COÖRDINATION COMPOUNDS OF BORON BROMIDE AND BORON IODIDE

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Boron bromide and boron iodide have been reported to form fewer coördination compounds than boron trichloride and boron trifluoride. A comparison of similar compounds formed by these halides indicates that the acceptor property of the boron atom in these halides is best with boron trifluoride and becomes systematically weaker to boron iodide. This is to be expected, inasmuch as the electronegativity of the halogen atoms becomes smaller from fluorine to iodine; consequently the boron atom becomes more electronegative by induction with an increase in the molecular weight of the boron halide.

Coördination compounds have been reported with boron bromide and molecules in which nitrogen, phosphorus, and arsenic atoms of Group V, oxygen and sulfur atoms of Group VI, and chlorine and bromine atoms of Group VII behave as donors.

Only compounds with ammonia have been reported to form coördination compounds with boron iodide, and the existence of these compounds has been questioned.

In earlier papers the coördination compounds of boron trifluoride (6, 18) and boron trichloride (19) have been reviewed. Owing to the interesting relationships existing between the compounds of these two boron halides, it is of interest to review critically the molecular compounds formed by the bromide and iodide of boron and to compare the properties of these compounds with analogous compounds of the chloride or fluoride. These compounds will be discussed according to the group in the Periodic Table of which the donor atom is a member.

As was expected, and as was found to be the case with boron trifluoride and trichloride, no molecular compounds involving boron bromide or boron iodide have been reported in which the donor atom is a member of Group I, II, or III of the Periodic Table. With boron trifluoride it was postulated that the carbon atom was a donor to form an unstable, intermediate molecular compound with an organic molecule in condensation and polymerization reactions in which boron trifluoride is used as a catalyst (6, 18). However, no analogous compounds have been reported for the other halides of boron.

GROUP V

Nitrogen

It was reported as early as 1846 by Poggiale (23) that 1 volume of boron bromide reacts with 1.5 volumes of gaseous ammonia to produce a white, pulverulent solid which is somewhat volatile and has a sharp taste. This compound, $3NH_3 \cdot 2BBr_3$, decomposes in water forming ammonium bromide and ammonium borate. The analogous compound with boron trichloride, $3NH_3 \cdot 2BCl_3$, had been reported much earlier by Berzelius (2) and confirmed somewhat later by Martius

(21). It is difficult to account satisfactorily for the distribution of the electrons required to establish the bonds in these compounds.

Besson (5) later studied the reaction of dry gaseous ammonia with boron bromide and reported that the reaction proceeds with the liberation of a large quantity of heat and the formation of some boron nitride. In order to obtain a definite compound Besson found it necessary to avoid a rise in temperature.

More recently, Pohland (24) studied the reaction of ammonia and boron bromide in the gas phase at a pressure of 5 mm. The reaction is exothermic and produces a white cloud of reaction product which contains 4.5 moles of ammonia per mole of boron bromide. This would correspond to the compound $9NH_3 \cdot 2BBr_3$. When the reaction product was heated in a vacuum to 300°C. ammonium bromide was found to be present.

Unfortunately the conditions were not adequately described by the earlier workers and therefore it is not possible to draw any definite conclusions with regard to the gas-phase reaction of ammonia with boron bromide except at reduced pressure. It is apparent however that the heat of reaction must be dissipated or the molecular compounds formed will decompose and, if the temperature is high enough, may be converted to boron nitride.

Joannis (16) allowed dry gaseous ammonia to react with precooled (−10°C.) liquid boron bromide. Under these conditions he reported that he obtained boron imide and ammonium bromide as products. At 0°C. Joannis observed that this reaction proceeded according to the equation:

$$2BBr_3 + 27NH_3 \rightarrow 6(NH_4Br \cdot 3NH_3) + B_2(NH)_3$$

The product $NH_4Br \cdot 3NH_3$ was identified by its vapor pressure, which was close to that reported by Troost (32). Upon warming to 20°C., $NH_4Br \cdot 3NH_3$ dissociates with the evolution of 9 moles of ammonia per mole of boron bromide, thus:

$$2BBr_3 + 27NH_3 \rightarrow 18NH_3 + 6NH_4Br + B_2(NH)_3$$

Several years later Stock and Holle (27) studied the reaction of gaseous ammonia with an excess of precooled, vigorously stirred boron bromide. Under these conditions, boron bromide was always occluded in the reaction product, which immediately underwent hydrolysis.

From the above work, it appears that gaseous ammonia reacts with liquid boron bromide to produce boron imide and ammonium bromide.

In order to dilute the reactants, Besson (5) studied the reaction of gaseous ammonia with a solution of boron bromide in carbon tetrachloride. By introducing precooled (0°C.) dry gaseous ammonia into the solution, also at 0°C., he obtained a white precipitate which was freed of the excess solvent by passing preheated (50–60°C.) dry air through the reaction vessel. The white amorphous product was found by analysis to have a composition in agreement with the formula $4NH_3 \cdot BBr_3$. This compound when heated in an atmosphere of dry hydrogen at 150°C. begins to decompose, without sublimation, to form boron nitride and ammonium bromide in accordance with the equation:

$$4NH_3 \cdot BBr_3 \rightarrow BN + 3NH_4Br$$

The obtainment of boron bromide by heating confirms the earlier observation of Besson that the heat evolved when the reactant gases are mixed produces boron nitride. Water and alkalies decompose $4NH_3 \cdot BBr_3$. At 10°C. the compound absorbs ammonia up to the ratio of 2 moles of compound per mole of ammonia, thus producing $9NH_3 \cdot 2BBr_3$ (*vide supra*). Besson, however, considered this absorption to be of a physical nature, although the resultant product is analogous to $9NH_3 \cdot 2BCl_3$, which he had reported earlier (3).

