COÖRDINATION COMPOUNDS OF BORON TRICHLORIDE. I

A Review

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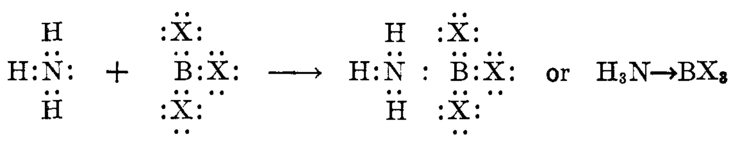
I. INTRODUCTION

In an earlier paper (3) the coördination compounds of boron trifluoride were reviewed. Many molecular compounds of boron trifluoride have been reported, and it is of interest to compare the number of these with the number of similar compounds formed with boron trichloride. Hackspill (29) and Moissan (45), in their reviews of the chemistry of boron trichloride, report only a few coördination compounds of boron trichloride. A survey of the literature reveals that boron trichloride forms fewer coördination compounds than boron trifluoride. This may be accounted for in several ways. First, boron trichloride has a larger molecule than boron trifluoride. The chlorine atom is larger than the fluorine atom; therefore the chlorine nuclei are farther from the boron atom in boron trichloride and thus less firmly attached than are the fluorine atoms in boron trifluoride. Evidence of this is abundant in the reactions of these two boron halides with organic compounds, in which boron trichloride readily splits out hydrogen chloride to form organo-boron chloride compounds, while boron trifluoride readily coördinates with organic compounds to form molecular compounds. Also, owing to the difference in size of the chlorine and fluorine atoms, steric hindrance to the formation of coördination compounds might be more readily encountered with boron trichloride than with boron trifluoride.

Secondly, in molecular compounds the boron halide molecule is electronegative, owing to the acceptance of a pair of electrons by the boron atom. For example:



$$\begin{array}{ccccccc} \mathrm{H} & & :\ddot{\mathrm{X}}: & & \mathrm{H}\;\;:\ddot{\mathrm{X}}: & & \\ \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}: & + & \underset{\cdot\cdot}{\ddot{\mathrm{B}}}:\underset{\cdot\cdot}{\ddot{\mathrm{X}}}: & \longrightarrow & \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}\,:\,\underset{\cdot\cdot}{\ddot{\mathrm{B}}}:\underset{\cdot\cdot}{\ddot{\mathrm{X}}}: & \text{or} & \mathrm{H_3N \rightarrow BX_3} \\ \mathrm{H} & & :\underset{\cdot\cdot}{\mathrm{X}}: & & \mathrm{H}\;\;:\underset{\cdot\cdot}{\mathrm{X}}: & & \end{array}$$

Since fluorine is more electronegative than chlorine, boron trifluoride will be more electronegative than boron trichloride; thus boron trifluoride should form molecular compounds with greater ease.

There are only seven elements which in their compounds have been reported to be donors to the boron atom of boron trichloride. These elements are nitrogen, phosphorus, and arsenic in Group V of the Periodic Table, oxygen and sulfur in Group VI, and fluorine and chlorine in Group VII. All of these elements except arsenic are found to be donors to boron trifluoride (3). In addition, carbon and argon are donors to boron trifluoride.

The greatest difference between boron trichloride and boron trifluoride is found in their reactions with organic compounds, as described above.

In this paper the coördination compounds of boron trichloride will be discussed with respect to the group in the Periodic Table of which the donor atom is a member.

II. GROUPS 0 TO IV

No research has been reported with the rare gases in Group 0 analogous to the argon–boron trifluoride study of Booth and Willson (5). It would be interesting to see if argon or krypton will coördinate with boron trichloride.

The literature reveals no coördination compound studies involving the members of Groups I to IV and boron trichloride. The same situation is found with boron trifluoride, although in this case it is postulated that certain organic compounds and boron trifluoride form intermediate coördination compounds in which the carbon atom is the donor (3).

III. GROUP V

Nitrogen, phosphorus, and arsenic in their respective compounds serve as donors to the boron atom of boron trichloride in forming coördination compounds. The nitrogen atom in ammonia, substituted ammonias, and cyanides coördinates with boron trichloride. Phosphine and the chlorides of phosphorus are the compounds in which the phosphorus atom serves as the donor to the boron atom of boron trichloride. Arsine is reported to form a molecular compound with boron trichloride. In this compound the arsenic is the donor atom.

