

to involve the s electrons in bonding is not compensated by the energy released in forming the 2 additional bonds. The argument is difficult to quantify since the requisite energy terms are not known. Thus it is unrealistic to use the simple ionic bond model (p. 79) to calculate the heat of formation of MX_3 because compounds like TlCl_3 are not ionic, i.e. $[\text{Tl}^{3+}(\text{Cl}^-)_3]$ — the energy for the ionization of $\text{M}(\text{g})$ to $\text{M}^{3+}(\text{g})$ is greater than 5000 kJ mol^{-1} for each element and substantial covalent interaction between M^{3+} and X^- would also be expected. In the absence of semi-empirical bond energy data or *ab initio* MO calculations it is only possible to note that the higher oxidation state becomes progressively less stable with respect to the lower oxidation state as atomic number increases within the group. This is seen, for example, by comparing the standard electrode potentials in aqueous solution for M^{III} and M^{I} in Table 7.5. Similarly, from the somewhat fragmentary data available, it appears that the enthalpy of formation of the anhydrous halides remains approximately constant for MX but diminishes irregularly from Al to Tl for MX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The overall result depends not only on the simple Born–Haber terms (p. 82) but also on a combination of several other factors including changes in structure and bond type, covalency effects, enthalpies of hydration, entropy effects, etc., and a quantitative rationalization of all the data has not yet been achieved.

Group 13 metals furnish a good example of the general rule that an element is more electropositive in its lower than in its higher oxidation state: the lower oxide and hydroxide are more basic and the higher oxide and hydroxide more acidic. The reasons for this behaviour are similar to those already discussed when comparing Group 2 with Group 1 (p. 111) and turn on the relative magnitude of ionization energies, cationic size, hydration enthalpy and entropy, etc. Again, the higher the charge on an aquo cation $[\text{M}(\text{H}_2\text{O}_x)]^{n+}$ the more readily will it act as a proton donor (p. 51).

Other group trends will emerge in subsequent sections. However, it is worth noting here an

important vestigial structural relation of these elements to the icosahedral units in elementary boron (p. 142). Thus, the structures of both β -rhombohedral boron and the cubic alloy phase Al_5CuLi_3 can be constructed from 60-vertex truncated icosahedra, although linked in very different ways in the 3-dimensional crystalline lattice. Likewise, Ga_{12} icosahedra have been found in intermetallic phases such as RbGa_7 , CsGa_7 , Li_2Ga_7 , K_3Ga_{13} and $\text{Na}_{22}\text{Ga}_{39}$. This has led to the proposal⁽³⁾ that the Group 13 elements should be given the collective epithet of ‘icosagens’.

7.3 Compounds

7.3.1 Hydrides and related complexes^(4–8)

The extensive covalent cluster chemistry of the boron hydrides finds no parallel with the heavier elements of Group 13. AlH_3 is a colourless, involatile solid which is extensively polymerized via Al–H–Al bonds; it is thermally unstable above $150\text{--}200^\circ$, is a strong reducing agent and reacts violently with water and other protic reagents to liberate H_2 . Several crystalline and amorphous modifications have been described and the structure of $\alpha\text{-AlH}_3$ has been determined by X-ray and neutron diffraction:⁽⁹⁾ each Al is octahedrally surrounded by 6 H atoms at 172 pm and the Al–H–Al angle is 141° . The participation of each Al in 6 bridges, and the equivalence of all

³ R. B. KING, *Inorg. Chim. Acta* **181**, 217–25 (1991).

⁴ E. WIBERG and E. AMBERGER, *Hydrides of the Elements of Main Groups I–IV*, Chaps. 5 and 6, pp. 381–461, Elsevier, Amsterdam, 1971.

⁵ N. N. GREENWOOD Chap. 3 in E. A. V. EBSWORTH, A. G. MADDOCK, and A. G. SHARPE (eds.), *New Pathways in Inorganic Chemistry*, pp. 37–64, Cambridge University Press, Cambridge, 1968.

⁶ A. R. BARRON and G. WILKINSON, *Polyhedron* **5**, 1897–1915 (1986).

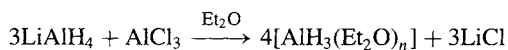
⁷ B. M. BULYCHEV, *Polyhedron* **9**, 387–408 (1990).

⁸ C. JONES, G. A. KOUSATONIS and C. L. RASTON, *Polyhedron* **12**, 1829–48 (1993).

⁹ J. W. TURLEY and H. W. RINN, *Inorg. Chem.* **8**, 18–22 (1969).

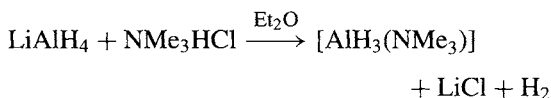
Al–H distances suggests that 3-centre 2-electron bonding occurs as in the boranes (p. 157). The closest Al...Al distance is 324 pm, which is appreciably shorter than in metallic Al (340 pm), but there is no direct metal–metal bonding and the density of AlH₃ (1.477 g cm⁻³) is markedly less than that for Al (2.699 g cm⁻³); this is because in Al metal all 12 nearest neighbours are at 340 pm whereas in AlH₃ there are 6 Al at 324 and 6 at 445 pm.

AlH₃ is best prepared by the reaction of ethereal solutions of LiAlH₄ and AlCl₃ under very carefully controlled conditions:⁽¹⁰⁾



The LiCl is removed and the filtrate, if left at this stage, soon deposits an intractable etherate of variable composition. To avoid this, the solution is worked up with an excess of LiAlH₄ and some added LiBH₄ in the presence of a large excess of benzene under reflux at 76–79°C. Crystals of α-AlH₃ soon form. Slight variations in the conditions lead to other crystalline modifications of unsolvated AlH₃, 6 of which have been identified.

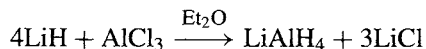
AlH₃ readily forms adducts with strong Lewis bases (L) but these are more conveniently prepared by reactions of the type



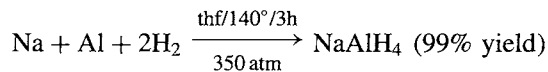
[AlH₃(NMe₃)] has a tetrahedral structure and can take up a further mole of ligand to give [AlH₃(NMe₃)₂]; this was the first compound in which Al was shown to adopt a 5-coordinate trigonal bipyramidal structure⁽¹¹⁾ Such complexes are now of interest since their thermal decomposition can be used to prepare ultra-thin carbon-free Al films by chemical

vapour deposition on GaAs semiconductor devices.⁽¹²⁾

LiAlH₄ is a white crystalline solid, stable in dry air but highly reactive towards moisture, protic solvents, and many organic functional groups. It is readily soluble in ether (~29 g per 100 g at room temperature) and is normally used in this solvent. LiAlH₄ has proved to be an outstandingly versatile reducing agent since its discovery some 50 y ago^(13,14) (see Panel opposite). It can be prepared on the laboratory (and industrial) scale by the reaction



On the industrial (multitonne) scale it can also be prepared by direct high-pressure reaction of the elements or preferably via the intermediate formation of the Na analogue.



The Li salt can then be obtained by metathesis with LiCl in Et₂O. The X-ray crystal structure of LiAlH₄ shows the presence of tetrahedral AlH₄ groups (Al–H 155 pm) bridged by Li in such a way that each Li is surrounded by 4H at 188–200 pm (cf. 204 pm in LiH) and a fifth H at 216 pm. The bonding therefore deviates considerably from the simple ionic formulation Li⁺AlH₄⁻ and there appears to be substantial covalent bonding as found in other complex hydrides (p. 67).

Other complex hydrides of Al are known including Li₃AlH₆, M^IAlH₄ (M^I = Li, Na, K, Cs), M^{II}(AlH₄)₂ (M^{II} = Be, Mg, Ca), Ga(AlH₄)₃, M^I(AlH₃R), M^I(AlH₂R₂), M^I[AlH(OEt)₃], etc. (see Panel). The important complex Al(BH₄)₃ has already been mentioned (p. 169); it is a colourless liquid, mp –64.5°, bp +44.5°. It is best prepared

¹⁰ F. M. BROWER, N. E. MATZEK, P. F. REIGLER, H. W. RINN, C. B. ROBERTS, D. L. SCHMIDT, J. A. SHOVER and K. TERADA, *J. Am. Chem. Soc.* **98**, 2450–3 (1976).

¹¹ G. W. FRASER, N. N. GREENWOOD and B. P. STRAUGHAN, *J. Chem. Soc.* 3742–9 (1963). C. W. HEITSCH, C. E. NORDMAN, and R. W. PARRY, *Inorg. Chem.* **2**, 508–12 (1963).

¹² A. T. S. WEE, A. J. MURRELL, N. K. SINGH, D. O'HARE and J. S. FORD, *J. Chem. Soc., Chem. Commun.*, 11–13 (1990).

¹³ A. E. FINHOLD, A. C. BOND, and H. J. SCHLESINGER, *J. Am. Chem. Soc.* **9**, 1199–203 (1947).

¹⁴ N. G. GAYLORD, *Reduction with Complex Metal Hydrides*, Interscience, New York, 1956, 1046 pp. J. S. PIZEY, *Lithium Aluminium Hydride*, Ellis Horwood, Ltd., Chichester, 1977, 288 pp.