Stock (25) observed that the compound $AsH_3 \cdot BBr_3$ (*vide infra*) reacts with ammonia at 10°C. to produce $9NH_3 \cdot 2BBr_3$. It is to be noted that the temperature is the same as employed by Besson (5) and that the identical product is obtained. Stock observed that the combining ratio of ammonia to boron bromide varies inversely with the reaction temperature. At −25°C. for example, $9NH_3 \cdot 2BBr_3$ absorbs sufficient ammonia to become a liquid, which upon warming evolves the excess ammonia.

Joannis (15) studied the reaction of ammonia and boron chloride by allowing gaseous boron chloride diluted with hydrogen to react with liquid ammonia. He bubbled hydrogen through boron chloride at 0°C. and introduced the gases into liquid ammonia at −70°C. to −50°C. Under these conditions he obtained a white precipitate in the liquid ammonia. The excess ammonia was removed by allowing the reaction vessel to warm to −23°C. According to Joannis the reaction proceeds as indicated by the equation:

$$BCl_3 + 15NH_3 \rightarrow B(NH_2)_3 + 3(NH_4Cl \cdot 3NH_3)$$

Upon warming the product to 0°C., 9 moles of ammonia are liberated. The reaction between ammonia and boron chloride at 0°C. is represented therefore by the equation:

$$BCl_3 + 6NH_3 \rightarrow 3NH_4Cl + B(NH_2)_3$$

In view of this experimental work and that which he did with gaseous ammonia and liquid boron bromide, Joannis questioned the formation of $4NH_3 \cdot BBr_3$ and $9NH_3 \cdot 2BBr_3$ by the reactions reported above. He suggested that it was quite probable that the reaction products were mixtures of boron amide and ammonium bromide.

Stock and Holle (27) studied the reaction between liquid boron bromide and liquid ammonia. The boron bromide was allowed to drip into liquid ammonia with the formation of soluble ammonium bromide and insoluble boron amide. Upon heating the product to 750°C., ammonium bromide sublimed leaving boron nitride.

Apparently the reaction between ammonia and boron bromide is highly sensitive to the experimental conditions. At high dilution (for example, in the gas phase or when a diluent is used with the liquid boron bromide) and at lower temperatures the evidence favors the existence of molecular compounds. However, these compounds are seemingly very unstable to heat and are easily decomposed at moderate temperatures to form boron amide and ammonium bromide. At higher temperatures, boron nitride is formed. When the ammonia and boron bromide reactants are more concentrated (for example, liquid-phase reactions) apparently the reaction is so exothermic that any molecular compounds which might be formed at first are instantaneously decomposed to produce boron amide and ammonium bromide. These reaction products when heated similarly produce boron nitride.

It is quite clear that the reaction between ammonia and boron bromide proceeds vigorously and is exothermic and that the resultant molecular compounds are quite unstable. Their stability is seemingly less than that of the boron chloride compounds, which in turn are less stable than the compounds of ammonia and boron trifluoride.

The only molecular compounds of boron iodide reported in the literature are those with ammonia. Besson (5) observed that dry gaseous ammonia unites with boron iodide with the evolution of a considerable quantity of heat. As he observed with the analogous reaction with boron bromide above, a rise in temperature favors the formation of boron nitride. Precooled (0°C.) ammonia when introduced into a solution of boron iodide in carbon tetrachloride at 0°C. yields a white precipitate immediately upon the surface of the solution. Removal of the carbon tetrachloride by a current of warm dry air (50–60°C.) leaves an amorphous white solid, which was found upon analysis to have a composition corresponding to the formula $5NH_3 \cdot BI_3$.

This compound is unstable in the presence of light, slowly turning to a yellow color with the liberation of a small quantity of iodine. Iodine is produced also when the compound is heated in a current of hydrogen. The compound is quickly decomposed by water. A current of dry gaseous ammonia at 0°C. converts $5NH_3 \cdot BI_3$ into a pasty mass which eventually completely liquefies. Besson reported the composition of this product to be $15NH_3 \cdot BI_3$. At 0°C. this product is unstable and gradually evolves ammonia when maintained in a current of dry air to reproduce the compound $5NH_3 \cdot BI_3$.

Later, Joannis (15) stated that he believed the reactions of ammonia with boron iodide were of the same nature as those which he had observed for ammonia and boron chloride and that the above products were actually mixtures of boron amide and ammonium iodide. As pointed out above, the concentration of the reactants and the reaction temperatures employed alter these reactions and it could well be that the reaction under certain conditions would proceed in either of the ways reported by Joannis or Besson.

Table 1 summarizes the molecular compounds reported to be formed by ammonia with the boron halides.

Inasmuch as the boron atom becomes more positive as the molecular weight of the boron halide decreases, and inasmuch as the size of the molecule becomes smaller, it would be expected that the ratio of ammonia to boron halides in the molecular compounds should increase as the molecular weight of the boron halide decreases. As a consequence of the increased positive charge on the boron, more ammonia molecules should associate owing to an induced positive

TABLE 1

Molecular compounds of ammonia and the boron halides

Ratio of NH_3/BX_3	1	1.5	2	3	4	4.5	5	15
BF_3	$NH_3 \cdot BF_3$		$2NH_3 \cdot BF_3$	$3NH_3 \cdot BF_3$				
BCl_3		$3NH_3 \cdot 2BCl_3$				$9NH_3 \cdot 2BCl_3$		
BBr_3		$3NH_3 \cdot 2BBr_3$			$4NH_3 \cdot BBr_3$	$9NH_3 \cdot 2BBr_3$		
BI_3							$5NH_3 \cdot BI_3$	$15NH_3 \cdot BI_3$

charge on the hydrogen atoms of the ammonia coördinating with the boron. This association should be favored also because steric hindrance is less likely to be encountered with the smaller halogen atoms. The reverse seems to be the case, as shown in table 1, and this along with the great instability reported for the compounds of the heavier boron halides seems to favor the postulates of Joannis that boron amide and ammonium halide are the products obtained in these cases. It is strange that more analogous compounds have not been reported for the boron halides with ammonia.