A. Nitrogen

According to Berzelius (1) 1 volume of boron trichloride combines with 1.5 volumes of ammonia to form the white solid $3NH_3 \cdot 2BCl_3$. Martius (41) prepared this compound by passing dry ammonia into cooled liquid boron trichloride. The compound does not fume in air, is less volatile than ammonium chloride, and sublimes without decomposition. It reacts with water to produce hydrochloric acid, ammonium chloride, and ammonium borate.

Besson (2) reported that ammonia displaces phosphine from the compound $PH_3 \cdot BCl_3$ at 8°C. to produce $9NH_3 \cdot 2BCl_3$. This compound changes slightly when exposed to air, but does not lose ammonia below 50°C. It reacts rapidly with water, producing an alkaline solution. Joannis (33) thought this substance to be a mixture of $6NH_4Cl + B_2(NH)_3$ and proposed that the above-mentioned results were due to the complexity of the reactions taking place. He concluded that mixtures of boron-substituted ammonias with ammonium chloride had been formed instead of coördination compounds.

By bubbling hydrogen through cooled (0°C.) liquid boron trichloride and then into cooled liquid ammonia Joannis (33) studied the reaction between ammonia and boron trichloride between −70°C. and −50°C. A white precipitate formed immediately in the liquid ammonia. The temperature of the bath was then raised to −23°C. and the excess ammonia evaporated. Examination of the product showed that fifteen molecules of ammonia had been fixed. At −23°C. the following reaction was thought to occur:

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

Nine molecules of ammonia were evolved when the product was heated to 0°C. The vapor pressure of the resulting products was the same as that of the compound $NH_4Cl \cdot 3NH_3$. During this reaction neither hydrogen nor nitrogen was evolved; therefore six molecules of ammonia rearranged to form three amido groups and three ammonium groups:

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

All of this early work on the reaction between ammonia and boron trichloride seems questionable. If coördination compounds are formed, why has $NH_3 \cdot BCl_3$ not been found? Boron trifluoride forms $NH_3 \cdot BF_3$, $2NH_3 \cdot BF_3$, and $3NH_3 \cdot BF_3$ (3).

Substituted ammonias, such as trialkylamines, have been reported to coördinate with boron trichloride. Wiberg and Sütterlin found that boron trichloride and trimethylamine react at −40°C. to yield $(CH_3)_3N \cdot BCl_3$. This compound melts at 243°C. and is stable up to 250°C. (69). These authors also prepared this compound by the thermal decomposition of $BCl_2OCH_3 \cdot N(CH_3)_3$:

$$3[BCl_2OCH_3 \cdot N(CH_3)_3] \rightarrow 2[(CH_3)_3N \cdot BCl_3] + B(OCH_3)_3 + N(CH_3)_3$$

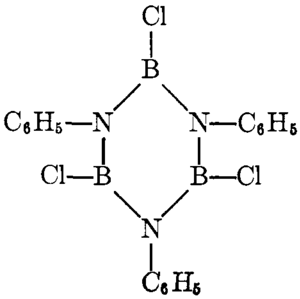
The corresponding ethyl derivative, $(C_2H_5)_3N \cdot BCl_3$, has been mentioned by Quill (49), but no experimental details were given. Gustavson (23, 27) investigated the reaction of ethylamine and boron trichloride. The product obtained melts and sublimes when heated. At 200°C. it decomposes, yielding ethyl chloride and boron nitride.

In the aromatically substituted ammonias, Rideal (52) has reported that one mole of aniline reacts with one mole of boron trichloride, producing a white solid, melting at 175°C. and having the composition C_6H_5NBCl. The reaction can be expressed as follows:

$$BCl_3 + C_6H_5NH_2 \rightarrow C_6H_5NBCl + 2HCl$$

Jones and Kinney (34) prepared the compound $C_6H_5NH_2 \cdot BCl_3$ by the reaction of aniline and boron trichloride in benzene at −15°C. The coördination compound decomposes in air. It begins to melt at 100°C. but decomposes at 120°C.

