Chapter 13

THE GROUP IIIB(13) ELEMENTS: ALUMINUM, GALLIUM, INDIUM, AND THALLIUM

13-1 Introduction

Aluminum is the commonest metallic element in the earth's crust and occurs in rocks such as felspars and micas. More accessible deposits are hydrous oxides such as bauxite ($Al_2O_3 \cdot n\, H_2O$) and cryolite (Na_3AlF_6). The elements Ga and In occur only in traces in Al and Zn ores. Thallium, also a rare element, is recovered from flue dusts from the roasting of pyrite and other sulfide ores.

Aluminum metal has many uses and some salts, such as the sulfate ($\sim 10^8$ kg/year in the USA), are made on a large scale. Gallium finds some use in solid state devices as GaAs. Thallium is used mainly as the Tl^{III} carboxylates in organic synthesis.

The position of the elements and their relation to the Sc, Y, La group is discussed in Chapter 8, where Table 8-3 gives some important properties of the elements.

The elements are more metallic than boron, and their chemistry in compounds is more ionic. Nevertheless, many of the compounds are on the borderline of ionic–covalent character. All four elements give trivalent compounds, but the univalent state becomes increasingly important for Ga, In, and Tl. For Tl the two states are about equally important and the redox system Tl^{I}–Tl^{III} dominates the chemistry. The Tl^+ ion is well defined in solutions.

The main reason for the existence of the univalent state is the decreasing strengths of bonds in MX_3; thus, for the chlorides, the mean bond energies are Ga(242), In(206), and Tl(153) kJ mol^{-1}. Hence, there is an increasing drive for Reaction 13-1.1 to occur.

$$MX_3 = MX + X_2 \qquad (13\text{-}1.1)$$

The compounds of MX_3 or MR_3 resemble similar BX_3 compounds in that they are Lewis acids, with strengths decreasing in the order $B > Al > Ga > In \sim Tl$. However, while all BX_3 compounds are planar monomers, the halides of the other elements have crystal structures in which the coordination number is increased. Coordination numbers of four occur in bridged dimers such as $Cl_2Al(\mu\text{-}Cl)_2AlCl_2$ and $(AlMe_3)_2$, whereas with bulky ligands, monomeric three-coordinate compounds may be formed, for example, $Ga(SR)_3$, where Ar =

2,4,6-*t*-BuC_6H_2. Adducts of the Lewis acids MX_3 can be five-coordinate, an example being $(Me_3N)_2AlH_3$.

Each of the elements forms an aqua ion, $[M(H_2O)_6]^{3+}$, and gives simple salts and complex compounds, where virtually all of the metals are octahedrally coordinated.

13-2 Occurrence, Isolation, and Properties of the Elements

Aluminum is prepared on a vast scale from bauxite, $Al_2O_3 \cdot n\,H_2O$ ($n = 1$–3). This is purified by dissolution in aqueous NaOH (giving $Al(OH)_4^-$), filtration to remove Fe and other insoluble hydroxides, and finally by precipitation of $Al(OH)_3 \cdot 3\,H_2O$ on cooling. The dehydrated product is dissolved in molten cryolite and the melt at 800–1000 °C is electrolyzed. Aluminum is a hard, strong, white metal. Although highly electropositive, it is nevertheless resistant to corrosion because a hard, tough film of oxide is formed on the surface. Thick oxide films are often electrolytically applied to aluminum, a process called anodizing; the fresh films can be colored by pigments. Aluminum is soluble in dilute mineral acids, but is "passivated" by concentrated HNO_3. If the protective effect of the oxide film is broken, for example by scratching or by amalgamation, rapid attack can occur even by water. The metal is readily attacked by hot aqueous NaOH, halogens, and various nonmetals.

The elements Ga, In, and Tl are usually obtained by electrolysis of aqueous solutions of their salts; for Ga and In this possibility arises because of large overvoltages for hydrogen evolution of these metals. These elements are soft, white, comparatively reactive metals, dissolving readily in acids. Thallium dissolves only slowly in H_2SO_4 or HCl, since the Tl^I salts formed are only sparingly soluble. Gallium, like Al, is soluble in aqueous NaOH. The elements react rapidly at room temperature (or on warming) with the halogens and with nonmetals such as sulfur.

