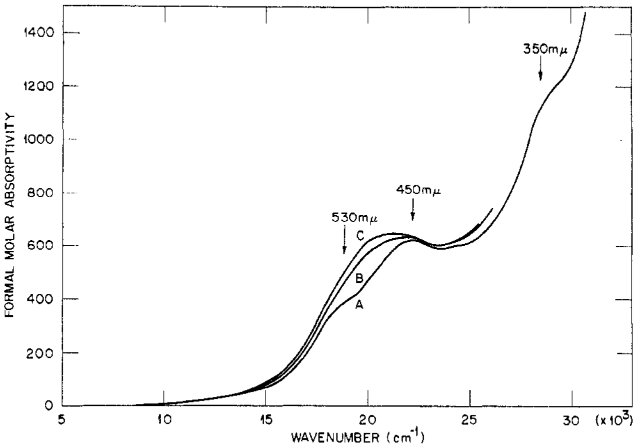

Figure 1.—Spectra of reaction mixtures: (A) 0.0146 molar excess bismuth in the $AlCl_3$–NaCl eutectic in equilibrium with bismuth metal at 250°. (B) 0.00403 molar excess bismuth with an initial $BiCl_3$ concentration of 0.107 $M$ contained in molten $NaAlCl_4$ saturated with NaCl at 250° and in equilibrium with bismuth metal. The absorbance of unreacted $BiCl_3$ has been subtracted from this spectrum. (C) 0.00259 molar excess bismuth with an initial $BiCl_3$ concentration of 0.107 $M$ in molten $NaAlCl_4$ saturated with NaCl at 250° but *not* in equilibrium with bismuth metal. The absorbance of unreacted $BiCl_3$ has been subtracted from this spectrum.

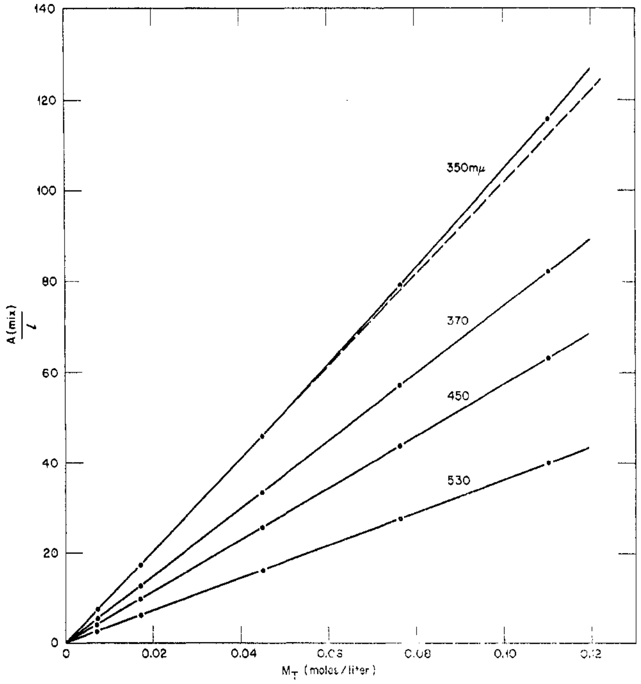

Figure 2.—Relations between the concentration of total bismuth in the $AlCl_3$–NaCl eutectic (in equilibrium with solid bismuth metal at 250°) and the total absorbance at representative wavelengths.

The corresponding mass action formula is

$$K_{\text{III}} = [\text{Bi}_{4n}{}^{n+}]/[\text{Bi}^{3+}]^{n/3} \qquad (2)$$

where $K_{\text{III}}$ is the equilibrium quotient, which is a constant if Henry's law is obeyed.

**Determination of** $n$.—An obvious way to obtain the value of $n$ would be to measure $[Bi_{4n}^{n+}]$ and $[Bi^{3+}]$ for a number of mixtures with different values of $M_T$. However, the measurements described above show that

Table I

Amounts of Bismuth Metal and Bismuth Trichloride Consumed to Form III in 63 Mole % $AlCl_3$–NaCl at 250°

| Moles of Bi metal × $10^4$ | Moles of $BiCl_3$ × $10^4$ | Moles of Bi/mole of $BiCl_3$ |
|---|---|---|
| 0.9782 | 0.09030 | 10.8 |
| 2.689 | 0.2485 | 10.8 |
| 4.621 | 0.4221 | 11.0 |
| 6.692 | 0.6141 | 10.9 |