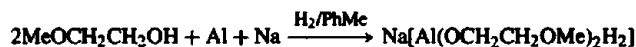
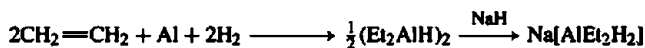
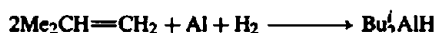
Synthetic Reactions of LiAlH_4 ^(4,14)

LiAlH_4 is a versatile reducing and hydrogenating reagent for both inorganic and organic compounds. With inorganic halides the product obtained depends on the relative stabilities of the corresponding tetrahydroaluminate, hydride and element. For example, BeCl_2 gives $\text{Be}(\text{AlH}_4)_2$, whereas BCl_3 gives B_2H_6 and HgI_2 gives Hg metal. The halides of Cu, Ag, Au, Zn, Cd and Hg give some evidence of unstable hydrido species at low temperatures but all are reduced to the metal at room temperature. The halides of main groups 14 and 15 yield the corresponding hydrides since the AlH_4 derivatives are unstable or non-existent. Thus SiCl_4 , GeCl_4 and SnCl_4 yield MH_4 and substituted halides such as $\text{R}_n\text{SiX}_{4-n}$ give $\text{R}_n\text{SiH}_{4-n}$. Similarly, PCl_3 (and PCl_5), AsCl_3 and SbCl_3 afford MH_3 but BiCl_3 is reduced to the metal. PhAsCl_2 gives PhAsH_2 and Ph_2SbCl gives Ph_2SbH , etc. Less work has been done on oxides but COCl_2 yields MeOH , NO yields hyponitrous acid $\text{HON}=\text{NOH}$ (which can be isolated as the Ag salt), and CO_2 gives $\text{LiAl}(\text{OMe})_4$ or $\text{LiAl}(\text{OCH}_2\text{O})_2$ depending on conditions.

The real importance of LiAlH_4 stems from the applications in organic syntheses. Its commercial introduction dates from 1948. By 1951 the number of functional groups that were known to react was 23 and this rose to more than 60 by the 1970s. Despite this, the heyday of LiAlH_4 seems to have been reached in the late 1960s and it has now been replaced in many systems by the more selective borohydrides (p. 167) or by organometallic hydrides (see below). Reaction is usually carried out in ether solution, followed by hydrolysis of the intermediate so formed when appropriate. Typical examples are listed below.

Compound	Product	Compound	Product
Reactive $>\text{C}=\text{C}<$	$>\text{CH}-\text{CH}<$	RCOSR	RCH_2OH
$\text{RCH}=\text{CH}_2$	$[\text{Al}(\text{CH}_2\text{CH}_2\text{R})_4]^-$	RCSNH_2	RCH_2NH_2
C_2H_2	$[\text{AlH}(\text{CH}=\text{CH}_2)_3]^-$	RSCN	RSH
$\text{RC}\equiv\text{CH}$	$\text{RCH}=\text{CH}_2$	R_2SO	R_2S
RX	RH (not aryl)	R_2SO_2	R_2S
ROH	$[\text{Al}(\text{OR})_4]^-$ or $[\text{AlH}(\text{OR})_3]^-$	RSO_2X	RSH
RCHO	RCH_2OH	$\text{ROSO}_2\text{R}'$, $(\text{ArOSO}_2\text{R}')$	RH , (ArOH)
R_2CO	R_2CHOH	RSO_2H	$\text{RSSR} + \text{RSH}$
Quinone	Hydroquinone	RNC or RNCO	RNHMe
RCO_2H or $(\text{RCO})_2\text{O}$	RCH_2OH	or RNCS	
or RCOX		RCN	RCH_2NH_2 or RCHO
$\text{RCO}_2\text{R}'$	$\text{RCH}_2\text{OH} + \text{R}'\text{OH}$	$\text{R}_2\text{C}=\text{NOH}$	R_2CHNH_2
Lactones, i.e. $\text{O}(\text{CH}_2)_n\text{C}=\text{O}$	Diols, i.e. $\text{HO}(\text{CH}_2)_{n+1}\text{OH}$	R_3NO	R_3N
RCONH_2	RCH_2NH_2 (also 2° , 3°)	R_2NNO	R_2NNH_2
Epoxides $\text{O}(\text{CR}_2)\text{CHR}$	$\text{R}_2\text{C}(\text{OH})\text{CH}_2\text{R}$	RNO_2 , RNHOH or RN_3	RNH_2
SCR_2-CR_2	$\text{R}_2\text{C}(\text{SH})\text{CHR}_2$	ArNO_2	$\text{ArN}=\text{NAr}$
RSSR	RSH		

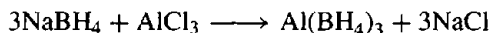
More recently, LiAlH_4 has been eclipsed as an organic reducing agent by the emergence of several cheaper organo-aluminium hydrides which are also safer and easier to handle than LiAlH_4 . Pre-eminent among these are Bu_2AlH and $\text{Na}[\text{AlEt}_2\text{H}_2]$ which were introduced commercially in the early 1970s and $\text{Na}[\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})_2\text{H}_2]$, VTRIDE[®], which became available in bulk during 1979. All three reagents can be prepared directly:



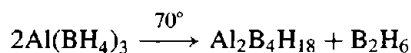
All three are substantially cheaper than LiAlH_4 and are now produced on a far larger scale as indicated in the table overleaf. Data refer to US industrial use in 1980 and even larger markets are available outside the chemical industry (e.g. in polymerization catalysis).

Compound	Production/kg	Price/\$ kg ⁻¹	\$ per kg 'H'
LiAlH ₄	6 000	88.00	835.00
Bu ₂ AlH	195 000	5.10	715.00
Na[AlEt ₂ H ₂]	91 000	11.00	605.00
Na[Al(OCH ₂ CH ₂ OMe) ₂ H ₂]	123 000	6.25	638.00

in the absence of solvent by the reaction



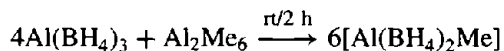
Al(BH₄)₃ was the first fluxional compound to be recognized as such (1955) and its thermal decomposition led to a new compound which was the first to be discovered and structurally characterized by means of nmr:



This binuclear complex is also fluxional and has the structure shown in Fig. 7.4a. Al(BH₄)₃ reacts readily with NMe₃ to give a 1:1 adduct in which Al adopts the unusual pentagonal bipyramidal

bipyramidal 7-fold coordination as shown in Fig. 7.4b.⁽¹⁵⁾

At room temperature Al(BH₄)₃ reacts quantitatively in the gas phase with Al₂Me₆ (p. 259) to give [Al(η²-BH₄)₂Me] (mp -76°) in which one of the BH₄ groups of the parent compound has been replaced by a Me group:



Electron diffraction studies in the gas phase reveal an unusual structure in which the 5-coordinate Al atom has square-pyramidal

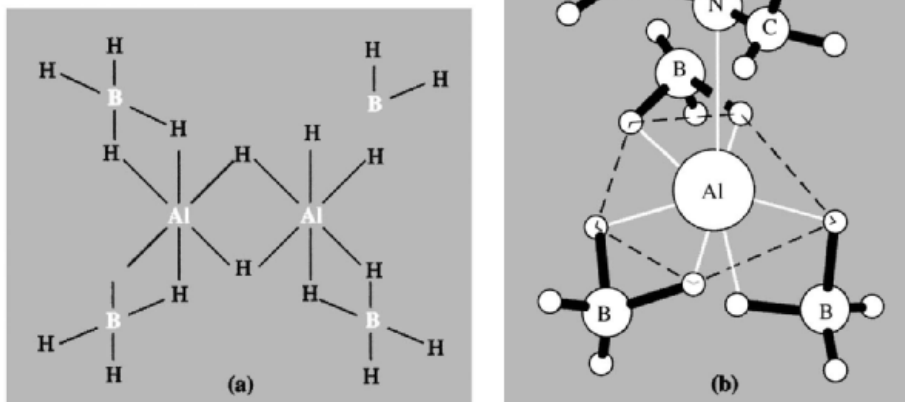


Figure 7.4 (a) Structure of Al₂B₄H₁₈ showing 6-coordinate Al, (b) Structure of the adduct Me₃N·Al(BH₄)₃ showing 7-coordinate pentagonal bipyramidal Al.

¹⁵ N. A. BAILEY, P. H. BIRD and M. G. H. WALLBRIDGE, *Chem. Commun.*, 286-7 (1966); *Inorg. Chem.* 7, 1575-81 (1968).

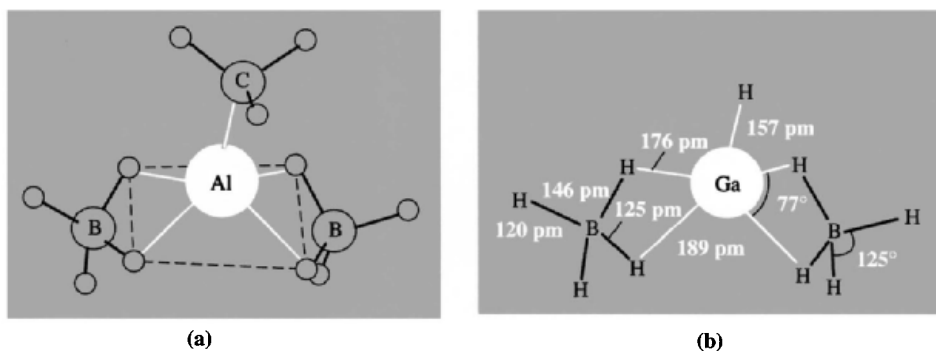


Figure 7.5 (a) Structure of $[\text{MeAl}(\eta^2\text{-BH}_4)_2]$ as revealed by electron diffraction, and (b) structure and key dimensions of $[\text{HGa}(\eta^2\text{-BH}_4)_2]$ as determined by low temperature X-ray diffractometry.