When the compound is heated in boiling benzene, boron trichloride is evolved. Triphenyltrichlorotriboron nitride forms in the benzene filtrate, crystallizing in long needles which sinter at 255–260°C. and melt with decomposition at 265–270°C. The determination of the molecular weight indicates that the substance is trimolecular. The authors propose the structure:



It is possible to write the formula of an isomer which would be a coördination compound of boron trichloride, $(C_6H_5N)_3B_2 \cdot BCl_3$. However, the cyclic formula is favored by the mode of preparation of the compound. With water, the three chlorine atoms of the compound are replaced by three hydroxyl groups. Complete hydrolysis yields aniline and boric acid.

Jones and Kinney (34) studied the reaction of dimethylaniline with boron trichloride in benzene at −15°C. A colorless solid, $C_6H_5N(CH_3)_2 \cdot BCl_3$, is obtained which softens at 125–130°C. and melts completely at 146°C. The melt crystallizes at 144–145°C. The solid fumes in air and is insoluble in cold water.

p-Toluidine–boron trichloride, $p\text{-}CH_3C_6H_4NH_2 \cdot BCl_3$, has been reported by Kinney and Kolbezen (35), who prepared it in benzene as a solvent. It melts with evolution of hydrogen chloride at 159–160°C. By distilling all of the hydrogen chloride out of the benzene filtrate, tri-*p*-tolyltrichlorotriboron nitride $(p\text{-}CH_3C_6H_4NBCl)_3$ is isolated. Kinney and Kolbezen reported that this compound softens at 304°C. and melts at 308–309°C. with decomposition. Its structure can be formulated as a cyclic compound or as an addition compound, in analogy to triphenyltrichlorotriboron nitride. The authors suggest the cyclic structure.

Martius (41) passed hydrogen cyanide gas into cooled liquid boron trichloride and obtained a white solid which changed to a brown liquid at ordinary temperature. He examined it no further but inferred that a molecular compound had been formed. Gustavson (23, 27) found that neither the silver nor the potassium salts of hydrogen cyanide react with boron trichloride.

Substitution of a methyl group for the hydrogen atom in hydrogen cyanide seems to improve the donor properties of the nitrogen atom. A coördination compound between acetonitrile and boron trichloride, $CH_3CN \cdot BCl_3$, has been reported by Nespital and coworkers (46, 61, 62). It is a white crystalline compound melting at 169°C.

Replacement of the hydrogen atom of hydrogen isocyanide with a chlorine atom seems to improve the donor properties of the nitrogen atom. Dry cyanogen chloride was bubbled through cold boron trichloride and a white crystalline substance resulted which, when analyzed for chlorine, seemed to have the composition $CNCl \cdot BCl_3$. Martius listed $CN_2Cl \cdot BCl_3$, but the analysis gave 79.7 and 79.2 per cent chlorine, values which are in good agreement with the formula $CNCl \cdot BCl_3$ (41).

Geuther (19, 20) found that nitrogen tetroxide reacted with boron trichloride to produce a solid substance suspended in the liquid phase, while yellow crystals condensed on the walls of the reaction vessel. When the material was distilled after standing for 2 days, volatile yellow crystals condensed in the receiver. Upon exposure to air, the crystals evolved a brownish red vapor. The distillate appeared to contain a solution of the crystals in boron trichloride. The composition of the crystals corresponded to $NOCl \cdot BCl_3$. The reaction can be expressed by the following equation:

$$16BCl_3 + 6N_2O_4 \rightarrow 12(NOCl \cdot BCl_3) + 2B_2O_3 + 3O_2$$

The crystals were rhombic octahedra or prisms which dissolved in water with production of chlorine, boric acid, and nitric acid. They melted at 23–24°C. forming two liquid layers, the upper of which appeared to be boron trichloride containing a small portion of the molecular compound, while the lower layer consisted of the fused coördination compound and a small quantity of nitrosyl chloride. Upon cooling, the two layers reunited to produce $NOCl \cdot BCl_3$. The synthesis of this compound from nitrosyl chloride and boron trichloride has not been reported. The similarity of this compound, $NOCl \cdot BCl_3$, to the one previously discussed, $CNCl \cdot BCl_3$, is interesting. In both compounds the chlorine atom is attached to the nitrogen atom, the only difference being the oxygen or carbon atoms which are also attached to the nitrogen atom. The carbon, oxygen, or chlorine atom might be the donor atom, but the properties of similar boron trifluoride compounds suggest the nitrogen atom rather than the carbon, chlorine, or doubly bound oxygen. The same property might be expected with boron trichloride.