Johnson (17) studied the reactions of boron bromide with substituted ammonia compounds. He slowly passed methylamine and ethylamine, respectively, into a solution of boron bromide in carbon tetrachloride. By so doing he avoided any appreciable rise in temperature and obtained amorphous white products which upon analysis were found to have compositions in agreement with the formulas $(CH_3NH)_2BBr$ and $C_2H_5NHBBr_2$.

Using isoamylamine and aniline, he modified his technique by making a solution of the amine in carbon tetrachloride and adding a solution of boron bromide in carbon tetrachloride to the former. By cooling the reaction vessel with ice a violent reaction was avoided, although considerable heat was generated. By very slow addition of the solution of boron bromide, yellow to orange precipitates were formed at first, but after 1 mole of boron bromide had been added, amorphous white precipitates were obtained. These precipitates upon analysis were found to have compositions which may be represented by the formulas $i\text{-}C_5H_{11}NH_2 \cdot BBr_3$ and $C_6H_5NH_2 \cdot BBr_3$ (17).

Isoamylamine–boron bromide does not dissociate very rapidly below 40°C., turns a light yellow color in the sunlight, and is hydrolyzed energetically, especially by an alkaline solution, e.g., sodium hydroxide. When warmed rapidly, the compound appears to melt with immediate decomposition. It will ignite and burn vigorously with a green colored flame.

Aniline–boron bromide fumes strongly in air and is rapidly hydrolyzed to produce boric acid and aniline hydrobromide. Hydrolysis in an alkaline solution yields aniline oil.

On the basis of his work, Johnson (17) concluded that the lower primary amines tend to allow more than one molecule of the amine to react with one molecule of boron bromide to split out hydrogen bromide with the resultant formation of a heterogeneous imide. With five or more carbon atoms, the primary amines tend to form molecular compounds. This statement seems unproven, inasmuch as reactions with propyl- and butyl-amines are not reported to have been studied.

Using the same technique, Johnson (17) found that secondary amines react in a manner somewhat similar to the primary amines. The lone hydrogen atom of the aliphatic secondary amines (dimethyl-, dipropyl-, and diamyl-amines) readily splits out to form hydrogen bromide, giving rise to the stable products $(CH_3)_2NBBr_2$, $(C_3H_7)_2NBBr_2$, and $(C_5H_{11})_2NBBr_2$.

Piperidine and diphenylamine, however, form molecular compounds with boron bromide. Using carbon tetrachloride as a mutual solvent, piperidine and boron bromide were allowed to react to produce a very light yellow precipitate.

The precipitate was washed with carbon tetrachloride and dried in a current of either dry air or dry hydrogen. The product upon analysis was found to have a composition most simply expressed as $3(C_5H_{10}NH)\cdot BBr_3$. The product is unstable under ordinary conditions and is transformed into a stable product with the evolution of hydrogen bromide. The stable product is best obtained by exposing a thin layer of $3(C_5H_{10}NH)\cdot BBr_3$ to the action of calcium chloride and sodium hydroxide in a desiccator. The stable product was found by analysis to have a composition in agreement with the formula $2(C_5H_{10}NH)\cdot C_5H_{10}NBBr_2$. This substance dissolves in several organic solvents, apparently without decomposition, to produce greenish-yellow solutions possessing fluorescing properties.

Using a similar procedure, diphenylamine reacted with boron bromide to yield a voluminous, snow-white product which is more stable under ordinary conditions than the other secondary amine compounds. The formula of this compound was found by analysis to be $3(C_6H_5)_2HN\cdot BBr_3$.

It seems odd that 3 moles of these secondary amines can easily coördinate with 1 mole of boron bromide. Evidently these secondary amines associate, although the fact that there are three moles of amine and three bromine atoms might suggest hydrogen bonding. However, with bromine at these temperatures, this does not seem probable.

In this study of the reactions of tertiary amines with boron bromide, Johnson (17) found that a simple molecular compound usually forms at first, which later decomposes by splitting out an alkyl bromide. A stable molecular compound forms with quinoline, whereas with alkyl or mixed alkyl phenyl amines, less stable coördination compounds are formed. The conclusion follows that the size of the aromatic nucleus attached to the nitrogen atom and the stability of the resulting molecular compound are related.

When gaseous trimethylamine was introduced into a solution of boron bromide in carbon tetrachloride, an exothermic reaction occurred immediately with the formation of a small quantity of precipitate. Copious white fumes were evolved from the reaction liquid, and it was apparent that a general decomposition was occurring, perhaps with solution of the initial product. Attempts made to crystallize the product as a definite compound were unsuccessful.

With carbon tetrachloride as a common solvent, triethylamine and boron bromide were allowed to react. Heat was liberated and a white precipitate formed at first which later dissolved in the warm carbon tetrachloride. Fine, long, slender prisms which readily formed large irregular translucent masses were deposited upon cooling the solution. By permitting the carbon tetrachloride solution to stand for a period of time, bunches of "cotton batting-like" crystals formed and floated about in the solvent. These crystals were exceedingly thin long needles, having a length at least two hundred times their diameter. They were found to be relatively unstable when washed and dried, particularly at temperatures above 50°C. After being analyzed, the crystals were assigned the formula $(C_2H_5)_3N\cdot BBr_3$. The crystals readily, but not violently, underwent hydrolysis in water.

Boron bromide evidently does not react with triethanolamine, inasmuch as it was found that a solution of boron bromide in triethanolamine did not react with magnesium after being heated with it in a sealed tube at 120°C. for 3 hr. (9).

Dimethylaniline reacts rapidly with boron bromide, forming masses of small, translucent crystals which are somewhat soluble in carbon tetrachloride (17). The reaction is exothermic. To prevent hydrolysis, dry air must be used to dry the crystals. The hydrolysis with cold water is rapid but not violent and produces an oil, a white insoluble substance, and a small quantity of gas. According to the analysis, the product is dimethylaniline–boron bromide, $C_6H_5N(CH_3)_2 \cdot BBr_3$. When stored over sodium hydroxide and calcium chloride in a desiccator placed near a steam radiator, this compound evolved methyl bromide, leaving $C_6H_5NCH_3BBr_2$.