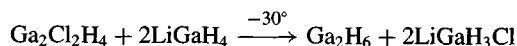
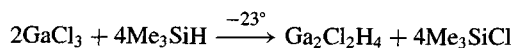
geometry (Fig. 7.5a).⁽¹⁶⁾ The heavy atoms CAIB_2 are coplanar and the symmetry is close to C_{2v} . A similar structure (Fig. 7.5b) has been found by X-ray diffraction for $[\text{Ga}(\eta^2\text{-BH}_4)_2\text{H}]$, which was prepared by the dry reaction of LiBH_4 and GaCl_3 at -45°C ,⁽¹⁷⁾ and this geometry is emerging as a notable structural feature of many AlH_4^- complexes (see next paragraph).

Many complexes in which AlH_4^- acts as a dihapto (or bridging bis-dihapto) ligand to transition metals have recently been characterized. These are usually stabilized by coligands such as tertiary phosphines or η^5 -cyclopentadienyls and are readily prepared by treating the corresponding chloro-complexes with LiAlH_4 in ether. Typical examples, frequently dimeric, are:⁽⁶⁾ $[\{(\text{C}_5\text{H}_5)_2\text{Y}(\text{AlH}_4\cdot\text{thf})\}_2]$, $[\{(\text{C}_5\text{Me}_5)_2\text{Ti}(\text{AlH}_4)\}_2]$ (Fig. 7.6a), $[\{(\text{C}_5\text{Me}_5)_2\text{Ta}(\text{AlH}_4)\}_2]$, $[\{(\text{PMe}_3)_3\text{-H}_3\text{W}\}_2\text{-}\mu\text{-(}\eta^2, \eta^2\text{-AlH}_5\text{)}]$ (Fig. 7.6b), $[\{(\text{dmpe})_2\text{-Mn}(\text{AlH}_4)\}_2]$ and $[\{(\text{PPH}_3)_3\text{HRu}(\text{AlH}_4)\}_2]$. A few transition metal tetrahydroaluminates $[\text{M}(\text{AlH}_4)_n]$ are also known but their structures have not yet been determined by X-ray crystallography, e.g.:⁽⁶⁾ $[\text{Y}(\text{AlH}_4)_3]$, $[\text{Ti}(\text{AlH}_4)_4]$, $[\text{Nb}(\text{AlH}_4)_5]$ and $[\text{Fe}(\text{AlH}_4)_2]$.

¹⁶ M. T. BARLOW, C. J. DAIN, A. J. DOWNS, P. D. P. THOMAS and D. W. H. RANKIN, *J. Chem. Soc., Dalton Trans.*, 1374–8 (1980). See also A. J. DOWNS and L. A. JONES, *Polyhedron* **13**, 2401–15 (1994) for a description of the polymeric Al analogue, $[\text{Al}(\text{BH}_4)_2\text{H}]$.

¹⁷ M. T. BARLOW, C. J. DAIN, A. J. DOWNS, G. S. LAUREN-SON and D. W. H. RANKIN, *J. Chem. Soc., Dalton Trans.*, 597–602 (1982).

The synthesis and characterization of gallane, the binary hydride of gallium, has proved even more elusive than that of alane, AlH_3 . Success was finally achieved^(18,19) by first preparing dimeric monochlorogallane, $\{\text{H}_2\text{Ga}(\mu\text{-Cl})\}_2$,⁽²⁰⁾ and then reducing a freshly prepared sample of this liquid with freshly prepared LiGaH_4 under solvent-free conditions in an all-glass apparatus at -30°C :



The volatile product, obtained in about 5% yield, condensed as a white solid at -50° and had a vapour pressure of about 1 mmHg at -63° . Gallane decomposes into its elements at ambient temperatures. In the vapour phase it has a diborane-like structure, Ga_2H_6 , with Ga-H_t 152 pm, Ga-H_μ 171 pm, $\text{Ga}\cdots\text{Ga}$ 258 pm and angle GaHGa 98° (electron diffraction).⁽¹⁹⁾ In the solid state gallane tends to aggregate via Ga-H-Ga bonds to give $(\text{GaH}_3)_n$ with n , perhaps equal to 4 but, in contrast to the structure

¹⁸ A. J. DOWNS, M. J. GOODE and C. R. PULHAM, *J. Am. Chem. Soc.* **111**, 1936–7 (1989).

¹⁹ C. R. PULHAM, A. J. DOWNS, M. J. GOODE, D. W. H. RANKIN and H. E. ROBERTSON, *J. Am. Chem. Soc.* **113**, 5149–62 (1991).

²⁰ M. J. GOODE, A. J. DOWNS, C. R. PULHAM, D. W. H. RANKIN and H. E. ROBERTSON, *J. Chem. Soc., Chem. Commun.*, 768–9 (1988).

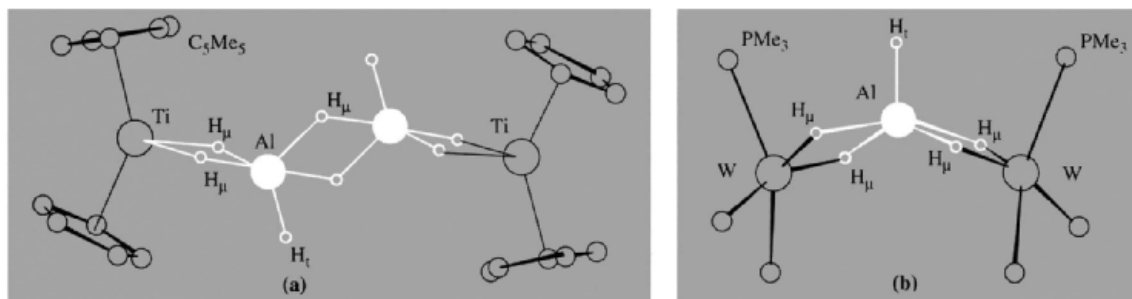
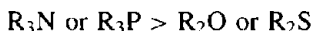
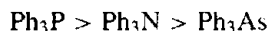
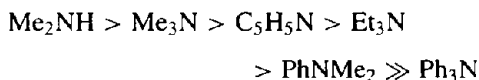


Figure 7.6 (a) The structure of $[\{(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\mu\text{-H})_2\text{Al}(\text{H}_t(\mu\text{-H}))_2\}]_2$; the Me groups have been omitted for clarity. (b) The structure of $[\{(\text{PMe}_3)_3\text{H}_3\text{W}\}_2-\mu\text{-}(\eta^2, \eta^2\text{-AlH}_5)]$; the Me groups have been omitted for clarity and the three H atoms on each W were not located with certainty.

of $\alpha\text{-AlH}_3$ (p. 227), some terminal Ga– H_t bonds remain.

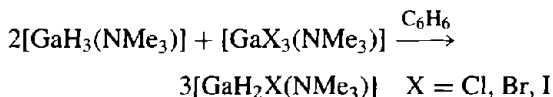
The known reactions of gallane appear mostly to parallel those of diborane (p. 165). Thus, at -95° , NH_3 causes unsymmetrical cleavage to give $[\text{H}_2\text{Ga}(\text{NH}_3)_2]^+[\text{GaH}_4]^-$ whereas NMe_3 effects symmetrical cleavage to give $\text{Me}_3\text{N}\cdot\text{GaH}_3$ or $(\text{Me}_3\text{N})_2\text{GaH}_3$ according to the amount used.⁽¹⁹⁾ These last two adducts were already well known. $\text{Me}_3\text{N}\cdot\text{GaH}_3$ can readily be prepared as a colourless crystalline solid, mp 70.5° , by the reaction of ethereal solutions of LiGaH_4 and Me_3NHCl .⁽²¹⁾ It is one of the most stable complexes of GaH_3 and, like its Al analogue, can take up a further mole of ligand to give the trigonal bipyramidal 2:1 complex.⁽²²⁾ Numerous other complexes have been prepared and the stabilities of the 1:1 adducts decrease in the following sequences:⁽⁵⁾



²¹ N. N. GREENWOOD, A. STORR and M. G. H. WALLBRIDGE, *Proc. Chem Soc.* 249 (1962).

²² N. N. GREENWOOD, A. STORR and M. G. H. WALLBRIDGE, *Inorg. Chem.* 2, 1036–9 (1963). D. F. SHRIVER and R. W. PARRY, *Inorg. Chem.* 2, 1039–42 (1963).

Complexes of the type $[\text{GaH}_2\text{X}(\text{NMe}_3)]$ and $[\text{GaHX}_2(\text{NMe}_3)]$ are readily prepared by reaction of HCl or HBr on the GaH_3 complex at low temperatures or by reactions of the type



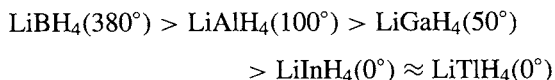
The relative stabilities of these various complexes can be rationalized in terms of the factors discussed on p. 198. A few mixed hydrides have also been characterized, e.g. galladiborane, $\text{H}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$,⁽²³⁾ and *arachno*-2-gallatettraborane(10), $\text{H}_2\text{GaB}_3\text{H}_8$,⁽²⁴⁾ as well as derivatives such as tetramethyldigallane, $\text{Me}_2\text{Ga}(\mu\text{-H})_2\text{GaMe}_2$.⁽²⁵⁾

InH_3 and TlH_3 appear to be too unstable to exist in the uncoordinated state though they may have transitory existence in ethereal solutions at low temperatures. A similar decrease in thermal stability is noted for the tetrahydro complexes; e.g. the temperature at which the Li salts decompose rapidly, follows the sequence

²³ C. R. PULHAM, P. T. BRAIN, A. J. DOWNS, D. W. H. RANKIN and H. E. ROBERTSON, *J. Chem. Soc., Chem. Commun.*, 177–8 (1990).