13-3 Oxides

The only oxide of aluminum is *alumina* (Al_2O_3). However, this simplicity is compensated by the occurrence of polymorphs and hydrated materials whose nature depends on the conditions of preparation. There are two forms of anhydrous Al_2O_3: α-Al_2O_3 and γ-Al_2O_3. Other trivalent metals (e.g., Ga or Fe) form oxides that crystallize in these same two structures. Both have close-packed arrays of oxide ions but differ in the arrangement of the cations.

α-Al_2O_3 is stable at high temperatures and also indefinitely metastable at low temperatures. It occurs in nature as the mineral corundum and may be prepared by heating γ-Al_2O_3 or any hydrous oxide above 1000 °C. Gamma-Al_2O_3 is obtained by dehydration of hydrous oxides at low temperatures (~450 °C). Alpha-Al_2O_3 is hard and is resistant to hydration and to attack by acids. Gamma-Al_2O_3 readily absorbs water and dissolves in acids; the aluminas used for chromatography and conditioned to different reactivities are γ-Al_2O_3. Large quantities of α-Al_2O_3 are used in industry as a support material for heterogeneous catalysts.

There are several hydrated forms of alumina of stoichiometries from $AlO \cdot OH$ to $Al(OH)_3$. Addition of ammonia to a boiling solution of an aluminum salt produces a form of AlO·OH known as *boehmite.* A second form of AlO·OH occurs in nature as the mineral *diaspore.* The true *hydroxide,* $Al(OH)_3$, is obtained as a crystalline white precipitate when CO_2 is passed into alkaline "aluminate" solutions.

The oxides of Ga and In are similar, but Tl gives only brown-black Tl_2O_3, which decomposes to Tl_2O at 100 °C.

The elements form *mixed oxides* with other metals. Aluminum oxides containing only traces of other metal ions include ruby (Cr^{3+}) and blue sapphire (Fe^{2+}, Fe^{3+}, and Ti^{4+}). Synthetic ruby, blue sapphire, and white sapphire (gem-quality corundum) are manufactured in large quantities. Mixed oxides containing macroscopic proportions of other elements include the minerals *spinel* ($MgAl_2O_4$) and *crysoberyl* ($BeAl_2O_4$). The *spinal structure* (Section 4-8) is important as a prototype for many other $M^{II}M_2^{III}O_4$ compounds. Compounds such as $NaAlO_2$, which can be made by heating Al_2O_3 with sodium oxalate at 1000 °C, are also ionic mixed oxides.

13-4 Halides

All four halides of each element are known, with one exception. The compound TlI_3, obtained by adding iodine to thallium(I) iodide, is not thallium(III) iodide, but rather thallium(I) triiodide, $Tl^I(I_3)$. This situation may be compared with the nonexistence of iodides of other oxidizing cations, such as Cu^{2+} and Fe^{3+}, except that here a lower-valent compound fortuitously has the same stoichiometry as the higher-valent one. The coordination numbers of the halides are shown in Table 13-1. The fluorides of Al, Ga, and In are ionic and high melting (>950 °C), whereas the chlorides, bromides, and iodides have lower melting points. There is some correlation between melting points and coordination number, since the halides with coordination number four consist of discrete dinuclear molecules (Fig. 13-1) and the melting points are low. Thus, the three chlorides have the following melting points: $AlCl_3$, 193 °C (at 1700 mm Hg); $GaCl_3$, 78 °C; $InCl_3$, 586 °C. In the vapor, aluminum chloride is also dimeric so that there is a radical change of coordination number on vaporization. The dimer structures persist in the vapor phase at temperatures close to the boiling points but at higher temperatures dissociation occurs, giving triangular monomers analogous to the boron halides.

The covalent halides dissolve readily in nonpolar solvents such as benzene, in which they are dimeric. As Fig. 13-1 shows, the configuration of halogen atoms about each metal atom is distorted tetrahedral. The formation of such dimers is attributable to the tendency of the metal atoms to complete their octets.