Pyridine, an example of a strongly basic organic compound of the heterocyclic nitrogen–carbon type, reacts with boron bromide in a carbon tetrachloride medium to produce a light, amorphous, snow-white precipitate (17). After the carbon tetrachloride has been removed, the product may be handled in air for some time without appreciable decomposition. Upon heating, the dissociation pressure rises rapidly with the temperature and at 120°C. the compound becomes "brown and crispy." By analysis the compound was found to be pyridine–boron bromide, $C_5H_5N \cdot BBr_3$. If pyridine–boron bromide is stored over sodium hydroxide and calcium chloride, hydrogen bromide is evolved to yield a more stable powder, $C_5H_4NBBr_2$.

Similarly, quinoline and boron bromide react to form the white product $C_9H_7N \cdot BBr_3$ (17). Less heat is liberated in this reaction than in the one above with pyridine. This compound is more stable under ordinary conditions than $C_5H_5N \cdot BBr_3$. It is decomposed relatively slowly in a cold alkaline solution.

The compounds formed by amines with boron halides are compared in table 2.

Pohland (24) observed a vigorous reaction when boron bromide was condensed over hydrogen cyanide and the reactants were allowed to warm to room temperature. Under these conditions sufficient heat is evolved to cause the hydrogen cyanide to polymerize. However, if the reaction is carried out under a greatly reduced pressure, white, sharp, needle-shaped crystals are obtained having the composition $HCN \cdot BBr_3$. This result is obtained regardless of which reactant is present in excess. The crystals are volatile at room temperature and melt in a closed tube at 70°C. with decomposition. The compound is decomposed by moisture, evolving gases having odors resembling hydrogen bromide and hydrogen cyanide.

Johnson (17) allowed methyl cyanide to react with boron bromide dissolved in carbon tetrachloride in a cooled reaction vessel. A beautiful, flaky, snow-white product, which is slightly soluble in carbon tetrachloride and may be recrystallized therefrom, was obtained. The dried powder was found by analysis to be methyl cyanide–boron bromide, $CH_3CN \cdot BBr_3$. At low temperatures the compound is stable but at 30°C. it dissociates rapidly. It quickly decomposes in water.

In 1866 Gautier (11) reported that boron trichloride reacts very rapidly with

TABLE 2

Molecular compounds formed by amines with boron halides

BF_3	BCl_3	BBr_3	BI_3
$(CH_3)_3N \cdot BF_3$	$(CH_3)_3N \cdot BCl_3$		None
$(C_2H_5)NH_2 \cdot BF_3$			
$(C_2H_5)_2NH \cdot BF_3$			
$(C_2H_5)_3N \cdot BF_3$	$(C_2H_5)_3N \cdot BCl_3$	$(C_2H_5)_3N \cdot BBr_3$	
$2(C_2H_5)_3N \cdot BF_3$			
		$i\text{-}C_5H_{11}NH_2 \cdot BBr_3$	
$(CH_2)_6N_4 \cdot 4BF_3$			
$C_{23}H_{26}N_2O_4 \cdot 4H_2O \cdot 2BF_3$			
$CH_3CONH_2 \cdot BF_3$			
$C_6H_5NH_2 \cdot BF_3$	$C_6H_5NH_2 \cdot BCl_3$	$C_6H_5NH_2 \cdot BBr_3$	
$C_6H_5N(CH_3)_2 \cdot BF_3$	$C_6H_5N(CH_3)_2 \cdot BCl_3$	$C_6H_5N(CH_3)_2 \cdot BBr_3$	
$p\text{-}CH_3C_6H_4NH_2 \cdot BF_3$(?)	$p\text{-}CH_3C_6H_4NH_2 \cdot BCl_3$		
$C_6H_5(CH_3CO)NH \cdot BF_3$			
$C_6H_5(CH_3CO)NCH_3 \cdot BF_3$			
$C_6H_5NHNa \cdot BF_3$			
$C_6H_5NHK \cdot BF_3$			
		$3(C_6H_5)_2NH \cdot BBr_3$	
$C_6H_5CH{=}NC_6H_5 \cdot BF_3$			
$C_6H_5C(NOH)CH_3 \cdot BF_3$			
$p\text{-}CH_3C_6H_4C(NOH)C_6H_5 \cdot BF_3$			
$C_5H_5N \cdot BF_3$		$C_5H_5N \cdot BBr_3$	
$C_5H_5N \cdot 2BF_3$			
$(CH_2)_5HN \cdot BF_3$		$3(CH_2)_5HN \cdot BBr_3$	
$C_9H_7N \cdot BF_3$		$C_9H_7N \cdot BBr_3$	

ethyl cyanide to produce a white crystalline compound which was found by analysis to have the formula $C_2H_5CN \cdot BCl_3$. The crystals are prisms which are perpendicular to a rhombic base. Upon heating, the crystals melt without appreciable decomposition, although they are quite volatile. Owing to decomposition a small portion of residue remains. When strongly heated, the crystals evolve acidic vapors smelling like cyanogen. The compound undergoes hydrolysis with the formation of hydrochloric acid, boric acid, and ethyl cyanide.

Gautier reported that a similar compound is obtained with boron bromide. Evidently the composition of this compound is $C_2H_5CN \cdot BBr_3$. Johnson (17) prepared this compound in the same manner in which he prepared methyl cyanide–boron bromide. He observed that the ethyl cyanide reacted with boron bromide with the evolution of more heat and that the product was more stable to heat and to hydrolysis than the methyl derivative.