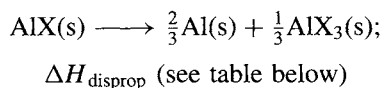
²⁴ C. R. PULHAM, A. J. DOWNS, D. W. H. RANKIN and H. E. ROBERTSON, *J. Chem. Soc., Chem. Commun.*, 1520–1 (1990). B. J. DUKE and H. F. SCHAEFER, *J. Chem. Soc., Chem. Commun.*, 123–4 (1991).

²⁵ P. L. BAXTER, A. J. DOWNS, M. J. GOODE, D. W. H. RANKIN and H. E. ROBERTSON, *J. Chem. Soc., Chem. Commun.*, 805–6 (1986).



7.3.2 Halides and halide complexes

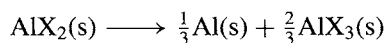
Several important points emerge in considering the wide range of Group 13 metal halides and their complexes. Monohalides are known for all 4 metals with each halogen though for Al they occur only as short-lived diatomic species in the gas phase or as cryogenically isolated solids. This may seem paradoxical, since the bond dissociation energies for Al–X are substantially greater than for the corresponding monohalides of the other elements and fall in the range 655 kJ mol⁻¹ (AlF) to 365 kJ mol⁻¹ (AlI). The corresponding values for the gaseous TlX decrease from 460 to 270 kJ mol⁻¹ yet it is these latter compounds that form stable crystalline solids. In fact, the instability of AlX in the condensed phase at normal temperatures is due not to the weakness of the Al–X bond but to the ready disproportionation of these compounds into the even more stable AlX₃:



The reverse reaction to give the gaseous species AlX(g) at high temperature accounts for the enhanced volatility of AlF₃ when heated in the presence of Al metal, and the ready volatilization of Al metal in the presence of AlCl₃. Using calculations of the type outlined on p. 82 the standard heats of formation of the crystalline monohalides AlX and their heats of disproportionation have been estimated as:

Compound (s)	AlF	AlCl	AlBr	AlI
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	-393	-188	-126	-46
$\Delta H_{\text{disprop}}^\circ/\text{kJ mol}^{-1}$	-105	-46	-50	-59

The crystalline dihalides AlX₂ are even less stable with respect to disproportionation, value of $\Delta H_{\text{disprop}}$ falling in the range -200 to -230 kJ mol⁻¹ for the reaction



Very recently the first AlII compound to be stable at room temperature, the tetrameric complex [AlII(NEt₃)₄], has been prepared and shown to feature a planar Al₄ ring with Al–Al 265 pm, Al–I 265 pm and Al–N 207 pm.^(25a)

Aluminium trihalides

AlF₃ is made by treating Al₂O₃ with HF gas at 700° and the other trihalides are made by the direct exothermic combination of the elements. AlF₃ is important in the industrial production of Al metal (p. 219) and is made on a scale approaching 700 000 tonnes per annum world wide. AlCl₃ finds extensive use as a Friedel–Crafts catalyst (p. 236): its annual production approaches 100 000 tpa and is dominated by Western Europe, USA and Japan. The price for bulk AlCl₃ is about \$0.35/kg.

AlF₃ differs from the other trihalides of Al in being involatile and insoluble, and in having a much greater heat of formation (Table 7.6). These differences probably stem from differences in coordination number (6 for AlF₃; change from 6 to 4 at mp for AlCl₃; 4 for AlBr₃ and AlI₃) and from the subtle interplay of a variety of other factors mentioned below, rather than from any discontinuous change in bond type between the fluoride and the other halides. Similar differences dictated by change in coordination number are noted for many other metal halides, e.g. SnF₄ and SnX₄ (p. 381), BiF₃ and BiX₃ (p. 559), etc., and even more dramatically for some oxides such as CO₂ and SiO₂. In AlF₃ each Al is surrounded by

Table 7.6 Properties of crystalline AlX₃

Property	AlF ₃	AlCl ₃	AlBr ₃	AlI ₃
MP/°C	1290	192.4	97.8	189.4
Sublimation pt (1 atm)/°C	1272	180	256	382
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	1498	707	527	310

^{25a}A. ECKER and H.-G. SCHNÖCKEL, *Z. anorg. allg. Chem.* **622**, 149–52 (1996).

a distorted octahedron of 6 F atoms and the 1:3 stoichiometry is achieved by the corner sharing of each F between 2 octahedra. The structure is thus related to the ReO_3 structure (p. 1047) but is somewhat distorted from ideal symmetry for reasons which are not understood. Maybe the detailed crystal structure data are wrong.⁽²⁶⁾ The relatively "open" lattice of AlF_3 provides sites for water molecules and permits the formation of a range of nonstoichiometric hydrates. In addition, well-defined hydrates $\text{AlF}_3 \cdot n\text{H}_2\text{O}$ ($n = 1, 3, 9$) are known but, curiously, no hexahydrate corresponding to the familiar $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$. In the gas phase at 1000°C the AlF_3 molecule has trigonal planar symmetry (D_{3h})⁽²⁷⁾ with Al–F 163.0(3) pm which is considerably shorter than in the solid phase 170–190 pm (for 6-coordinate Al).

The complex fluorides of Al^{III} (and Fe^{III}) provide a good example of a family of structures with differing stoichiometries all derived by the sharing of vertices between octahedral $\{\text{AlF}_6\}$ units;⁽²⁶⁾ edge sharing and face sharing are not observed, presumably because of the destabilizing influence of the close (repulsive) approach of 2 Al atoms each of which carries a net partial positive charge. Discrete $\{\text{AlF}_6\}$ units occur in cryolite, Na_3AlF_6 , and in the garnet structure $\text{Li}_3\text{Na}_3\text{Al}_2\text{F}_{12}$ (i.e. $[\text{Al}_2\text{Na}_3(\text{LiF}_4)_3]$, see p. 348) but it is misleading to think in terms of $[\text{AlF}_6]^{3-}$ ions since the Al–F bonds are not appreciably different from the other M–F bonds in the structure. Thus the Na_3AlF_6 structure is closely related to perovskite ABO_3 (p. 963) in which one-third of the Na and all the Al atoms occupy octahedral $\{\text{MF}_6\}$ sites and the remaining two-thirds of the Na occupy the 12-coordinate sites. When two opposite vertices of $\{\text{AlF}_6\}$ are shared the stoichiometry becomes $\{\text{AlF}_5\}$ as in $\text{Ti}_2^{\text{I}}\text{AlF}_5$ (and $\text{Ti}_2^{\text{I}}\text{GaF}_5$). The sharing of 4 equatorial vertices of $\{\text{AlF}_6\}$ leads to the stoichiometry $\{\text{AlF}_4\}$ in $\text{Ti}^{\text{I}}\text{AlF}_4$. The same structural motif is found in each of

the "isoelectronic" 6-coordinate layer lattices of $\text{K}_2\text{Mg}^{\text{II}}\text{F}_4$, $\text{KAl}^{\text{III}}\text{F}_4$ and $\text{Sn}^{\text{IV}}\text{F}_4$, none of which contain tetrahedral $\{\text{MF}_4\}$ units.

More complex patterns of sharing give intermediate stoichiometries as in $\text{Na}_5\text{Al}_3\text{F}_{14}$ which features layers of $\{\text{Al}_3\text{F}_{14}^{5-}\}$ built up by one-third of the $\{\text{AlF}_6\}$ octahedra sharing 4 equatorial vertices and the remainder sharing 2 opposite vertices. Again, $\text{Na}_2\text{MgAlF}_7$ comprises linked $\{\text{AlF}_6\}$ and $\{\text{MgF}_6\}$ octahedra in which 4 vertices of $\{\text{AlF}_6\}$ and all vertices of $\{\text{MgF}_6\}$ are shared. Likewise, $\text{Sm}^{\text{II}}\text{AlF}_5$ features $\{\text{Al}_2\text{F}_{10}^{4-}\}$ bioctahedra and linear chains of *trans* corner-sharing $\{\text{AlF}_6\}$,⁽²⁸⁾ and $\text{Ba}_3\text{Al}_2\text{F}_{12}$ has a tetrameric $\{(\text{F}_4\text{AlF}_{2/2})_4^{8-}\}$ ring, i.e. $[\text{Ba}_6\text{F}_4(\text{Al}_4\text{F}_{20})]$,⁽²⁹⁾ which is unique for fluorometallates, being previously encountered only in neutral molecules $(\text{MF}_5)_4$ where M is Nb, Ta (p. 990); Mo, W (p. 1020); Ru, Os (p. 1083). In all of these structures the degree of charge separation, though considerable, is unlikely to approach the formal group charges: thus AlF_3 should not be regarded as a network of alternating ions Al^{3+} and F^- nor, at the other extreme, as an alternating set of Al^{3+} and AlF_6^{3-} , and lattice energies calculated on the basis of such formal charges placed at the observed interatomic distances are bound to be of limited reliability. Equally, the structure is not well described as a covalently bonded network of Al atoms and F atoms, and detailed MO calculations would be required to assess the actual extent of charge separation, on the one hand, and of interatomic covalent bonding, on the other.