Table 13-1 Coordination Numbers of Metal Atoms in Group IIIB(13) Halides

	F	Cl	Br	I
Al	6	6	4	4
Ga	6	4	4	4
In	6	6	6	4
Tl	6	6	4	

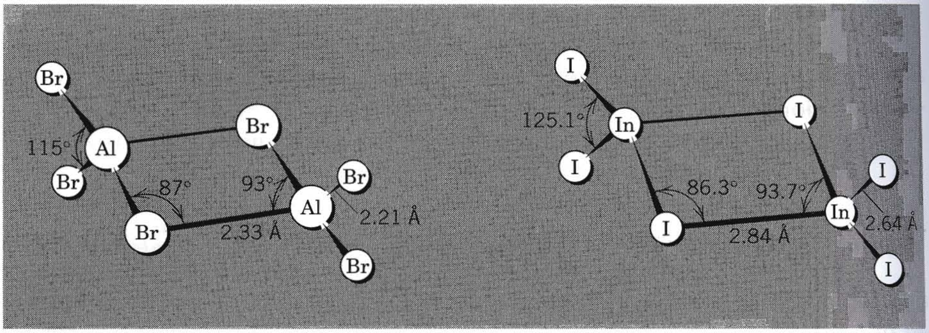


Figure 13-1 The structures of Al_2Br_6 and In_2I_6.

The thallium(III) halides vary considerably in thermal stability. Although TlF_3 is stable to 500 °C, $TlCl_3$ loses chlorine at about 40 °C forming TlCl, while $TlBr_3$ loses Br_2 at even lower temperatures to give first "$TlBr_2$," which is actually $Tl^I[Tl^{III}Br_4]$.

The trihalides (fluorides excepted) are strong Lewis acids, and this is one of the most important aspects of their chemistry, as well as that of other MR_3 compounds, such as the alkyls and AlH_3. Adducts are readily formed with Lewis bases (including halide ions). The dimeric halides are cleaved to give products such as $Cl_3AlN(CH_3)_3$ and $AlCl_4^-$.

Aluminum chloride and bromide especially are used as catalysts (Friedel–Crafts type) in a variety of reactions. The formation of $AlCl_4^-$ or $AlBr_4^-$ ions is essential to the catalytic action, since in this way carbonium ions are formed (Reaction 13-4.1).

$$RCOCl + AlCl_3 = RCO^+ + AlCl_4^- \quad \text{(ion pair)} \qquad (13\text{-}4.1)$$

and made available for reaction as in Reaction 13-4.2.

$$RCO^+ + C_6H_6 \longrightarrow [RCOC_6H_6]^+ \longrightarrow RCOC_6H_5 + H^+ \qquad (13\text{-}4.2)$$

13-5 The Aqua Ions, Oxo Salts, and Aqueous Chemistry

The elements Al, Ga, In, and Tl form well-defined octahedral aqua ions, $[M(H_2O)_6]^{3+}$, and many salts containing these ions are known, including hydrated halides, sulfates, nitrates, and perchlorates. Phosphates are sparingly soluble.

In aqueous solution, the octahedral ions $[M(H_2O)_6]^{3+}$ are quite acidic. For Reaction 13-5.1

$$[M(H_2O)_6]^{3+} = [M(H_2O)_5(OH)]^{2+} + H^+ \qquad (13\text{-}5.1)$$

the constants are K_a(Al), 1.12×10^{-5}; K_a(Ga), 2.5×10^{-3}; K_a(In), 2×10^{-4}; and K_a(Tl), $\sim 7 \times 10^{-2}$. Although little emphasis can be placed on the exact numbers, the orders of magnitude are important, for they show that aqueous solutions of the

M^{III} salts are subject to extensive hydrolysis. Indeed, salts of weak acids (sulfides, carbonates, cyanides, acetates, and the like) cannot exist in contact with water.

In addition to this hydrolysis reaction there is also a dimerization as in Reaction 13-5.2.

$$2\ AlOH^{2+}(aq) = [Al_2(OH)_2]^{4+}(aq) \qquad K = 600\ M^{-1}\ (30\ °C) \quad (13\text{-}5.2)$$

More complex species of the general formula $Al[Al_3(OH)_8]_m^{m+3}$ have also been postulated and some, such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and its gallium analog, have been identified in crystalline basic salts.