Phenyl cyanide and boron bromide produce a substance which is quite soluble in carbon tetrachloride. With difficulty, Johnson (17) obtained good crystals which had a composition corresponding to the formula $C_6H_5CN \cdot BBr_3$. The pure white powder when dry is hygroscopic and hydrolyzes rapidly.

Comparatively little heat is evolved when boron bromide is allowed to react with benzyl cyanide. An amorphous, translucent mass results which forms clusters of needles around the edges. The dried product absorbs considerable carbon tetrachloride and is soluble to some extent in it. It is difficult to obtain well-formed crystals from the solution. Carbon disulfide was found to be a poorer solvent. Both solvents were used by Johnson (17) to obtain a final product which had a faint yellow color which is considered to be characteristic. The product fumes in air and melts with decomposition. The formula of the product was found by analysis to be $C_6H_5CH_2CN \cdot BBr_3$.

Silver cyanide and boron bromide have been reported to react at 60°C. to produce a yellowish-brown insoluble solid having a composition best expressed as $AgCN \cdot BBr_3$. The product is decomposed by water and ethanol to produce hydrogen bromide and hydrogen cyanide. Similar products are obtained when the crystals hydrolyze in moist air. Pohland (24) found that the product is black in color and is insoluble in the usual solvents when the reaction is carried out at 100°C. The molecular compound when heated to 150°C. evolved cyanogen, bromine, and boron bromide.

The fact that boron bromide, which is a poorer acceptor molecule than boron chloride, forms the above compound with silver cyanide is significant, because many years prior to this research Gustavson (13, 14) reported that neither silver cyanide nor potassium cyanide reacted with boron chloride to give boron cyanide. He did not give the conditions of his investigations, however.

Cocksedge (8) allowed boron bromide to react with twice the theoretical amount of dried silver thiocyanate in a benzene medium. He obtained a colorless solution which gave glistening colorless crystals upon the removal of the solvent at ordinary temperatures in a current of dry air. The crystals as usually obtained from benzene are short rhombic crystals, but occasionally they are obtained as radiating needles.

Analysis of the crystals indicated they were boron thiocyanate, $B(CNS)_3$. At 100°C. the crystals darken considerably. The product hydrolyzes to give boric and hydrothiocyanic acids. Later, Pohland (24) repeated the work of Cocksedge and was unable to confirm his preparation of boron thiocyanate. Instead, he obtained a light-stable, yellow product which could not be silver bromide, the by-product in the preparation of boron thiocyanate by the above reaction.

The reported cyanide compounds with the boron halides are tabulated in table 3. The pseudo-halogen group, CN, is apparently a better donor to boron halides than the chlorine atom. Methyl chloride was found by Booth and Martin (7, 18, 20) not to coördinate with either boron trifluoride or boron chloride, whereas methyl cyanide coördinates, as shown above.

TABLE 3

Molecular compounds of cyanides and the boron halides

BF_3	BCl_3	BBr_3	BI_3
$HCN \cdot BF_3$	$HCN \cdot BCl_3$(?)	$HCN \cdot BBr_3$	None
$CH_3CN \cdot BF_3$	$CH_3CN \cdot BCl_3$	$CH_3CN \cdot BBr_3$	
	$C_2H_5CN \cdot BCl_3$	$C_2H_5CN \cdot BBr_3$	
$C_6H_5CN \cdot BF_3$		$C_6H_5CN \cdot BBr_3$	
		$C_6H_5CH_2CN \cdot BBr_3$	
$CH_3C_6H_4CN \cdot BF_3$			
		$AgCN \cdot BBr_3$	

Phosphorus

Proceeding in Group VA to phosphorus it is interesting to note that the ammonia analog, phosphine, has been reported by Besson to form a one-to-one molecular compound with boron bromide (4). Being more electropositive, it is natural that the phosphorus atom would donate electrons more easily than the nitrogen atom and that the tendency for association with phosphine would be less than with ammonia. Hence we do not find compounds with more than one phosphine molecule per boron bromide molecule, as was the case with ammonia. On the other hand, as a consequence of association, the nitrogen atom of one of the associated molecules becomes sufficiently positive to coördinate, whereas the nitrogen atom in a single ammonia molecule is not sufficiently electropositive to coördinate. Hence, a one-to-one compound between ammonia and boron bromide has not been isolated.

Besson (4) observed that boron bromide absorbs phosphine at ordinary temperatures, producing a very light, white, amorphous solid which fumes in air and is spontaneously inflammable. When placed in water the product violently decomposes, evolving phosphine. It is reported that one may handle the compound in an atmosphere of carbon dioxide only with difficulty; consequently its analysis is difficult. The compound was found to have a composition best expressed as $PH_3 \cdot BBr_3$, as determined by the volume of phosphine which reacted with a known weight of boron bromide.

The dissociation pressure of the compound is negligible at ordinary temperature but is appreciable at 150°C. In a current of hydrogen or carbon dioxide in a closed system, the compound may be sublimed. The sublimate appears as small, transparent, very refractive crystals. When heated to 300°C. the compound first turns yellow, then brown, with the evolution of hydrogen bromide and the formation of phosphorus tribromide. Boron trichloride and boron trifluoride are reported to form the following compounds with phosphine: $PH_3 \cdot BCl_3$, $PH_3 \cdot BF_3$, and $PH_3 \cdot 2BF_3$.

About a year later, Besson (5) reported that boron iodide and phosphine react to yield a crystalline compound. He indicated that later he would publish the details of this research, but a search of the literature does not disclose this information.

Tarible (30) reported that boron bromide reacts instantly with phosphorus trichloride to produce a white crystalline compound. Considerable heat is evolved in this reaction. The reaction was carried out under various conditions, primary of which was the varying of the ratio of boron bromide to phosphorus trichloride from 0.5 to 3. The most lively reaction was obtained when 2 moles of boron bromide were allowed to react with 1 mole of phosphorus trichloride. When 3 moles of boron bromide were used, the excess liquid boron bromide appeared above the crystalline product and was decanted, leaving the crystals which were dried in a current of carbon dioxide. The analytical results corresponded with the formula $PCl_3 \cdot 2BBr_3$.