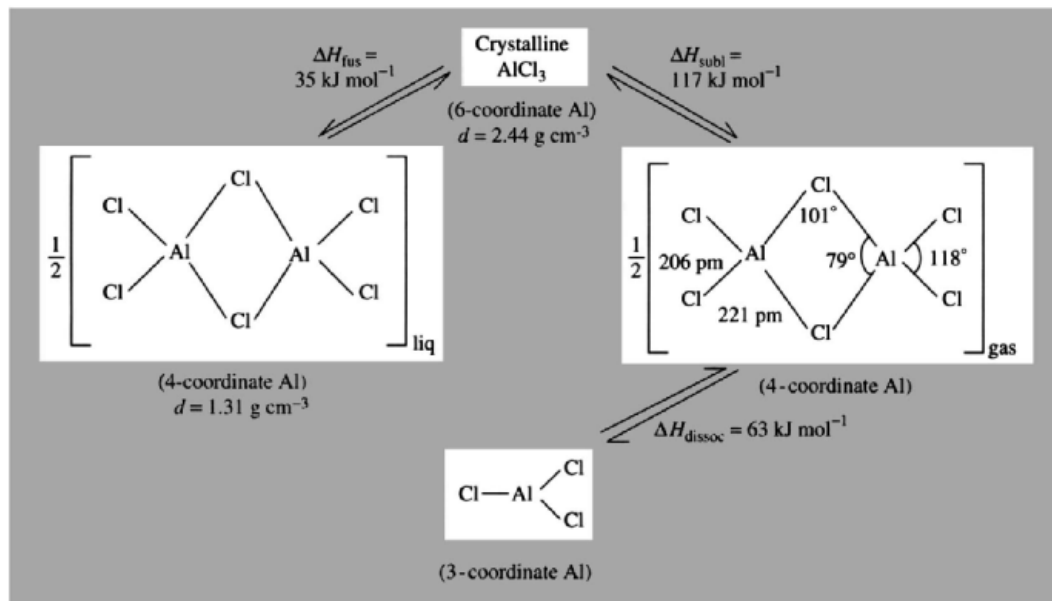
The structure of AlCl_3 is similarly revealing. The crystalline solid has a layer lattice with 6-coordinate Al but at the mp 192.4° the structure changes to a 4-coordinate molecular dimer Al_2Cl_6 ; as a result there is a dramatic increase in volume (by 85%) and an even more dramatic drop in electrical conductivity almost to zero. The mp therefore represents a substantial change in the nature of the bonding. The covalently bonded

²⁶ A. F. WELLS, *Structural Inorganic Chemistry*, 4th edn., Oxford University Press, Oxford, 1975, 1095 pp.

²⁷ M. HARGITTAI, M. KOLONITS, J. TREMMEL, J.-L. FOURQUET and G. FERREY, *Struct. Chem.* **1**, 75–8 (1989).

²⁸ J. KÖHLER, *Z. anorg. allg. Chem.* **619**, 181–8 (1993).

²⁹ R. DOMESLE and R. HOPPE, *Angew. Chem. Int. Edn. Engl.* **19**, 489–90 (1980).



molecular dimers are also the main species in the gas phase at low temperatures ($\sim 150\text{--}200^\circ$) but at higher temperature there is an increasing tendency to dissociate into trigonal planar AlCl_3 molecules isostructural with BX_3 (p. 196).

By contrast, Al_2Br_6 and Al_2I_6 form dimeric molecular units in the crystalline phase as well as in the liquid and gaseous states and fusion is not attended by such extensive changes in properties. In the gas phase $\Delta H_{\text{dissoc}} = 59 \text{ kJ mol}^{-1}$ for AlBr_3 and 50 kJ mol^{-1} for AlI_3 . In all these dimeric species, as in the analogous dimers Ga_2Cl_6 , Ga_2Br_6 , Ga_2I_6 and In_2I_6 , the $\text{M}\text{--}\text{X}_\tau$ distance is $10\text{--}20 \text{ pm}$ shorter than the $\text{M}\text{--}\text{X}_\mu$ distance; the external angle $\text{X}_\tau\text{MX}_\tau$ is in the range $110\text{--}125^\circ$ whereas the internal angle $\text{X}_\mu\text{MX}_\mu$ is in the range $79\text{--}102^\circ$.

The trihalides of Al form a large number of addition compounds or complexes and these have been extensively studied because of their importance in understanding the nature of Friedel–Crafts catalysis.^(30,31) The adducts vary enormously in stability from weak interactions to very stable complexes, and they also vary widely in their mode of bonding, structure and

properties. Aromatic hydrocarbons and olefins interact weakly though in some cases crystalline adducts can be isolated, e.g. the clathrate-like complex $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_6$, mp 37° (decomp). With mesitylene ($\text{C}_6\text{H}_3\text{Me}_3$) and the xylenes ($\text{C}_6\text{H}_4\text{Me}_2$) the interaction is slightly stronger, leading to dissociation of the dimer and the formation of weak monomeric complexes AlBr_3L both in solution and in the solid state. At the other end of the stability scale NMe_3 forms two crystalline complexes: $[\text{AlCl}_3(\text{NMe}_3)]$ mp 156.9° which features molecular units with 4-coordinate tetrahedral Al, and $[\text{AlCl}_3(\text{NMe}_3)_2]$ which has 5-coordinate Al with trigonal bipyramidal geometry and *trans* axial ligands. By contrast, the adduct $\text{AlCl}_3 \cdot 3\text{NH}_3$ has been shown by X-ray diffraction analysis to consist of elongated octahedra $[\text{AlCl}_2(\text{NH}_3)_4]^+$ and compressed octahedra $[\text{AlCl}_4(\text{NH}_3)_2]^-$, the

³⁰ N. N. GREENWOOD and K. WADE, Chap. 7 in G. A. OLAH (ed.), *Friedel–Crafts and Related Reactions*, Vol. 1, pp. 569–622, Interscience, New York, 1963.

³¹ K. WADE and A. J. BANISTER, Chap. 12 in *Comprehensive Inorganic Chemistry*, Vol. 1, pp. 993–1172, Pergamon Press, Oxford, 1973.

arrangement being further stabilized by a network of N-H...Cl hydrogen bonds.⁽³²⁾

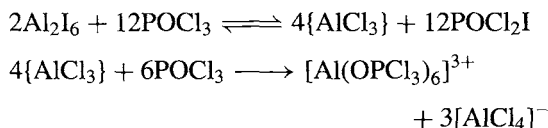
Alkyl halides interact rather weakly and vibrational spectroscopy suggests bonding of the type R-X...AlX₃. However, for readily ionizable halides such as Ph₃CCl the degree of charge separation is much more extensive and the complex can be formulated as Ph₃C⁺AlCl₄⁻. Acyl halides RCOX may interact either through the carbonyl oxygen, PhC(Cl)=O→AlCl₃, or through the halogen, RCOX...AlX₃ or RCO⁺AlX₄⁻. Again, vibrational spectroscopy is a sensitive, though not always reliable, diagnostic for the mode of bonding. X-ray crystal structures of several complexes have been obtained but these do not necessarily establish the predominant species in nonaqueous solvents because of the delicate balance between the various factors which determine the structure (p. 198). Even in the crystalline state the act of coordination may lead to substantial charge separation. For example, X-ray analysis has established that AlCl₃ICl₃ comprises chains of alternating units which are best described as ICl₂⁺ and AlCl₄⁻ with rather weaker interactions between the ions.

Another instructive example is the ligand POCl₃ which forms 3 crystalline complexes AlCl₃POCl₃ mp 186.5°, AlCl₃(POCl₃)₂ mp 164° (d), and AlCl₃(POCl₃)₆ mp 41° (d). Although the crystal structures of these adducts have not been established it is known that POCl₃ normally coordinates through oxygen rather than chlorine and very recently a Raman spectroscopic study of the 1:1 adduct in the gas phase suggests that it is indeed Cl₃P=O→AlCl₃ with C_s symmetry.⁽³³⁾ Also consistent with oxygen ligation is the observation that there is no exchange of radioactive ³⁶Cl when AlCl₃ containing ³⁶Cl is dissolved in inactive POCl₃. However, such solutions are good electrical conductors and spectroscopy reveals AlCl₄⁻ as a predominant solute species. The resolution of this apparent paradox was provided by means

of ²⁷Al nmr spectroscopy⁽³⁴⁾ which showed that ionization occurred according to the reaction

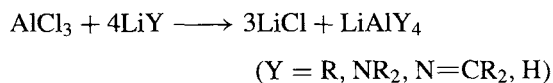
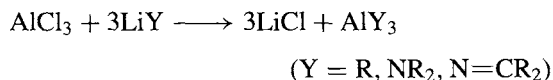


It can be seen that all the Cl atoms in [AlCl₄]⁻ come from the AlCl₃. It was further shown that the same two species predominated when Al₂I₆ was dissolved in an excess of POCl₃:



No mixed Al species were found by ²⁷Al nmr in this case.

AlCl₃ is a convenient starting material for the synthesis of a wide range of other Al compounds, e.g.:



Similarly, NaOR reacts to give Al(OR)₃ and NaAl(OR)₄. AlCl₃ also converts non-metal fluorides into the corresponding chloride, e.g.