An important class of aluminum salts, the *alums,* are structural prototypes and give their name to a large number of analogous salts formed by other elements. These salts have the general formula $MAl(SO_4)_2 \cdot 12\ H_2O$ in which M is practically any common univalent, monatomic cation except Li^+, which is too small to be accommodated without loss of stability of the structure. The crystals are made up of $[M(H_2O)_6]^+$, $[Al(H_2O)_6]^{3+}$, and two SO_4^{2-} ions. Salts of the same type, $M^IM^{III}(SO_4)_2 \cdot 12\ H_2O$, and having the same structures, are formed by other M^{3+} ions, including those of Ti, V, Cr, Mn, Fe, Co, Ga, In, Rh, and Ir. All such compounds are referred to as alums. The term is used so generally that those alums containing aluminum are redundantly designated aluminum alums.

Aluminum ions and complexes are environmentally important. The leaching of Al^{3+} from silicate rocks by acid rain leads to high concentrations in lakes. Such high concentrations are toxic to aquatic life. Although senile dementia (Alzheimer's disease) may have a genetic origin, a symptom is the accumulation of aluminum complexes in the brain. The Al^{3+} ion is known to bind to iron sites in human serum transferrin (Chapter 31), and citrates, which occur in blood plasma, lactates, and other complexing agents may be involved.

Thallium carboxylates, particularly the acetate and trifluoroacetate, which can be obtained by dissolution of the oxide in the acid, are extensively used in organic synthesis. The trifluoroacetate will directly thallate (cf. mercuration, Chapter 29) aromatic compounds to give aryl thallium ditrifluoroacetates [e.g., $C_6H_5Tl(OOCCF_3)_2$]. It also acts as an oxidant, for example, by converting para substituted phenols into *p*-quinones.

The hydroxides of aluminum and gallium are amphoteric:

$$Al(OH)_3(s) = Al^{3+} + 3\ OH^- \qquad K \approx 5 \times 10^{-33} \quad (13\text{-}5.3)$$

$$Al(OH)_3(s) = AlO_2^- + H^+ + H_2O \qquad K \approx 4 \times 10^{-13} \quad (13\text{-}5.4)$$

$$Ga(OH)_3(s) = Ga^{3+} + 3\ OH^- \qquad K \approx 5 \times 10^{-37} \quad (13\text{-}5.5)$$

$$Ga(OH)_3(s) = GaO_2^- + H^+ + H_2O \qquad K \approx 10^{-15} \quad (13\text{-}5.6)$$

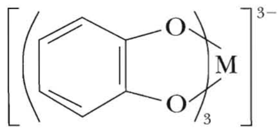
Like the oxides, these compounds also dissolve in bases as well as in acids. By contrast, the oxides and hydroxides of In and Tl are purely basic. According to Raman spectra, the main aluminate species from pH 8 to 12 appears to be an OH bridged polymer with octahedral Al, but at pH > 13 and concentrations below 1.5 *M* the tetrahedral $Al(OH)_4^-$ ion is present. Above 1.5 *M* there is condensation to give the ion $[(HO)_3AlOAl(OH)_3]^{2-}$. This occurs in the crystalline salt $K_2[Al_2O(OH)_6]$ which has an angular Al—O—Al bridge.

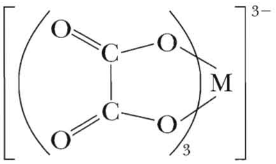
13-6 Coordination Compounds

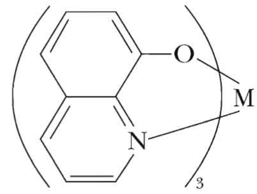
The trivalent elements form four-, five- and six-coordinate complexes, which may be cationic, like $[Al(H_2O)_6]^{3+}$ or $[Al(OSMe_2)_6]^{3+}$; neutral, for example, $AlCl_3(NMe_3)_2$; or anionic, like $[AlF_6]^{3-}$ and $[In(NCS)_6]^{3-}$.

One of the most important salts is *cryolite,* whose structure (Fig. 13-2) is adopted by many other salts that contain small cations and large octahedral anions and, with reversal of cations and anions, by many salts of the same type as $[Co(NH_3)_6]I_3$. It is closely related to the structures adopted by many compounds of the types $M_2^+[AB_6]^{2-}$ and $[XY_6]^{2+}Z_2^-$. The last two structures are essentially the fluorite (or antifluorite) structures (see Fig. 4-1), except that the anions (or cations) are octahedra whose axes are oriented parallel to the cube edges. The relationship of the two structures can be seen in Fig. 13-2, since the Na^+ ions have been indicated by both open ○ and marked ⊗ circles. If all of the marked circles (one at the center and one on each of the cube edges) in Fig. 13-2 are removed, the cryolite structure reduces to the $M_2^+[AB_6]^{2-}$ fluorite-type structure.