As would be expected, the colorless crystals fume in moist air and are completely hydrolyzed in water to yield phosphorous acid, boric acid, hydrogen bromide, and hydrogen chloride. The compound is soluble in its congeners, chloroform and carbon disulfide, but is insoluble in petroleum ether and vaseline oil. When heated, the compound partially sublimes at 40°C. and melts around 58°C. In a current of hydrogen the compound sublimes around 30°C. and is partially dissociated at 50°C. At red heat, oxygen reacts with $PCl_3 \cdot 2BBr_3$. Sulfur is unreactive with the compound below its dissociation temperature. Ammonia is absorbed by the compound in an exothermic reaction which yields a white crystalline product. Tarible found that hydrocarbons, ethers, alcohols, and organic acids react vigorously with the molecular compound.

Wiberg and Schuster (33) have studied the reaction of phosphorus trichloride and boron bromide more recently and were unable to confirm the above work of Tarible. The latter chemists allowed boron bromide and phosphorus trichloride to react in an apparatus maintaining a high vacuum and obtained a white crystalline product. The same product was obtained regardless of which reactant was present in excess. The excess reactant was distilled away from the product at −30°C. to prevent loss of the reaction product by sublimation. The reaction product was found to have a composition best expressed by the formula $PCl_3 \cdot BBr_3$.

The freshly prepared compound, $PCl_3 \cdot BBr_3$, melts at 42°C. and becomes a liquid when stored in a vacuum for several days. The crystals fume strongly in moist air and react vigorously with water producing a hissing noise and liberating considerable heat. The vapor pressure of the crystals was found to be 20 mm. at 18°C. and 21.5 mm. at 20°C.

Consideration of the bonds involved would surely favor the existence of $PCl_3 \cdot BBr_3$ over $PCl_3 \cdot 2BBr_3$.

The higher chloride, phosphorus pentachloride, does not react with boron bromide at ordinary temperatures, according to Tarible (30). However, if the reactants are placed in a sealed tube and heated to 150°C., yellow crystals, which are heavier than those of phosphorus pentachloride, are obtained. Tarible varied the molar ratios of the reactants in a manner similar to that described above for phosphorus trichloride. The compound upon analysis was found to have a composition in agreement with the formula $PCl_5 \cdot 2BBr_3$.

It is reported that the compound with the pentachloride is more stable than the analogous compound formed with the trichloride; this is probably due to the fact that the chlorine atom is the donor instead of the phosphorus atom. The pentachloride molecular compound is colorless, inasmuch as the pale yellow color obtained in the sealed tube disappears upon recrystallization from a solution of the crystals in boron bromide. Tarible attributed the color to traces of chlorine present in the phosphorus pentachloride. The compound is soluble in boron bromide and carbon disulfide but insoluble in petroleum ether and vaseline oil. Like the trichloride molecular compound, $PCl_5 \cdot 2BBr_3$ hydrolyzes in moist air and in water forming phosphoric and boric acids and evolving hydrogen bromide and chloride. The coördination compound is partially sublimed at 100°C. under atmospheric pressure and melts around 151°C. with slight decomposition. At elevated temperatures it sublimes in a current of hydrogen without decomposition. It is attacked by oxygen only at red heat. Below the dissociation temperature the compound is not attacked by sulfur, but ammonia is absorbed energetically and exothermally to produce a white amorphous powder. Hydrocarbons, ethers, alcohols, and organic acids react vigorously with the coordination compound.

Although the chlorine atom of phosphorus pentachloride is considered the donor atom in $PCl_5 \cdot 2BBr_3$, it was discussed at this point owing to its similarity to phosphorus trichloride.

Although oxygen is probably the donor in the compound formed by phosphoryl chloride and boron bromide, this compound will be discussed with the phosphorus chlorides. Oddo and Tealdi (22) allowed phosphoryl chloride and boron bromide to react and obtained a white crystalline product which was dried under reduced pressure on a clay plate supported over calcium oxide and sulfuric acid. Analysis of the crystalline product indicated the existence of the compound $POCl_3 \cdot BBr_3$. The compound hydrolyzes energetically and is easily decomposed, especially by potassium hydroxide. When heated, it decomposes prior to melting.

Tarible (29) found that phosphorus tribromide and phosphorus pentabromide form molecular compounds with boron bromide but unlike the phosphorus chlorides, the molar ratio is one to one. He observed that 1 mole of boron bromide when added to 1 mole of phosphorus tribromide produced a white crystalline compound which melted around 60°C. However, if carbon disulfide solutions of the two reactants were mixed and half of the solvent removed by distillation, the remaining solution produced either short thick crystals or needle-like crystals, depending upon the conditions of cooling. The crystals were freed from the solvent by a current of dry carbon dioxide and when analyzed were found to have the composition $PBr_3 \cdot BBr_3$. This crystalline product melted at 61°C.

As would be expected, the crystals fume in moist air and are very easily decomposed by water, producing boric and phosphorous acids and hydrogen bromide. The crystals are soluble in carbon disulfide and chloroform. When heated, they sublime with partial dissociation in a current of hydrogen. The compound is slightly decomposed by a current of oxygen at ordinary temperatures but ignites below red heat forming phosphoric oxide, boric oxide, and bromine. It was found that sulfur does not react with the crystals below their dissociation temperature. In a current of chlorine gas the compound is converted to $PCl_5 \cdot BCl_3$ by the displacement of bromine. Bromine, iodine, and other non-metals do not appear to react with the compound. Hydrogen chloride, hydrogen bromide, and hydrogen iodide do not react with the crystals but ammonia is absorbed exothermically to form a white crystalline compound. As reported for $PCl_3 \cdot 2BBr_3$, vigorous reactions are obtained with hydrocarbons, ethers, alcohols, and organic acids with $PBr_3 \cdot BBr_3$.