This type of transhalogenation reaction, which is common amongst the halides of main group elements, always proceeds in the direction which pairs the most electropositive element with the most electronegative, since the greatest amount of energy is evolved with this combination.⁽³⁵⁾

The major industrial use of AlCl₃ is in catalytic reactions of the type first observed in 1877 by C. Friedel and J. M. Crafts. AlCl₃ is now extensively used to effect alkylations (with RCl, ROH or RCH=CH₂), acylations (with RCOCl), and

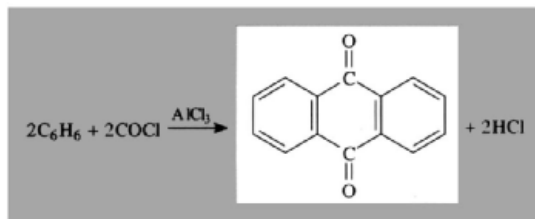
³² H. JACOBS and B. NÖCKER, *Z. anorg. allg. Chem.* **619**, 73-6 (1993).

³³ S. BOGHOSIAN, D. A. KARYDIS and G. A. VOYIATZIS, *Polyhedron* **12**, 771-82 (1993).

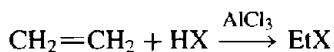
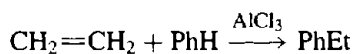
³⁴ R. G. KIDD and D. R. TRUAX, *J. Chem. Soc., Chem. Commun.*, 160-1 (1969).

³⁵ F. SEEL, *Atomic Structure and Chemical Bonding*, 4th edn. translated and revised by N. N. GREENWOOD and H. P. STADLER, Methuen, London, 1963, pp. 83-4.

various condensation, polymerization, cyclization, and isomerization reactions.⁽³⁶⁾ The reactions are examples of the more general class of electrophilic reactions that are catalysed by metal halides and other Lewis acids (electron pair acceptors). Of the 30 000 tonnes of AlCl_3 produced annually in the USA, about 15% is used in the synthesis of anthraquinones for the dyestuffs industry:



A further 15% of the AlCl_3 is used in the production of ethyl benzene for styrene manufacture, and 13% in making EtCl or EtBr (for PbEt_4):

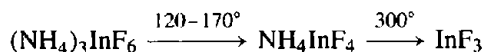


The isomerization of hydrocarbons in the petroleum industry and the production of dodecyl benzene for detergents accounts for a further 10% each of the AlCl_3 used.

Trihalides of gallium, indium and thallium

These compounds have been mentioned several times in the preceding sections. As with AlX_3 (p. 233), the trifluorides are involatile and have much higher mps and heats of formation than the other trihalides;⁽³¹⁾ e.g. GaF_3 melts above 1000° , sublimes at $\sim 950^\circ$ and has the 6-coordinate FeF_3 -type structure, whereas GaCl_3 melts at 77.8° , boils at 201.2° , and has the 4-coordinate molecular structure Ga_2Cl_6 . GaF_3 and

InF_3 are best prepared by thermal decomposition of $(\text{NH}_4)_3\text{MF}_6$, e.g.:



Preparations using aqueous HF on $\text{M}(\text{OH})_3$, M_2O_3 , or M metal give the trihydrate. TlF_3 is best prepared by the direct fluorination of Tl_2O_3 with F_2 , BrF_3 or SF_4 at 300° . Trends in the heats of formation of the Group 13 trihalides show the same divergence from BX_3 , AlX_3 and the Group 3 trihalides as was found for trends in other properties such as I_M , E° and χ (pp. 223–5) and for the same reasons. For example, the data for ΔH_f° for the trifluorides and tribromides are compared in Fig. 7.7 from which it is clear that the trend noted for the sequence B, Al, Sc, Y, La, Ac is not followed for the Group 13 metal trihalides which become progressively less stable from Al to Tl.

The volatile trihalides MX_3 form several ranges of addition compounds MX_3L , MX_3L_2 , MX_3L_3 , and these have been extensively studied because of the insight they provide on the relative influence of the underlying d^{10} electron configuration on the structure and stability of the complexes. With halide ions X^- as ligands the stoichiometry depends sensitively on crystal lattice effects or on the nature of the solvent and the relative concentration of the species in solution. Thus X-ray studies have established the tetrahedral ions $[\text{GaX}_4]^-$, $[\text{InCl}_4]^-$, etc., and these persist in ethereal

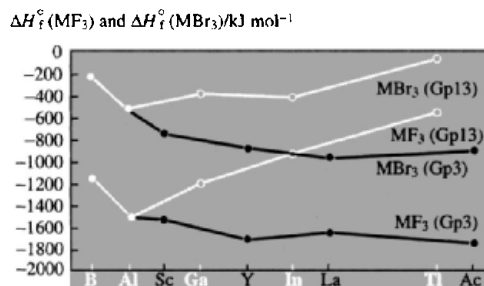


Figure 7.7 Trends in the standard enthalpies of formation ΔH_f° for Groups 3 and 13 trihalides as illustrated by data for MF_3 and MB_3 .

³⁶ G. A. OLAH (ed.), *Friedel-Crafts and Related Reactions*, Vols. 1–4, Interscience, New York, 1963. See especially Chap. 1, Historical, by G. A. OLAH and R. E. A. DEAR, and Chap. 2, Definition and scope by G. A. OLAH.

solution, though in aqueous solution $[\text{InCl}_4]^-$ loses its T_d symmetry due to coordination of further molecules of H_2O . $[\text{NEt}_4]_2[\text{InCl}_5]$ is remarkable in featuring a square-pyramidal ion of C_{4v} symmetry (Fig. 7.8) and was one of the first recorded examples of this geometry in nontransition element chemistry (1969), cf SbPh_5 on p. 598 and the hydrido aluminate species on p. 231. The structure is apparently favoured by electrostatic packing considerations though it also persists in nonaqueous solution, possibly due to the formation of a pseudo-octahedral solvate $[\text{InCl}_5\text{S}]^{2-}$. It will be noted that $[\text{InCl}_5]^{2-}$ is not isostructural with the isoelectronic species SnCl_5^- and SbCl_5 which have the more common D_{3h} symmetry. Substituted 5-coordinate chloroderivatives of In^{III} and Tl^{III} often have geometries intermediate between square pyramidal and trigonal bipyramidal.⁽³⁷⁾

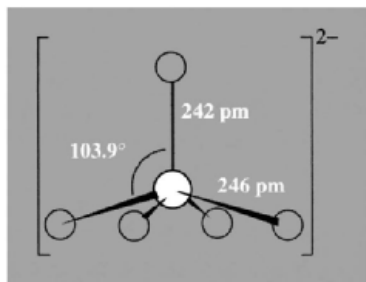
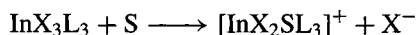


Figure 7.8 The structure of $[\text{InCl}_5]^{2-}$ showing square-pyramidal (C_{4v}) geometry. The $\text{In}-\text{Cl}_{\text{apex}}$ distance is significantly shorter than the $\text{In}-\text{Cl}_{\text{base}}$ distances and In is 59 pm above the basal plane; this leads to a $\text{Cl}_{\text{apex}}-\text{In}-\text{Cl}_{\text{base}}$ angle of 103.9° which is very close to the theoretical value required to minimize $\text{Cl}\cdots\text{Cl}$ repulsions whilst still retaining C_{4v} symmetry (103.6°) calculated on the basis of a simple inverse square law for repulsion between ligands. $[\text{NEt}_4]_2[\text{TlCl}_5]$ is isomorphous with $[\text{NEt}_4]_2[\text{InCl}_5]$ and presumably has a similar structure for the anion.

³⁷ R. O. DAY and R. R. HOLMES, *Inorg. Chem.* **21**, 2379–82 (1982). H. BORGHOLTE, K. DEHNICKE, H. GOESMANN and D. FENSKE, *Z. anorg. allg. Chem.* **600**, 7–14 (1991).

With neutral ligands, L, GaX_3 tend to resemble AlX_3 in forming predominantly MX_3L and some MX_3L_2 , whereas InX_3 are more varied.⁽³⁸⁾ InX_3L_3 is the commonest stoichiometry for N and O donors and these are probably predominantly 6-coordinate in the solid state, though in coordinating solvents (S) partial dissociation into ions frequently occurs:



More extensive ionization occurs if, instead of the halides X^- , a less strongly coordinating anion Y^- such as ClO_4^- or NO_3^- is used; in such cases the coordinating stoichiometry tends to be 1:6, e.g. $[\text{InL}_6]^{3+}(\text{Y}^-)_3$, $\text{L} = \text{Me}_2\text{SO}$, Ph_2SO , $(\text{Me}_2\text{N})_2\text{CO}$, $\text{HCO}(\text{NMe}_2)$, $\text{P}(\text{OMe})_3$, etc. Bulky ligands such as PPh_3 and AsPh_3 tend to give 1:4 adducts $[\text{InL}_4]^{3+}(\text{Y}^-)_3$. The same effect of ionic dissociation can be achieved in 1:3 complexes of the trihalides themselves by use of bidentate chelating ligands (B) such as en, bipy, or phen, e.g. $[\text{InB}_3]^{3+}(\text{X}^-)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCO}, \text{NCS}, \text{NCSe}$). InX_3 complexes having 1:2 stoichiometry also have a variety of structures. Trigonal bipyramidal geometry with axial ligands is found for InX_3L_2 , where $\text{L} = \text{MNE}_3$, PME_3 , PPh_3 , Et_2O , etc. By contrast, the crystal structure of the 1:2 complex of InI_3 with Me_2SO shows that it is fully ionized as $[\text{cis}-\text{InI}_2(\text{OSMe}_2)_4]^+[\text{InI}_4]^-$, and fivefold coordination is avoided by a disproportionation into 6- and 4-coordinate species. Complexes having 1:1 stoichiometry are rare for InX_3 ; InCl_3 forms $[\text{InCl}_3(\text{OPCl}_3)]$, $[\text{InCl}_3(\text{OCMe}_2)]$ and $[\text{InCl}_3(\text{OCPh}_2)]$ and py forms a 1:1 (and a 1:3) adduct with InI_3 . Frequently, of course, a given donor–acceptor pair combines in more than one stoichiometric ratio.