Many of the important octahedral complexes are those containing chelate rings. Some typical structures contain β-diketones, pyrocatechol (Structure 13-I), dicarboxylic acids (Structure 13-II), and 8-quinolinol (Structure 13-III).


13-I


13-II


13-III

The neutral complexes are soluble in organic solvents, but insoluble in water. The acetylacetonates have low melting points (<200 °C) and vaporize without de-

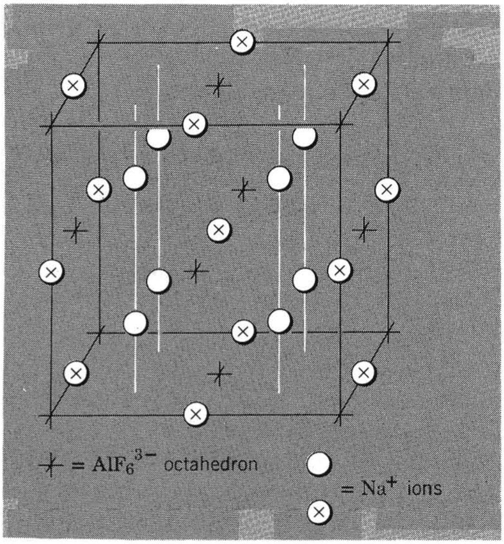


Figure 13-2 The cubic structure of cryolite (Na_3AlF_6).

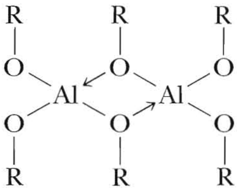
composition. The anionic complexes are isolated as the salts of large univalent cations. The 8-quinolinolates are used for analytical purposes.

The four elements form *alkoxides*, but only those of aluminum and gallium are important. The isopropoxide of aluminum is widely used in organic chemistry to catalyze the reduction of aldehydes and ketones by alcohols or vice versa (Meerwein–Ponndorf–Oppenauer–Verley reactions). Alkoxides can be made by Reactions 13-6.1 and 13-6.2.

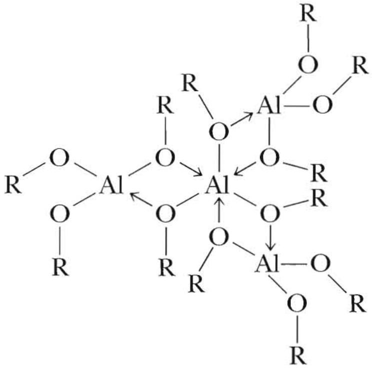
$$\mathrm{Al} + 3\,\mathrm{ROH} \xrightarrow[\text{catalyst, warm}]{1\%\ \mathrm{HgCl_2}\ \text{as}} (\mathrm{RO})_3\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2} \qquad (13\text{-}6.1)$$

$$\mathrm{AlCl_3} + 3\,\mathrm{RONa} \xrightarrow{\mathrm{ROH}} (\mathrm{RO})_3\mathrm{Al} + 3\,\mathrm{NaCl} \qquad (13\text{-}6.2)$$

The *tert*-butoxide has the dimeric structure typical of $M_2(OR)_6$ compounds both in the crystalline form and in solution (Structure 13-IV). The commonly used isopropoxide has different oligomers, one of which is the tetramer shown in Structure 13-V. This compound can be regarded as an Al^{3+} ion coordinated by three $[Al(OR)_4]^-$ groups. Other alkoxides normally form dimers and trimers, but where R groups are very bulky, three-coordinate monomers can be formed.



13-IV



13-V

Terminal and bridging alkoxyl groups can be distinguished by nmr spectra. Other alkoxides form dimers and trimers.