in the $AlCl_3$–NaCl eutectic mixture the concentration of $BiCl_3$ is so much smaller than that of $Bi_{4n}{}^{n+}$ that we cannot estimate $[Bi^{3+}]$ to within a useful accuracy (*i.e.*, $K_{III}$ is a large number). It is this fact, of course, that permitted us to establish eq 1. Consequently, we considered the possibility of using as a solvent an $AlCl_3$–NaCl mixture with a composition well removed from that of the eutectic in the hope that $K_{III}$ would have a more favorable value. Choices of suitable solvent compositions are highly limited because of the need to keep the chloride ion concentration buffered. At the eutectic composition, $Cl^-$ is buffered by the presence of chloride-bridged chloroaluminate ions as previously discussed.[2] The buffering reaction is probably $Cl^- + Al_2Cl_7^- = 2AlCl_4^-$. Such mixtures are to be regarded as "acidic" in the Lewis sense.

There is also a "basic" composition at which we expect $Cl^-$ to be buffered; namely, $AlCl_3$–NaCl melts saturated with solid NaCl. In order to understand the nature of such a melt it is helpful to examine the phase diagram for the $AlCl_3$–NaCl system.[5] Slightly to the NaCl-rich side of the compound $NaAlCl_4$, the liquidus curve (which corresponds to melts saturated with solid NaCl) rises very steeply from 150°. We found that the melt saturated with NaCl at 250° contained about 50.4 mole % NaCl and 49.6 mole % $AlCl_3$. Such a melt may be regarded as a dilute solution of NaCl in liquid $NaAlCl_4$. Because of the steepness of the liquidus curve the solubility product of NaCl in liquid $NaAlCl_4$ changes only slightly with temperature near 250°. Thus, since the sodium ion concentration is very large, the chloride ion concentration will be approximately constant with respect to small changes in temperature as well as changes in concentration of dilute solutes such as $BiCl_3$.

Two kinds of experiments were performed in which $NaAlCl_4$ saturated with NaCl served as the solvent. In the first kind of experiment a small amount of bismuth metal was added to a solution of $BiCl_3$ and reaction proceeded until all of the bismuth was consumed. Then more bismuth was added, and still more, until finally there was unreacted metal in equilibrium with the solution. The spectrum was measured after each addition. Typical results are shown by curves B and C in Figure 1. This experiment began with an initial $BiCl_3$ concentration of 0.107 *M*. Curve C shows the reaction product spectrum after enough metal had reacted to attain an $M_E$ value of 0.00259 *M*, still far short of enough to give equilibrium with the metal phase. Curve B shows the reaction product spectrum after enough metal had reacted so that the solution was in equilibrium with the metal phase. At this point $M_E$ was 0.00403 *M*. Both spectra are somewhat similar to curve A and the similarity increases as the extent of reduction increases.

In the second kind of experiment, we began with a sample of solvent containing bismuth metal as a separate phase. Successive additions of $BiCl_3$ were made to the solvent and after each addition the mixture was equilibrated and its spectrum measured. The $BiCl_3$ concentration never got large enough to consume all of the metal phase. Curve B in Figure 1 is typical of spectra at the highest $BiCl_3$ concentrations studied. For lower concentrations of $BiCl_3$ the shapes of the spectra were intermediate to curves A and B, so that at low $BiCl_3$ concentrations the spectra of reaction products were fairly close to the spectrum of $Bi_{4n}{}^{n+}$ in the $AlCl_3$–NaCl eutectic.

The results of these experiments lead us to suppose that $Bi_{4n}{}^{n+}$ is a primary reaction product when $NaAlCl_4$–NaCl serves as the solvent because of the similarity between the reaction product spectrum in this medium and that of $Bi_{4n}{}^{n+}$ in the $AlCl_3$–NaCl eutectic. However, the reaction product spectrum varies somewhat with solution composition so that we also suppose that there is an additional product (or products). The qualitative behavior shows that the ratio between the concentration of this additional product and the concentration of $Bi_{4n}{}^{n+}$ decreases with the extent of reduction in the first kind of experiment and increases as the concentration of $BiCl_3$ increases in the second kind of experiment.

It is very important that in the above experiments a relatively substantial concentration of unreacted $BiCl_3$ was present. This fact was established qualitatively by the presence of the intense ultraviolet bands of $Bi^{3+}$ and quantitatively by measuring the amount of bismuth metal that reacted with a known amount of $BiCl_3$ in solution as discussed in more detail below.

We now proceed to a quantitative analysis of the data for the second kind of experiment, in which solutions of $BiCl_3$ were equilibrated with a metal phase. The objective of this analysis is to determine the value of *n* so as to fix the formula of $Bi_{4n}{}^{n+}$. The first step is to show that the spectra obey the rules for an equilibrium between two reaction products. Then, using equations appropriate to a two-product equilibrium we deduce *n*.