The thermochemistry of the Group 13 trihalide complexes has been extensively studied^(30,31,39) and several stability sequences have been

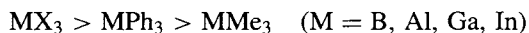
³⁸ A. J. CARTY and D. J. TUCK, *Prog. Inorg. Chem.* **19**, 243–337 (1975).

³⁹ N. N. GREENWOOD *et al.*, *Pure Appl. Chem.* **2**, 55–9 (1961); *J. Chem. Soc. A*, 267–70, 270–3, 703–6 (1966); *J. Chem. Soc. A*, 753–6 (1968); 249–53, 2876–8 (1969); *Inorg. Chem.* **9**, 86–90 (1970), and references therein. R. C. GEARHART, J. D. BECK and R. H. WOOD, *Inorg. Chem.* **14**, 2413–6 (1975).

established which can be interpreted in terms of the factors listed on p. 198. In addition, Ga and In differ from B and Al in having an underlying d^{10} configuration which can, in principle, take part in $d_{\pi}-d_{\pi}$ back bonding with donors such as S (but not N or O); alternatively (or additionally), some of the trends can be interpreted in terms of the differing polarizabilities of B and Al, as compared to Ga and In, the former pair behaving as class-a or "hard" acceptors whereas Ga and In frequently behave as class-b or "soft" acceptors. Again, it should be emphasized that these categories tend to provide descriptions rather than explanations. Towards amines and ethers the acceptor strengths as measured by gas-phase enthalpies of formation decrease in the sequence $MCl_3 > MBr_3 > MI_3$ for $M = Al, Ga$ or In . Likewise, towards phosphines the acceptor strength decreases as $GaCl_3 > GaBr_3 > GaI_3$. However, towards the "softer" sulfur donors Me_2S , Et_2S and C_4H_8S , whilst AlX_3 retains the same sequence, the order for GaX_3 and InX_3 is reversed to read $MI_3 > MBr_3 > MCl_3$. A similar reversal is noted when the acceptor strengths of individual AlX_3 are compared with those of the corresponding GaX_3 : towards N and O donors the sequence is invariably $AlX_3 > GaX_3$ but for S donors the relative acceptor strength is $GaX_3 > AlX_3$. These trends emphasize the variety of factors that contribute towards the strength of chemical bonds and indicate that there are no unique series of donor or acceptor strengths when the acceptor atom is varied, e.g.:

- towards $MeCO_2Et$: $BCl_3 > AlCl_3 > GaCl_3 > InCl_3$
 towards py: $AlPh_3 > GaPh_3 > BPh_3 \approx InPh_3$
 towards py: $AlX_3 > BX_3 > GaX_3$ ($X = Cl, Br$)
 towards Me_2S : $GaX_3 > AlX_3 > BX_3$ ($X = Cl, Br$)

Regularities are more apparent when the acceptor atom remains constant and the attached groups are varied; e.g., for all ligands so far studied the acceptor strength diminishes in the sequence



It has also been found that halide-ion donors (such as X^- in AlX_4^- and GaX_4^-) are more than

twice as strong as any neutral donor such as X in M_2X_6 , or N, P, O and S donors in MX_3L .⁽³⁹⁾ Finally, the complexity of factors influencing the strength of such bonds can be gauged from the curious alternation of the gas-phase enthalpies of dissociation of the dimers M_2X_6 themselves; e.g. $\Delta H_{298}^\circ(\text{dissoc})$ for Al_2Cl_6 , Ga_2Cl_6 and In_2Cl_6 are respectively 126.8, 93.9 and 121.5 kJ mol^{-1} .⁽⁴⁰⁾ The corresponding entropies of dissociation ΔS_{298}° are 152.3, 150.4 and 136.0 J mol^{-1} .

The trihalides of Tl are much less stable than those of the lighter Group 13 metals and are chemically quite distinct from them. TlF_3 , mp 550° (decomp), is a white crystalline solid isomorphous with $\beta\text{-BiF}_3$ (p. 560); it does not form hydrates but hydrolyses rapidly to $Tl(OH)_3$ and HF. Nor does it give TlF_4^- in aqueous solution, and the compounds $LiTlF_4$ and $NaTlF_4$ have structures related to fluorite, CaF_2 (p. 118): in $NaTlF_4$ the cations have very similar 8-coordinate radii (Na 116 pm, Tl 100 pm) and are disordered on the Ca sites (Ca 112 pm); in $LiTlF_4$, the smaller size of Li (~83 pm for eightfold coordination) favours a superlattice structure in which Li and Tl are ordered on the Ca sites. Na_3TlF_6 has the cryolite structure (p. 234).

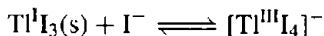
$TlCl_3$ and $TlBr_3$ are obtained from aqueous solution as the stable tetrahydrates and $TlCl_3 \cdot 4H_2O$ can be dehydrated with $SOCl_2$ to give anhydrous $TlCl_3$, mp 155°; it has the YCl_3 -type structure which can be described as $NaCl$ -type with two-thirds of the cations missing in an ordered manner.

TlI_3 is an intriguing compound which is isomorphous with NH_4I_3 and CsI_3 (p. 836); it therefore contains the linear I_3^- ion[†] and is a compound of Tl^I rather than Tl^{III} . It is obtained as black crystals by evaporating an equimolar solution of TlI and I_2 in concentrated aqueous Hl . The formulation $Tl^I(I_3^-)$ rather than $Tl^{III}(I^-)_3$ is consistent with the standard reduction potentials $E^\circ(Tl^{III}/Tl^I) + 1.26 \text{ V}$ and $E^\circ(\frac{1}{2}I_2/I^-) + 0.54 \text{ V}$,

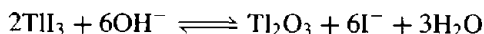
⁴⁰ K. KRAUSZE, H. OPPERMAN, U. BRUHN and M. BALARIN, *Z. anorg. allg. Chem.* **550**, 116–22 (1987).

[†] Note that this X-ray evidence by itself does not rule out the possibility that the compound is $[I-Tl^{III}-I]^+I^-$.

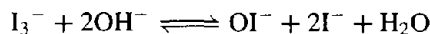
which shows that uncomplexed Tl^{III} is susceptible to rapid and complete reduction to Tl^{I} by I^- in acid solution. The same conclusion follows from a consideration of the I_3^-/I^- couple for which $E^\circ = +0.55 \text{ V}$. Curiously, however, in the presence of an excess of I^- , the Tl^{III} state is stabilized by complex formation



Moreover, solutions of TlI_3 in MeOH do not show the visible absorption spectrum of I_3^- and, when shaken with aqueous Na_2CO_3 , give a precipitate of Tl_2O_3 , i.e.:



This is due partly to the great insolubility of Tl_2O_3 ($2.5 \times 10^{-10} \text{ g l}^{-1}$ at 25°) and partly to the enhanced oxidizing power of iodine in alkaline solution as a result of the formation of hypoiodate:



Consistent with this, even KI_3 is rapidly decolorized in alkaline solution. The example is a salutary reminder of the influence of pH, solubility, and complex formation on the standard reduction potentials of many elements.

Numerous tetrahedral halogeno complexes $[\text{Tl}^{\text{III}}\text{X}_4]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been prepared by reaction of quaternary ammonium or arsonium halides on TlX_3 in nonaqueous solution, and octahedral complexes $[\text{Tl}^{\text{III}}\text{X}_6]^{3-}$ ($\text{X} = \text{Cl}, \text{Br}$) are also well established. The binuclear complex $\text{Cs}_3[\text{Tl}_2^{\text{III}}\text{Cl}_9]$ is an important structural type which features two TlCl_6 octahedra sharing a common face of 3 bridging Cl atoms (Fig. 7.9); the same binuclear complex structure is retained when Tl^{III} is replaced by Al^{III} , V^{III} , Cr^{III} and Fe^{III} and also in $\text{K}_3\text{W}_2\text{Cl}_9$ and $\text{Cs}_3\text{Bi}_2\text{I}_9$, etc.

Lower halides of gallium, indium and thallium

Like AlX (p. 233), GaF and InF are known as unstable gaseous species. The other monohalides are more stable. GaX can be obtained as reactive sublimates by treating GaX_3 with

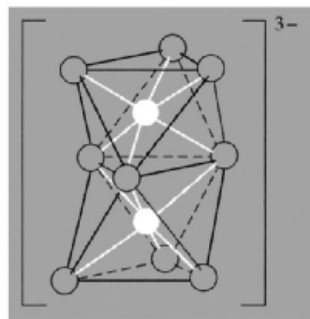


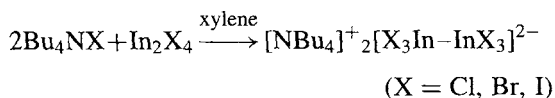
Figure 7.9 The structure of the ion $[\text{Tl}_2\text{Cl}_9]^{3-}$ showing two octahedral TlCl_6 units sharing a common face: $\text{Tl}-\text{Cl}$, 254 pm, $\text{Tl}-\text{Cl}_\mu$, 266 pm. The $\text{Tl}\cdots\text{Tl}$ distance is nonbonding (281 pm. cf. $2 \times \text{Tl}^{\text{III}} = 177 \text{ pm}$).