In view of the numerous compounds containing nitrogen which coördinate with boron trichloride, it appears that the nitrogen atom is able to coördinate regardless of its environment.

B. Phosphorus

Besson (2) observed that phosphine and boron trichloride unite below 20°C. to produce a white solid, $PH_3 \cdot BCl_3$. Upon exposure to air, the substance rapidly decomposes, and with water it reacts vigorously producing phosphine, boric acid, and hydrochloric acid. Dissociation of the compound begins at 20°C. under atmospheric pressure. If the products of dissociation are slowly cooled, the compound is obtained in bulky, colorless, highly refractive crystals. Gamble and Gilmont (14) prepared $PH_3 \cdot BCl_3$ by the reaction of diborane diphosphine and hydrogen chloride under pressure above 0°C. It is strange that an analogous compound between ammonia and boron trichloride has not been reported.

Tarible (60) reported the formation of a double chloride in the reaction of chlorine with $P_2I_4 \cdot 2BBr_3$. He gave no formula for the compound, but if one assumes that all of the halogen atoms are displaced, the compound $P_2Cl_4 \cdot 2BCl_3$ results. However, P_2Cl_4 is difficult to prepare and therefore this assumption is questionable.

With phosphorus trichloride, Stieber (56) obtained the coördination compound $PCl_3 \cdot BCl_3$ as a white crystalline solid.

Phosphorus pentachloride–boron trichloride, $PCl_5 \cdot BCl_3$, has been prepared in two ways by Tarible (59). Chlorine displaces the bromine from $PBr_3 \cdot BBr_3$ at ordinary temperature, and the bromine from $PBr_5 \cdot BBr_3$ in the cold. Chlorine is the donor atom in $PCl_5 \cdot BCl_3$, but owing to its relationship to phosphorus trichloride, it is discussed at this point.

Apparently the replacement of the hydrogen atoms by chlorine atoms does not materially affect the donor properties of the central phosphorus atom.

C. Arsenic

Arsine and boron trichloride produce no compound at room temperature or at 0°C. However, Stieber (56) obtained a white crystalline compound, $AsH_3 \cdot BCl_3$, at −80°C. A melting point is unobtainable since the compound dissociates at −40°C. with the evolution of arsine.

IV. GROUP VI

Oxygen and sulfur in their compounds are reported as donor atoms to the boron atom of boron trichloride. With such organic compounds as alcohols, ketones, acids, acid anhydrides, and esters, boron trichloride readily splits out hydrogen chloride. Boron trifluoride, in contrast, readily coördinates with such compounds (3). However, coördination compounds with boron trichloride are reported with acid chlorides, phenols, ethers, and dioxane.

A. Oxygen—inorganic

Gaseous and liquid boron trichloride react with water, forming hydrochloric acid and boric acid (10, 11, 38, 72). This reaction is quite different from those observed for the hydrides of the elements of Group V. Dumas (10) observed that a solid hydrate is formed if the quantity of water used is very small. When the hydrate was heated in a stream of hydrogen, hydrochloric and boric acids were obtained. The work of Dumas has never been confirmed (45). On the other hand, boron trifluoride is decomposed by water, producing hydrofluoric and boric acids, but with limited quantities of water is reported to form $BF_3 \cdot H_2O$,$BF_3 \cdot 2H_2O$, and $BF_3 \cdot 3H_2O$ (3).

The existence of the oxychloride of boron, BOCl, is very questionable. The percentage composition of this compound is the same as that of a mixture of boric anhydride and boron trichloride, $B_2O_3 \cdot BCl_3$. In the research cited below, no molecular weights were determined, and there is no evidence that either BOCl or $B_2O_3 \cdot BCl_3$ exists, although the authors postulate the synthesis of the oxychloride of boron.

Gustavson (26, 27) stated that equivalent quantities of boron trichloride and boric anhydride combine, when heated in a sealed tube at 150°C., to form boron oxychloride. He assigned no formula to this compound. The same product is obtained by heating boric anhydride and phosphorus pentachloride at 140–150°C. for 3 to 4 days in a sealed tube. Lorenz (39) tried to confirm this reaction and reported the product to be a mixture consisting of $7B_2O_3 + 2BCl_3$.