13-7 Hydrides

The salts containing the tetrahedral anion AlH_4^-, which is similar in some ways to BH_4^-, are important hydrides of Al. Gallium also forms a tetrahydrido anion. The thermal and chemical stabilities of these tetrahydrido anions vary with the ability of the MH_3 groups to act as an H^- acceptor, as in Reaction 13-7.1.

$$MH_3 + H^- = MH_4^- \qquad (13\text{-}7.1)$$

The order is B > Al > Ga. Thus $LiGaH_4$ decomposes slowly even at 25 °C to LiH, Ga, and H_2 and is a milder reducing agent than $LiAlH_4$. Similarly, although BH_4^- is stable in water, the Al and Ga salts are rapidly and often explosively hydrolyzed by water.

$$MH_4^- + 4\,H_2O = 4\,H_2 + M(OH)_3 + OH^- \qquad (13\text{-}7.2)$$

The most important compound is *lithium tetrahydridoaluminate,* which is widely used in both organic and inorganic chemistry as a reducing agent. It accomplishes many otherwise tedious or difficult reductions, for example, —CO_2H to —CH_2OH. It is a nonvolatile, crystalline solid, which is white when pure but is usually gray. It is stable below 120 °C and is soluble in diethyl ether, THF, and glymes.

Both aluminum and gallium salts are made by reaction of the chloride with lithium hydride, as in Reaction 13-7.3.

$$4\,LiH + MCl_3 \xrightarrow{(C_2H_5)_2O} LiMH_4 + 3\,LiCl \qquad (13\text{-}7.3)$$

The sodium salt can be obtained by direct interactions of the elements, as in Reaction 13-7.4.

$$Na + Al + 2\,H_2 \xrightarrow[150\,^\circ C\ 2000\ psi]{THF} NaAlH_4 \qquad (13\text{-}7.4)$$

The addition of toluene precipitates $NaAlH_4$ which can be converted to the lithium salt by recrystallization from ether in the presence of LiCl, as in Reaction 13-7.5.

$$NaAlH_4 + LiCl \xrightarrow{(C_2H_5)_2O} NaCl(s) + LiAlH_4 \qquad (13\text{-}7.5)$$

Donor Adducts of the Hydrides

There is an extensive range of complex hydrides that may be regarded as arising from the Lewis acid behavior of the MH_3 fragments. These adducts may be formed with donor molecules (e.g., NR_3 and PR_3) or with anions (e.g., H^-) as in Reaction 13-7.3 above. The various adducts are similar to the borane adducts, the stability order being B > Al > Ga. The most studied adducts are the trialkylamine alanes (alane = AlH_3). Trimethylamine in ether, at room temperature or below, gives both 1:1 and 1:2 adducts, as in Reactions 13-7.6 through 13-7.9.

$$Me_3N{-}AlCl_3 + 3\,LiH \longrightarrow Me_3N{-}AlH_3 + 3\,LiCl \qquad (13\text{-}7.6)$$

$$Me_3NH^+Cl^- + LiAlH_4 \longrightarrow Me_3N{-}AlH_3 + LiCl + H_2 \qquad (13\text{-}7.7)$$

$$3\,LiAlH_4 + AlCl_3 + 4\,NMe_3 \longrightarrow 4\,Me_3N{-}AlH_3 + 3\,LiCl \qquad (13\text{-}7.8)$$

$$Me_3NAlH_3 + Me_3N \longrightarrow (Me_3N)_2AlH_3 \qquad (13\text{-}7.9)$$

The monotrimethylamine alane adduct is a white, volatile, crystalline solid (mp 75 °C), that is readily hydrolyzed. It is monomeric and tetrahedral. The bis amine product of Reaction 13-7.9 is trigonal bipyramidal, with axial N atoms. Tetrahydrofuran also gives both a 1:1 and a 2:1 adduct, but ether, presumably for steric reasons, forms only a mono adduct.

Similar monoamine gallane adducts exist. These have strong Ga—H bonds, making them less sensitive to hydrolysis than are the aluminum analogs. The diamine adduct $(Me_3N)_2GaH_3$ is stable only below –60 °C.

13-8 Lower Valent Compounds

Since the outer-electron configuration is ns^2np^1, univalent compounds are, in principle, possible. Aluminum forms such species only at high temperature in the gas phase, for example,

$$\mathrm{AlCl_3(s)} + 2\,\mathrm{Al(s)} \rightleftharpoons 3\,\mathrm{AlCl(g)} \qquad (13\text{-}8.1)$$

Some gallium(I) and indium(I) compounds are known. The so-called dichloride "$GaCl_2$" is actually $Ga^{I}[Ga^{III}Cl_4]$.