Tarible (29) observed that carbon disulfide solutions of boron bromide and phosphorus pentabromide produced a crystalline product when mixed. The reaction is exothermic. The product is not very soluble in cold carbon disulfide but is soluble when warmed. Small white crystals were obtained by recrystallization from carbon disulfide. The analysis of these crystals indicated that their composition was $PPr_5 \cdot BBr_3$.

The crystals turn yellow if placed in a sealed tube shortly after preparation. They fume in moist air and are decomposed energetically by water, forming phosphoric and boric acids along with hydrogen bromide. When heated in air the compound starts to volatilize at 105°C. The product melts at 140°C. in a sealed tube. A current of pure dry hydrogen does not react with the compound at ordinary temperatures, but upon heating the compound volatilizes and is entrained by the hydrogen. The crystals burn when heated to red heat in a current of oxygen. Chlorine displaces the bromine to produce $PCl_5 \cdot BCl_3$ exothermically. Ammonia reacts with $PBr_5 \cdot BBr_3$ with the evolution of heat to produce a white crystalline product.

This compound was discussed at this point owing to its similarity to the compound formed with PBr_3. However, in $PBr_5 \cdot BBr_3$ the donor atom is considered to be bromine.

Tarible (31) also studied the reaction of boron bromide with phosphorus diiodide. He allowed boron bromide to react with a carbon disulfide solution of phosphorus diiodide and obtained a yellow crystalline solid in a dark red liquid.

The product upon analysis was found to have a composition in agreement with the formula $P_2I_4 \cdot 2BBr_3$. The same product was obtained also by placing the reactants in a sealed tube.

$P_2I_4 \cdot 2BBr_3$ is a golden-yellow crystalline solid which rapidly hydrolyzes and decomposes in water to produce boric and phosphorous acids along with hydrogen bromide and hydrogen iodide.

The compound is soluble in boron bromide, carbon disulfide, and chloroform but insoluble in petroleum ether and vaseline oil.

When heated to 130°C. the compound evolves iodine and at 145°C. begins to fuse. When heated in a current of hydrogen the product sublimes without decomposition. In a current of oxygen it burns to yield boric oxide, phosphorus pentoxide, bromine, and iodine. With sulfur the compound yields an iodide of sulfur. Chlorine displaces the halogens to produce double chloride compounds. The composition of these was not given by Tarible, but if all the halogens are displaced $P_2Cl_4 \cdot 2BCl_3$ would result. However, it is questionable if P_2Cl_4 would form. $P_2I_4 \cdot 2BBr_3$ absorbs ammonia at elevated temperatures to produce a white amorphous powder.

TABLE 4

Molecular compounds of boron halides with halides of phosphorus

BF_3	BCl_3	BBr_3	BI_3
None	$PCl_3 \cdot BCl_3$	$PCl_3 \cdot BBr_3$	None
		$PCl_3 \cdot 2BBr_3$(?)	
	$PCl_5 \cdot BCl_3$	$PCl_5 \cdot 2BBr_3$	
	$P_2Cl_4 \cdot 2BCl_3$(?)		
		$POCl_3 \cdot BBr_3$	
		$PBr_3 \cdot BBr_3$	
		$PBr_5 \cdot BBr_3$	
		$P_2I_4 \cdot 2BBr_3$	

It is interesting that Tarible (31) found that phosphorus triodide and boron bromide do not react at ordinary temperatures. However, if they are heated in a sealed tube a mixture of large crystals of iodine along with yellow crystals in a colored liquid is obtained. The following reaction is reported to take place:

$$2PI_3 + 2BBr_3 \rightarrow P_2I_4 \cdot 2BBr_3 + I_2$$

A summary of the molecular compounds formed by the boron halides and the phosphorus halides is given in table 4.

Arsenic

No compounds have been reported in which arsenic is the donor atom to boron trifluoride. However, arsine is reported to form the compound $AsH_3 \cdot BCl_3$ with boron trichloride. Stock (25) found that arsine does not react with boron bromide at room temperature nor at 0°C., just as is the case with boron trichloride. It made no difference if the reactants were allowed to mix in the gas phase or if arsine were introduced into a solution of boron bromide in carbon disulfide. However, if boron bromide is dropped slowly into liquid arsine at a temperature between −100° and −80°C. (in the absence of oxygen and water and preferably in the presence of hydrogen) a white amorphous solid is obtained. The solid is very refractive and forms glittering colorless crystals when sublimed in a vacuum. The crystals appear under low-power magnification as right-angled plates and prisms, the edges of which cut off planes to give the appearance of hexagonal crystals. The crystals were found by analysis to have the composition $AsH_3 \cdot BBr_3$.

$AsH_3 \cdot BBr_3$ is oxidized by oxygen at temperatures above −40°C. and is spontaneously inflammable in air, yielding hydrogen bromide, boric oxide, and arsenious oxide. Upon heating, the compound decomposes completely without melting. In a sealed tube kept in the dark at ordinary temperatures the compound decomposes in several weeks, yielding boron bromide, hydrogen, and arsenic. This decomposition is accelerated by heat. However, at 90°C. no reaction occurs between the boron and arsenic such as occurs between boron and phosphorus when $PH_3 \cdot BBr_3$ decomposes.

$AsH_3 \cdot BBr_3$ hydrolyzes to form boric acid, hydrogen bromide, and arsine. There is no apparent reaction between the compound and sulfuric acid, but with nitric acid a violent oxidation occurs. Chlorine causes the compound to burn with a light blue flame, leaving a snow-like residue which Stock postulates might be a compound formed by boron chloride and arsenic trichloride. This is contrary to the results published earlier by Tarible (*vide infra*). With bromine, the compound burns with a pale yellow flame. At −50°C. the compound reacts with arsenic trichloride, yielding arsenic, hydrogen chloride, boron chloride, and arsenic tribromide.