Councler (8, 9) claimed that $BOCl_3$ is obtained as a by-product in the preparation of boron trichloride. He described it as a yellowish green liquid which decomposes to boron trichloride, chlorine, and boric anhydride upon heating. With water, it hydrolyzes to give chlorine, boric acid, and hydrochloric acid. Lorenz (39) tried to prepare this compound from chlorine, boric anhydride, and charcoal, but obtained, instead, a liquid mixture of boron trichloride and benzene hexachloride. After the liquid mixture was distilled, the oxychloride remained as a white fibrous mass.

$$11B_2O_3 + 2BCl_3 \rightarrow 3B_8O_{11}Cl_2$$

Upon heating this compound, the above reaction is reversed (39). Wöhler and Deville (72) reported that a little boron oxychloride always forms in the reaction vessel in which chlorine reacts with boron to produce boron trichloride. A trace of water in the chlorine or a little boric anhydride in the boron was thought to be responsible for its formation.

More recently, Wiberg and coworkers (51, 67) have proposed that boron oxychloride, BOCl, is one of the products obtained when $BCl_2OC_2H_5$ is heated to 50°C. They did not isolate this compound nor has its existence been proved.

Gustavson (24, 28) discovered that phosphorus pentoxide and boron trichloride produce a crystalline compound when heated to 200°C. in a sealed tube for 2 to 3 days. This molecular compound, phosphoryl chloride–boron trichloride, $POCl_3 \cdot BCl_3$, is obtained also from phosphoryl chloride and boron trichloride, and from boric anhydride and phosphoryl chloride when heated in a sealed tube at 150°C. for 8 to 10 hr. It is a rhombic crystalline solid melting at 73°C. Its dissociation pressure and free energy have been determined (6). Upon distillation it decomposes, yielding phosphoryl chloride and boron trichloride. In water or moist air it is converted into phosphoric acid, boric acid, and hydrochloric acid (24, 28). Oddo and Tealdi (48) produced the same compound from boric anhydride and phosphoryl chloride but were unable to confirm its synthesis from phosphoryl chloride and boron trichloride. This latter synthesis should be checked.

Gustavson found that boron trichloride and sulfur trioxide react within 8 hr. at 150°C. in a sealed tube to form sulfuryl chloride and a molecular compound, $B_2O_3 \cdot SO_3$ (25). Recently Luchinskiĭ (40) has found that a white, flaky, gel-like precipitate is obtained when liquid sulfur trioxide is added to cooled boron trichloride. Analysis of the precipitate showed a composition corresponding to $2SO_3 \cdot BCl_3$. The compound decomposes at room temperature with the separation of a liquid. Quill (49) and Whittenberg (63) mention the compounds $SO_3 \cdot BCl_3$ and $SO_2 \cdot BCl_3$. Whittenberg (63) stated that sulfur dioxide and boron trichloride react to form a yellow liquid, which upon exposure to air becomes crystalline. The substance was not analyzed, but the suggestion was made that a complex compound forms, according to the following equation:

$$SO_2 + BCl_3 \rightarrow SO_2 \cdot BCl_3$$

The compound $SO_2 \cdot BF_3$ exists (4). A thermal analysis of the system sulfur dioxide–boron trichloride would be helpful.

B. Oxygen—organic

Whereas a large number of coördination compounds between organic compounds and boron trifluoride have been prepared (3), only a few are known between organic compounds and boron trichloride. Boron trichloride and organic compounds show a strong tendency to lose hydrogen chloride, forming organoboron chlorides. Possible explanations for such behavior were offered in the introduction of this paper.

(*1*) *Alcohols:* With alcohols, stepwise substitution of the chlorine atoms of boron trichloride occurs with the formation of boric esters. Berzelius (1) noted that boron trichloride dissolves in alcohol with the evolution of an ether-like odor. Later, Ncklès (47) prepared a "hydrated boron chloride ether" by the reaction of dry hydrogen chloride gas upon an absolute alcohol solution of boric anhydride. Schiff (54) could not confirm this reaction. Instead he obtained a mixture of ethanol, "boric acid ether," ethyl chloride, hydrogen chloride, and water. Councler (7, 8, 9) found that allyl alcohol, ethylene glycol, and benzyl alcohol react with boron trichloride with the evolution of hydrogen chloride.

Wiberg and coworkers (65, 66, 67, 69) synthesized the series of compounds $ROBCl_2$, $(RO)_2BCl$, and $(RO)_3B$ (where R is a methyl or an ethyl group) by the reaction between the alcohol and boron trichloride at −90°C. to −60°C. The suggestion is made that the alcohol apparently first forms a coördination compound, $ROH \cdot BCl_3$, which later loses hydrogen chloride. These addition compounds have not been isolated (69, 70).