Any reaction between bismuth metal and $BiCl_3$ in solution must be of the form

$$\left(\frac{3d - b}{3}\right)\mathrm{Bi(s)} + \frac{b}{3}\mathrm{Bi^{3+}(soln)} = \mathrm{Bi}_d{}^{b+}\mathrm{(soln)} \qquad (3)$$

Let us suppose that in molten $NaAlCl_4$–NaCl as solvent we have, in addition to $Bi_{4n}{}^{n+}$, one other reaction product, designated IV, with molar concentration [IV].

According to the law of additive absorbances

$$M_E\epsilon(\mathrm{prod.}) = A(\mathrm{prod.})/l = [\mathrm{Bi}_{4n}{}^{n+}]\epsilon_{III} + [\mathrm{IV}]\epsilon_{IV} \qquad (4)$$

where $\epsilon_{III}$ and $\epsilon_{IV}$ are the molar absorptivities of $Bi_{4n}{}^{n+}$ and IV, respectively. For brevity we denote the coef-

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(5) W. Fisher and A. L. Simon, *Z. Anorg. Allgem. Chem.*, **306**, 1 (1960).

ficients of Bi(metal) in eq 1 and 3 as $S_{III} = 11n/3$ and $S_{IV} = (3d - b)/3$, respectively. Then a material balance gives the relation

$$M_E = S_{III}[Bi_{4n}{}^{n+}] + S_{IV}[IV] \qquad (5)$$

Finally, defining $\epsilon_{III}{}^* = \epsilon_{III}/S_{III}$ and $\epsilon_{IV}{}^* = \epsilon_{IV}/S_{IV}$ and combining eq 4 and 5 we obtain

$$\epsilon(\text{prod.}) = x\epsilon_{III}{}^* + (1 - x)\epsilon_{IV}{}^* \qquad (6)$$

where $x = S_{III}[Bi_{4n}{}^{n+}]/M_E$.

Equation 6 is a special function that holds when there are two and only two reaction products.[6] This function specifies unique relations among the $\epsilon$(prod.) curves generated by varying the concentration of $BiCl_3$. Among these relations are: (1) all crossing points are isosbestic points; (2) $\epsilon$(prod.) at any one wavelength is a linear function of $\epsilon$(prod.) at any other wavelength; and (3) every $\epsilon$(prod.) curve is a weighted sum of any two $\epsilon$(prod.) curves.

Examination of the measured $\epsilon$(prod.) spectra generated by varying the concentration of $BiCl_3$ in equilibrium with a bismuth metal phase showed that eq 6 is obeyed and, hence, that the data could be treated according to the equations for an equilibrium between two reaction products. In some of these experiments the amount of metal that reacted was not determined from weighings because of experimental difficulties but from the absorbance at the isosbestic point near 450 m$\mu$.

Equation 2 may be written

$$\log\,[Bi_{4n}{}^{n+}] = \frac{n}{3}\log\,[Bi^{3+}] + \log K_{III} \qquad (7)$$

Applying the Bouguer–Beer law to this relation we obtain

$$\log A_{III}(\lambda_1) = \frac{n}{3}\log\,[Bi^{3+}] + \log K' \qquad (8)$$

where $A_{III}(\lambda_1)$ is the absorbance of $Bi_{4n}{}^{n+}$ at wavelength $\lambda_1$ and $K'$ is a constant.

It has been shown[2] that the absorbance of one of the products in a two-product system in which only the products absorb can be expressed as

$$A_{III}(\lambda_1) = \frac{A(\lambda_1) - g_{IV}A(\lambda_2)}{1 - g_{III}g_{IV}} \qquad (9)$$

where $A(\lambda_1)$ and $A(\lambda_2)$ are the measured total absorbances at $\lambda_1$ and $\lambda_2$, respectively, while $g_{III}$ and $g_{IV}$ are concentration-independent quantities given by the relations

$$g_{III} = A_{III}(\lambda_2)/A_{III}(\lambda_1) \qquad (10a)$$

$$g_{IV} = A_{IV}(\lambda_1)/A_{IV}(\lambda_2) \qquad (10b)$$

Substitution of eq 9 into eq 8 gives

$$\log\,[A(\lambda_1) - g_{IV}A(\lambda_2)] = \frac{n}{3}\log\,[Bi^{3+}] + \log K'' \qquad (11)$$

where $K''$ is a constant.