The compound is soluble in its reactants but insoluble in carbon disulfide. At 10°C. the compound reacts with ammonia to form $9NH_3 \cdot 2BBr_3$ (*vide supra*).

Arsenic trichloride was found by Tarible (31) to enter into a double decomposition with boron bromide with the liberation of a considerable quantity of heat. He observed also that boron bromide dissolves arsenic tribromide at 18°C. but that no compound is formed. The iodides of arsenic (AsI_3 and AsI_5) are soluble in boron bromide at temperatures between 180°C. and 200°C., but no reaction occurs in a sealed tube.

Antimony

Tarible (31) extended his study to the compounds of antimony and observed that boron bromide enters into double decomposition reactions which are exothermic with antimony trichloride and antimony pentachloride, as indicated by the following equations:

$$SbCl_3 + BBr_3 \rightarrow BCl_3 + SbBr_3$$

$$3SbCl_5 + 5BBr_3 \rightarrow 5BCl_3 + 3SbBr_3 + 3Br_2$$

Antimony tribromide and antimony triiodide are soluble in boron bromide with an alteration of their properties.

GROUP VI

Oxygen

From the reactions of the above molecular compounds of boron bromide and boron iodide it is quite evident that these halides readily hydrolyze to give boric acid and the corresponding hydrogen halide. In this respect these boron halides are like boron trichloride. On the other hand, boron trifluoride with limited quantities of water under suitable conditions forms three hydrates. This is probably due to the fact that fluorine is more electronegative than the other halogens and therefore forms stronger bonds with the central boron atom, which in turn forms a stronger dative bond with oxygen.

The only inorganic compound which has been reported to form a coördination compound with boron bromide in which the donor atom is considered to be the oxygen atom is phosphoryl chloride (*vide supra*).

The reactions of organic compounds with boron bromide are analogous to their reactions with boron trichloride. Instead of forming coördination compounds, as is the usual case with boron trifluoride, boron bromide cleaves ethers. Benton and Dillon (1) have observed that diethyl, diisopropyl, di-*n*-butyl, isopropyl, phenyl, *n*-butyl phenyl, 2-bromophenyl methyl, mesityl methyl, and benzyl *n*-propyl ethers are cleaved by boron bromide to give the corresponding alcohol or bromide in accordance with the equations:

$$R_2O + BBr_3 \rightarrow (RO)_3B + 3RBr$$

$$(RO)_3B + 3H_2O \rightarrow 3ROH + H_3BO_3$$

Sulfur

Stock and Poppenberg (28) allowed boron bromide to react with cold hydrogen sulfide and obtained a white crystalline product. Hydrogen bromide was evolved. Better results were obtained, however, by allowing hydrogen sulfide to react with a solution of boron bromide in either benzene or carbon disulfide at 0°C. (25). Using a 50 per cent solution of boron bromide in carbon disulfide at its boiling point, white needle-like crystals of $B_2S_3 \cdot H_2S$ were obtained.

Working with Blix, Stock studied the reaction further by allowing hydrogen sulfide to pass through boron bromide for 10 to 12 days to obtain $B_2S_3 \cdot H_2S$ (26). The reaction was observed to proceed rapidly at first, owing to the formation of a crystalline compound composed of boron bromide and boron sulfide. The reaction then proceeds very slowly, owing to the decomposition of this compound by additional hydrogen sulfide. $B_2S_3 \cdot BBr_3$ is more easily obtained when $B_2S_3 \cdot H_2S$ is dissolved in an excess of boron bromide and dried in a vacuum. The compound remaining, $B_2S_3 \cdot BBr_3$, forms colorless crystals which melt above 100°C. and decomposes into its components when strongly heated. If boron bromide is introduced into a solution of $B_2S_3 \cdot H_2S$ in carbon disulfide while heating, $B_2S_3 \cdot BBr_3$ is formed. $B_2S_3 \cdot BCl_3$ is prepared in an analogous manner.

These reactions are different from the reactions obtained between hydrogen sulfide and boron trichloride and boron trifluoride at lower temperatures.

Under these conditions and using the method of thermal analysis, Germann and Booth (12) found evidence for the existence of $H_2S \cdot BF_3$ and Martin (20) for $H_2S \cdot BCl_3$. The above evidence indicates that boron bromide and boron chloride at higher temperatures tend to undergo solvolysis with hydrogen sulfide, whereas boron trifluoride has not been reported to react in this way. This is in line with the general fact that boron trifluoride is a much better acceptor molecule for the formation of coördination compounds than the other boron halide molecules. Owing to the great electronegativity of the fluorine atom, the boron atom in boron trifluoride is more positive than in the other boron halides and therefore has a greater affinity for a pair of electrons from a donor atom.

GROUP VII

Chlorine

Poggiale (23) allowed chlorine to react with boron bromide and discovered that the bromine atoms were immediately displaced.

The chlorine atom is considered to be donor in the compound $PCl_5 \cdot 2BBr_3$, discussed above.

Bromine

The system Br_2–BBr_3 was studied by Cueilleron (9, 10) and was found to contain no maximum but only a simple eutectic at 80 per cent boron bromide and −60.4°C., thus indicating that bromine has no tendency to donate electrons to boron bromide to form a molecular compound.

The bromine atom is considered to be the donor atom in the compound $PBr_5 \cdot BBr_3$, discussed above. It is interesting to note that this is the only compound reported in the literature in which a bromine atom is a donor to a boron atom of a boron halide.

SUMMARY

It has been observed that the number of coördination compounds formed by the boron halides increases inversely with their molecular weights. The properties of analogous compounds of these halides indicate that the electrophilic character of the boron atom in these molecules is strongest in boron trifluoride and becomes progressively weaker in the chloride, bromide, and iodide.

Compounds containing nitrogen, phosphorus, arsenic, oxygen, sulfur, chlorine, and bromine have been reported to act as donors to boron tribromide.

Boron iodide has been reported to form some compounds with ammonia only. These compounds are of unusual composition and their existence is somewhat doubtful.

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