Kinney, Thompson, and Cheney (36) prepared a similar compound, diisoamyloxyboron chloride, $(C_5H_{11}O)_2BCl$, from isoamyl alcohol and boron trichloride.

Fischer and Taurinsch (13) prepared compounds of boron trichloride and benzeneazo-*p*-phenol by carrying out the reaction in carbon disulfide. The compound $2C_6H_5N_2C_6H_4OH \cdot BCl_3$ decomposes at 166°C., and the compound $3C_6H_5N_2C_6H_4OH \cdot BCl_3$ decomposes at 158°C. Both compounds precipitated as fine red crystals in the carbon disulfide solution.

(*2*) *Ketones:* Schumacher (55) reported that boron trichloride reacts with diketone to produce boro-organic salts. Acetylacetone is reported to react with boron trichloride, splitting out hydrogen chloride and forming complex compounds (53). Ketones are reported to coördinate with boron trifluoride (3).

(*3*) *Acids:* Gustavson (23, 27) treated a mixture of acetic acid and acetic anhydride with boron trichloride and obtained a crystalline compound which hydrolyzed to give boric acid, acetic acid, hydrogen chloride, and acetyl chloride. Meerwein and Maier-Hüser (42) later found that acetic anhydride and boron trichloride react to give pyroboron acetate $[(CH_3COO)_2B]_2O$ and acetyl chloride. An addition compound is reported by them to be formed when boron trichloride vapor is introduced into cooled acetyl chloride. The compound $CH_3COCl \cdot BCl_3$ separates as long needle-like crystals melting between -70°C. and -60°C. At room temperature the compound completely dissociates, evolving boron trichloride.

In 1928, I. G. Farbenindustrie A.-G. obtained a patent for the use of an organic complex compound, such as formed by acetic acid with boron trifluoride, as a moth-proofing material. The claim that boron trichloride would be useful likewise infers the formation of a complex compound between acetic acid and boron trichloride (32).

(*4*) *Esters:* An ester, such as ethyl acetoacetate, when treated with boron trichloride evolves hydrogen chloride and forms a complex compound (53). Esters and boron trifluoride readily coördinate (3).

(*5*) *Ethers:* Ebelmen and Bouquet (12) in 1846 reported a reaction between ethyl ether and boron trichloride in which hydrogen chloride was evolved and a compound "ethyl protoborate" was formed. Similarly, methyl and amyl "protoborates" were formed.

Gattermann (15) first reported the coördination compound between ethyl ether and boron trichloride. He stated that boron trichloride is soluble in ether and forms a crystalline, difficultly fusible, double compound with it. According to Wiberg and coworkers (51, 68, 69, 70) boron trichloride reacts with ethers to form mono- and di-alkyl substitution products. With an excess of methyl ether at -80°C. $(CH_3)_2O \cdot BCl_3$ forms. It melts with decomposition at 76°C. to a colorless liquid. Its decomposition yields methyl chloride, BCl_2OCH_3, and boric anhydride. The ethyl ether compound, $(C_2H_5)_2O \cdot BCl_3$, melts at 56°C. to a clear liquid (46).

Comparison of the observed dipole moment of boron trichloride in dioxane with the moment calculated for $C_4H_8O_2 \cdot BCl_3$ indicates that coördination of boron trichloride with dioxane is almost complete (37).

C. Sulfur

Ralston and Wilkinson (50) have reported the coördination compound $12H_2S \cdot BCl_3$. The ratio was established by analysis of their product for boron, chlorine, and sulfur. Moissan (44) passed hydrogen chloride over boron trisulfide at 400°C. and obtained a boron trichloride and hydrogen sulfide mixture. A study of the system boron trichloride–hydrogen sulfide would determine if a one-to-one coördination compound is formed. The question naturally arises as to whether $H_2S \cdot BCl_3$ exists, since $12H_2S \cdot BCl_3$ and $H_2S \cdot BF_3$ (3) have been reported.

Stock and Blix (57) obtained the compound $B_2S_3 \cdot BCl_3$ as colorless crystals.

V. GROUP VII

Fluorine and chlorine in a few of their compounds are reported as serving as donor atoms to boron trichloride.