Thallium has a well-defined unipositive state. In aqueous solution it is distinctly more stable than Tl^{III}

$$\mathrm{Tl^{3+}} + 2\,\mathrm{e^-} = \mathrm{Tl^+} \qquad E^\circ = +1.25\ \mathrm{V} \qquad (13\text{-}8.2)$$

The Tl^+ ion is not very sensitive to pH, although the Tl^{3+} ion is extensively hydrolyzed to $TlOH^{2+}$ and the colloidal oxide, even at pH 1–2.5. The redox potential is, hence, very dependent on pH, as well as on the presence of complexing anions. For example, the presence of Cl^- stabilizes Tl^{3+} more (by formation of complexes) than Tl^+, and the potential is thereby lowered.

The colorless Tl^+ ion has a radius of 1.64 Å, comparable to those of K^+, Rb^+, and Ag^+ (1.52, 1.66, and 1.29 Å). Thus it resembles the alkali ions in some ways and the Ag^+ ion in others. It may replace K^+ in certain enzymes and has potential use as a probe for potassium. In crystalline salts, the Tl^+ ion is usually six or eight coordinate. The yellow hydroxide is unstable, giving the black oxide Tl_2O at about 100 °C. The oxide and hydroxide are soluble in water giving strongly basic solutions. These absorb CO_2 from the air, although TlOH is a weaker base than KOH. Many thallium(I) salts (e.g., Tl_2SO_4, Tl_2CO_3, or $TlCO_2CH_3$) have solubilities somewhat lower than those of the corresponding K^+ salts, but otherwise they are similar to and quite often isomorphous with them. Thallium(I) fluoride is soluble in water but the other halides are sparingly soluble. Thallium(I) chloride also resembles AgCl in being photosensitive and darkening on exposure to light, but differs in being insoluble in ammonia. All thallium compounds are exceedingly poisonous.

13-9 Summary of Periodic Trends for the Elements of Group IIIB(13)

By using the list of periodic chemical properties developed in Section 8-11, as well as properties mentioned in Chapters 12 and 13, we can now summarize the periodic trends in the properties of the elements of Group IIIB(13).

1. Boron
    - (a) Forms no simple B^{3+} cation.
    - (b) Forms covalent compounds almost exclusively, and all polyatomic ions have covalent bonds.
    - (c) Obeys the octet rule, the maximum covalence being four.
    - (d) Forms trivalent compounds that readily serve as Lewis acids.

   - (e) Frequently forms polyhedral structures: boranes and borates.
   - (f) Forms an oxide, B_2O_3, and a hydroxide, $B(OH)_3$, both of which are acidic.
   - (g) Forms covalent halides that are readily hydrolyzed.
   - (h) Forms numerous covalent hydrides, all of which are volatile, flammable, and readily hydrolyzed.
   - (i) Forms a stable and important hydride anion, BH_4^-.
2. Aluminum
   - (a) Readily forms an important 3+ ion, because it is electropositive.
   - (b) Is much more metallic than boron, and forms a greater number and variety of ionic substances.
   - (c) Forms both molecular and ionic substances, with coordination numbers of six and higher.
   - (d) Forms two oxides, only one of which is acidic.
   - (e) Forms a hydroxide that is weakly amphoteric, although mostly basic.
   - (f) Forms solid halides that are only partially hydrolyzable.
   - (g) Forms a polymeric hydride.
   - (h) Forms an anionic hydride (AlH_4^-) that is more reactive than BH_4^-.
3. Gallium, Indium, and Thallium
   - (a) Readily give the M^{3+} ion in solution, and have a rich coordination chemistry typical of metals.
   - (b) Form increasingly stable lower valent compounds, especially Tl^+.
   - (c) Increasingly form weaker covalent bonds on descent of the group, enhancing the formation of monovalent compounds.
   - (d) Form MX_3 halides that are increasingly aggregated in the solid state (through halide ion bridges) to give coordination numbers of four, six, and higher.
   - (e) Do not form important EH_4^- anions, except perhaps GaH_4^-.