We estimated $[Bi^{3+}]$ to be the initial concentration of $BiCl_3$, $M(BiCl_3, \text{intl})$, less the amount of $BiCl_3$ that would be consumed if $Bi_{4n}{}^{n+}$ were the exclusive reaction product. The validity of this estimate rests primarily on the fact that $M(BiCl_3, \text{intl})$ was so much larger than $M_E$ (0.107 *vs.* 0.00403 $M$ in a typical case) that $[Bi^{3+}]$ is approximately equal to $M(BiCl_3, \text{intl})$ no matter what the reaction products may be. Furthermore, the amount of IV formed at equilibrium is much smaller than the amount of $Bi_{4n}{}^{n+}$ so that its neglect can at most lead to very small errors.

We measured $A(\lambda_1)$ at 450 m$\mu$, where $Bi_{4n}{}^{n+}$ has an absorption maximum, and $A(\lambda_2)$ at 500 m$\mu$, which is near an absorption maximum for IV. An initial estimate of 0.5 for $g_{IV}$ was obtained from measurements at very low excess-bismuth concentrations. Finally, we plotted $\log\,[A(\lambda_1) - g_{IV}A(\lambda_2)]$ *vs.* $\log\,[Bi^{3+}]$ using $g_{IV}$ values in the range 0–0.8 with the results shown in Figure 3. The lines in this figure are straight and have a slope of $^2/_3$. They are fitted to pass through the experimental points for low values of $[Bi^{3+}]$. It will be seen that the data labeled C are very close to the line, which has a $g_{IV}$ value of 0.5.

It has been pointed out[2] that in a plot such as Figure 3 all of the points for any value of $g_{IV}$ will approach a straight line with a slope of $n/3$ at low values of log $[Bi^{3+}]$ and that the points with the correct value of $g_{IV}$ will lie on a straight line with slope $n/3$ at all ordinate values. In Figure 3 the sets of data A through D with $g_{IV}$ values of 0–0.7 approximate straight lines to within experimental error while set E with a $g_{IV}$ value of 0.8 shows an appreciable deviation from straight-line behavior. At higher values of $g_{IV}$ this deviation becomes

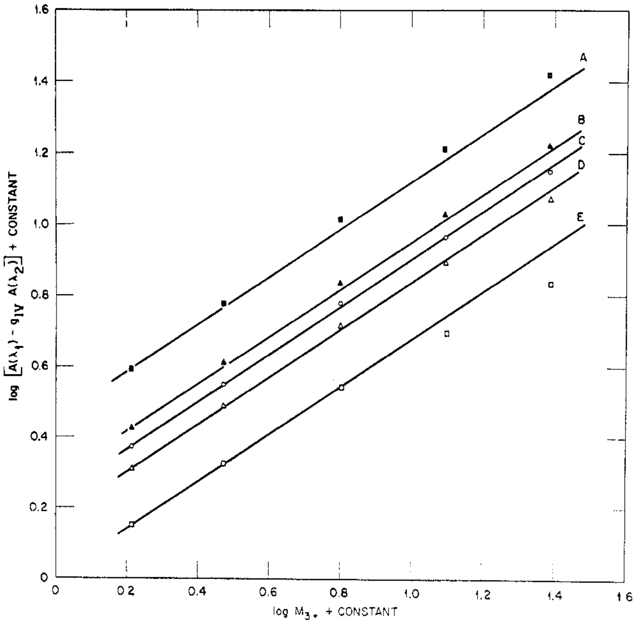

Figure 3.—A plot of experimental data in terms of quantities that occur in eq 11. The quantity $M_{3+}$ is the molar concentration of $BiCl_3$, *i.e.*, $[Bi^{3+}]$. Values of $\lambda_1$ and $\lambda_2$ were 450 and 500 m$\mu$, respectively. Values of $g_{IV}$ for various sets of points are: (A) 0.0, (B) 0.4, (C) 0.5, (D) 0.6, (E) 0.8. The straight lines were chosen to have the slope $^2/_3$ and to fit the data at small values of $[Bi^{3+}]$.

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(6) We note that eq 6 also holds if what we have designated as IV is actually a mixture of reaction products that are linearly related by a single reaction parameter. However, that will occur only if all of these products have the same value of $b$. This possibility makes no difference insofar as the evaluation of $n$ for $Bi_{4n}{}^{n+}$ is concerned.

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 $^{22}/_3$.

**Acknowledgment.**—We express our gratitude to Jorulf Brynestad with whom we discussed this research at length.

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

BY C. W. MAKOSKY, G. L. GALLOWAY,[2] AND G. E. RYSCHKEWITSCH

*Received May 24, 1967*

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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(1) Abstracted from an M.S. thesis submitted by C. W. Makosky to the Chemistry Department of St. Lawrence University. Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) To whom correspondence should be directed: Denison University, Granville, Ohio 43023

(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).