A. *Fluorine*

With triphenylfluoromethane, boron trichloride forms an addition compound of a deep yellow color. It appears to be more stable than the corresponding triphenylchloromethane compound described below. It was not analyzed, so no formula can be assigned to it (64). No other examples were found in which fluorine served as a donor atom. Perhaps this is due to the fact that boron trichloride behaves like a negative element in the formation of coördination compounds, and since fluorine is quite electronegative, coördination is not favored.

B. *Chlorine*

Chlorine and boron trichloride do not react at room temperature or at −80°C. (58). Graff (21) made a thermal analysis of the system chlorine–boron trichloride. He found no maximum and a eutectic only at 65.5 per cent boron trichloride by weight at −135.4°C. It is evident therefore that elemental chlorine will not donate to the boron atom of boron trichloride.

Graff (22) also studied the system hydrogen chloride–boron trichloride. He found no maximum and a eutectic only at 44 per cent boron trichloride by weight at −134.5°C.

Moissan (44), however, found that chlorine reacts with boron trisulfide to produce sulfur tetrachloride–boron trichloride, $SCl_4 \cdot BCl_3$. This compound is a liquid at ordinary temperatures, but melts at −23°C. Moissan mixed one mole of sulfur monochloride and one mole of boron trichloride at −23°C. and obtained no crystals. However, upon introducing chlorine into this mixture abundant crystals formed. Upon raising the temperature to room temperature, the crystals melted to a liquid. The crystals were probably $SCl_4 \cdot BCl_3$.

Hoffmann (30, 31) observed that a small quantity of an iridescent green sublimate, the analysis of which corresponds to $3FeCl_2 \cdot BCl_3$, was produced when ferroboride was heated in a stream of dry chlorine at a high temperature. It is strange that ferrous chloride should be formed under these conditions. The main product of the reaction was a reddish brown solid which analyzed to be $4FeCl_3 \cdot BCl_3$. In a similar manner, manganese boride produced a yellowish-brown product which, when analyzed, appeared to be $2MnCl_2 \cdot BCl_3$. In all of these compounds, the chlorine atom is thought to be the donor atom.

Wiberg and Heubaum (64) reported that boron trichloride and triphenylchloromethane react at room temperature and at 0°C. to form a deep yellow addition compound, the analysis of which corresponds to $(C_6H_5)_3CCl \cdot BCl_3$. When heated to 200°C. it turns a dark brown color but does not melt. When heated to 80°C. under vacuum it distils with decomposition.

Michaelis and Becker (43) found that chlorine decomposes monophenylboron chloride, $C_6H_5BCl_2$, at ordinary temperature to produce a mixture of monochlorobenzene and boron trichloride. At −18°C., however, monophenylboron chloride absorbs chlorine, producing monophenylboron tetrachloride, $C_6H_5BCl_4$.

This compound is very unstable and when removed from the cooling bath decomposes thus:

$$C_6H_5BCl_4 \rightarrow C_6H_5Cl + BCl_3$$

$$C_6H_5BCl_4 \rightarrow C_6H_5BCl_2 + Cl_2$$

On the basis of the first equation, the tetrachloride might be considered as a coördination compound of monochlorobenzene and boron trichloride, $C_6H_5Cl \cdot BCl_3$; however, $C_6H_5BCl_4$ is favored by the method of synthesis.

VI. SUMMARY

Boron trichloride forms relatively few coördination compounds in comparison with boron trifluoride. No coördination compounds are reported in which the donor atom is a member of Groups 0 to IV in the Periodic Table.

Of the Group V elements, nitrogen, phosphorus, and arsenic in their compounds are reported to be donors to boron trichloride.

In Group VI, oxygen and sulfur in their compounds are reported to form coordination compounds with boron trichloride. Organic oxygen compounds form very few coördination compounds with it. As a rule, the boron trichloride reacts with the organic compound with the evolution of hydrogen chloride and the formation of a substituted boron chloride.

Fluorine and chlorine in their compounds are the only members of Group VII reported to form coördination compounds with boron trichloride.

Only seven elements, nitrogen, phosphorus, arsenic, oxygen, sulfur, fluorine, and chlorine, comprising the upper right-hand corner of the Periodic Table, have been found in their compounds to be donors to the boron atom of boron trichloride, thus forming coördination compounds.

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