STUDY GUIDE

Study Questions

A. Review

1. What is bauxite, and how is it purified for Al production?
2. Why is aluminum resistant to air and water, even though it is very electropositive?
3. What are the formulas and structures of (a) corundum, (b) the mineral spinel?
4. What is the structure of the trihalide dimers, M_2X_6? What happens to these molecules at high temperatures?
5. What is an alum? What species are present in a crystalline alum?
6. For cryolite, give the formula, structure, and chief industrial use.
7. Compare the properties of B_2O_3 and Al_2O_3.
8. How is $LiAlH_4$ prepared? Why does it explode with water, while $NaBH_4$ does not?
9. Write equations to show that the hydroxides of Al and Ga are amphoteric.

B. Additional Exercises

1. Discuss the reasons why $Tl^{III}I_3$ is unstable relative to $Tl^{I}I_3$, whereas the opposite is true for Al, Ga, and In.
2. How might one establish that the true nature of "$GaCl_2$" is actually $Ga^{I}[Ga^{III}Cl_4]$?
3. Interaction of Al with alcohols using $HgCl_2$ as a catalyst gives alkoxides of Al that are tetrameric in solution. Write a structure for the aluminum–isopropoxide tetramer.
4. Show, with equations, how $AlCl_3$ functions as a Friedel–Crafts catalyst.
5. Why is the Tl^+/Tl^{3+} electrochemical potential sensitive to pH and to the presence of complexing anions?
6. Explain the preference shown in Table 13-1 of six coordination for fluorides and chlorides versus four coordination for bromides and iodides.
7. Give equations for the following:
   (a) Aluminum chloride plus PF_3.
   (b) Synthesis of $LiAlH_4$ starting with elements only.
   (c) Thermal decomposition of $LiGaH_4$.
   (d) Thermal decomposition of $TlCl_3$.
   (e) Hydrolysis of Al^{3+} salts.
   (f) Hydrolysis of $GaCl_3$.
   (g) Reaction of Al with ethanol.
   (h) Thermal decomposition of Tl_2O_3.
   (i) Reaction of Al_2Cl_6 with $N(CH_3)_3$.
   (j) Amphoteric behavior by aluminum hydroxide (two equations).
   (k) Reduction of $AlCl_3$ by Al, at high temperature.
   (l) Synthesis of $(Me_3N)_2GaH_3$.

C. Questions from the Literature of Inorganic Chemistry

1. Complexes of the type $InCl_3 \cdot 3\,L$ and $TlX_3 \cdot 2\,L$ were studied by B. F. G. Johnson and R. A. Walton, *Inorg. Chem.*, **1966,** *5,* 49–53.
   (a) Write balanced equations for the reactions that were employed in the syntheses of these two types of compounds.
   (b) Suggest a structure for $TlCl_4^-$, for $TlCl_3 \cdot 2$ py, and for $InCl_3 \cdot 3$ py.
2. What evidence do the authors present for the presence of a metal–metal bond in the compound $Ga_2I_4 \cdot 2(\text{diox})$? See J. C. Beamish, R. W. H. Small, and I. J. Worrall, *Inorg. Chem.*, **1979,** *18,* 220–223.
3. Consider the paper by E. R. Alton, R. G. Montemayer, and R. W. Parry, *Inorg. Chem.*, **1974,** *13,* 2267–2270.
   (a) Which of the Lewis bases featured in this study ($:PF_3$, $:PCl_3$, $:C{\equiv}O:$, or $:NH_3$) form complexes with the Lewis acids (i) BF_3 (ii) $AlCl_3$ (iii) $(CH_3)_3Al$?
   (b) What conclusions in reference to σ-base strength do the authors reach for PF_3 versus CO?
   (c) What is the *distortion energy* that the authors mention, and how can this concept be used to explain a higher stability for $F_3P{:}AlCl_3$ than for $F_3P{:}BF_3$?
4. Read about the synthesis of gallane and other materials in the article by A. J. Downs, M. J. Goode, and C. R. Pulham, *J. Am. Chem. Soc.*, **1989,** *111,* 1936–1937.
   (a) How was the starting material $[H_2GaCl]_2$ prepared?
   (b) How was the title compound prepared?
   (c) What reaction takes place between gallane and anhydrous HCl, and how was this

used for analysis of the chemical composition of the title compound?

(d) What is the significance of the fact that the title compound reacts at low temperature with an excess of trimethylamine to give a single product, $(Me_3N)_2GaH_3$?

(e) What compound is obtained from the thermal decomposition of $(Me_3N)_2GaH_3$?

SUPPLEMENTARY READING

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