2Ga : stability increases with increasing size of the anion and GaI melts at 271° . Stability is still further enhanced by coordination of the anion with, for example, AlX_3 to give $\text{Ga}^{\text{I}}[\text{Al}^{\text{III}}\text{X}_4]$. Likewise, the very stable "dihalides" $\text{Ga}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$, $\text{Ga}[\text{GaBr}_4]$, and $\text{Ga}[\text{GaI}_4]$ can be prepared by heating equimolar amounts of GaX_3 and Ga , or more conveniently by halogenation of Ga with the stoichiometric amount of Hg_2X_2 or HgX_2 . They form complexes of the type $[\text{Ga}^{\text{I}}\text{L}_4]^+[\text{Ga}^{\text{III}}\text{X}_4]^-$ with a wide range of N, As, O, S and Se donors. See also p. 264 for arene complexes of the type $[\text{Ga}^{\text{I}}(\text{ar})_n]^+[\text{Ga}^{\text{III}}\text{X}_4]^-$. Note, however, that the complexes with dioxan $[\text{Ga}_2\text{X}_4(\text{C}_4\text{H}_8\text{O}_2)_2]$, do in fact contain Ga^{II} and a $\text{Ga}-\text{Ga}$ bond, e.g. the chloro complex is a discrete molecule with $\text{Ga}-\text{Ga}$ 240.6 pm (cf. 239.0 pm in $\text{Ga}_2\text{Cl}_6^{2-}$);⁽⁴¹⁾ the coordination about each Ga atom is essentially tetrahedral and the compound surprisingly adopts an essentially eclipsed structure rather than the staggered structure of $\text{Ga}_2\text{Cl}_6^{2-}$. Likewise $[\text{Ga}_2\text{I}_4 \cdot 2\text{L}]$, where L is a wide range of organic ligands with N, P, O or S donor atoms, have been shown by vibration spectroscopy to have a $\text{Ga}-\text{Ga}$ bond.⁽⁴²⁾

⁴¹ J. C. BEAMISH, R. W. H. SMALL and I. J. WORRALL, *Inorg. Chem.* **18**, 220-3 (1979).

⁴² J. C. BEAMISH, A. BOARDMAN and I. J. WORRALL, *Polyhedron* **10**, 95-9 (1991).

Indium monohalides, InX , can be prepared as red crystals either directly from the elements or by heating In metal with HgX_2 at 320–350°. They have a TII-type structure (p. 242) with [1 + 4 + 2] rather than 6-fold coordination of In by X, leading to rather close $\text{In}^{\text{I}} \dots \text{In}^{\text{I}}$ contacts of 362, 356 and 357 pm respectively for $\text{X} = \text{Cl}, \text{Br}$ and I .⁽⁴³⁾ Again, InI is the most stable, and mixed halides of the type $\text{In}^{\text{I}}[\text{Al}^{\text{III}}\text{Cl}_4]$, $\text{In}^{\text{I}}[\text{Ga}^{\text{III}}\text{Cl}_4]$ and $\text{Tl}^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_4]$ are known. Numerous intermediate halides have also been reported and structural assignments of varying degrees of reliability have been suggested, e.g. $\text{In}^{\text{I}}[\text{In}^{\text{III}}\text{X}_4]$ for InX_2 ($\text{Cl}, \text{Br}, \text{I}$); and $\text{In}_3^{\text{I}}[\text{In}^{\text{III}}\text{Cl}_6]$ for In_2Cl_3 . In contrast to the chloride, In_2Br_3 has the unexpected structure $[(\text{In}^+)_2(\text{In}_2^{\text{II}}\text{Br}_6)^{2-}]$.⁽⁴⁴⁾ The compounds In_4X_7 and In_5X_7 (Cl, Br) and In_7Br_9 are also known. In all of these halides the observed stoichiometry is achieved by varying the ratio of In^{I} to In^{II} or In^{III} , e.g. $[(\text{In}^+)_5(\text{InBr}_4^-)_2(\text{InBr}_6^{3-})]$, $[(\text{In}^+)_3(\text{In}_2\text{Br}_6^{2-})\text{Br}^-]$ and $[(\text{In}^+)_6(\text{InBr}_6^{3-})(\text{Br}^-)_3]$.^(45,46) Compounds containing In^{II} were unknown until 1976 when the $[\text{In}_2\text{X}_6]^{2-}$ dianions having an ethane-like structure were prepared:⁽⁴⁷⁾



The analogous Ga compounds, e.g. $[\text{NET}_4]_2[\text{Cl}_3\text{-Ga-GaCl}_3]$, have been known for rather longer (1965). Oxidation of $\text{In}_2\text{X}_6^{2-}$ with halogens Y_2 yields the mononuclear mixed halide complexes InX_3Y^- and InX_2Y_2^- ($\text{X} \neq \text{Y} = \text{Cl}, \text{Br}, \text{I}$).⁽⁴⁸⁾

Thallium(I) is the stable oxidation state for the halides of this element (p. 226) and some physical properties are in Table 7.7. TlF is readily obtained by the action of aqueous HF on Tl_2CO_3 ; it is very soluble in water (in contrast to the other TlX) and has a distorted NaCl structure in which there are 3 pairs of Tl–F distances at 259, 275 and 304 pm. TlCl, TlBr and TlI are all prepared by addition of the appropriate halide ion to acidified solutions of soluble Tl^{I} salts (e.g. perchlorate, sulfate, nitrate). TlCl and TlBr have the CsCl structure (p. 80) as befits the large Tl^{I} cation and both salts (and TlI) are photosensitive (like AgX). Yellow TlI has a curious orthorhombic layer structure related to NaCl (Fig. 7.10), and this transforms at 175° or at 4.7 kbar to a metastable red cubic form with 8-iodine neighbours at 364 pm (CsCl type). This transformation is accompanied by 3% reduction in volume. Further application of pressure steadily reduces the volume and at pressures above about 160 kbar, when the volume has decreased by about 35%, the compound becomes a metallic conductor with a resistivity of the order of 10^{-4} ohm cm at room temperature and a positive temperature coefficient. TlCl and TlBr behave similarly. All three compounds are excellent insulators at normal pressures with negligible conductivity and an energy gap between the valence band and conduction band

⁴³ G. MEYER and T. STAFFEL, *Z. anorg. allg. Chem.* **574**, 114–8 (1989).

⁴⁴ T. STAFFEL and G. MEYER, *Z. anorg. allg. Chem.* **552**, 113–22 (1987).

⁴⁵ J. E. DAVIES, L. G. WATERWORTH and I. J. WORRALL, *J. Inorg. Nucl. Chem.* **36**, 805–7 (1974).

⁴⁶ T. STAFFEL and G. MEYER, *Z. anorg. allg. Chem.* **563** 27–37 (1988). See also correction in R. E. MARSH and G. MEYER, *Z. anorg. allg. Chem.* **582**, 128–30 (1990).

⁴⁷ B. H. FREELAND, J. L. HENCHER, D. G. TUCK and J. G. CONTRERAS, *Inorg. Chem.* **15**, 2144–6 (1976). See also D. G. TUCK, *Polyhedron* **9**, 377–86 (1990).

⁴⁸ J. E. DRAKE, J. L. HENCHER, L. N. KHASROU, D. G. TUCK and L. VICTORIANO, *Inorg. Chem.* **19**, 34–8 (1980).

Table 7.7 Some properties of TlX

Property	TlF	TlCl	TlBr	TlI
MP/°C	322	431	460	442
BP/°C	826	720	815	823
Colour	White	White	Pale yellow	Yellow
Crystal structure	Distorted NaCl	CsCl	CsCl	See text
Solubility/g per 100 g H ₂ O (°C)	80 (15°)	0.33 (20°)	0.058 (25°)	0.006 (20°)
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	–326	–204	–173	–124

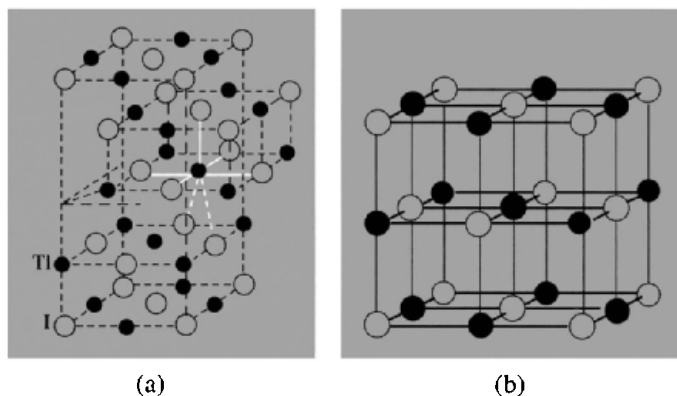


Figure 7.10 Structure of yellow TlI (a) showing its relation to NaCl (b). Tl has 5 nearest-neighbour I atoms at 5 of the vertices of an octahedron and then 2I + 2Tl as next-nearest neighbours; there is one I at 336 pm, 4 at 349 pm, and 2 at 387 pm, and the 2 close Tl–Tl approaches, one at 383 pm. InX (X = Cl, Br, I) have similar structures in their red forms.⁽⁴³⁾

of about 3 eV ($\sim 300 \text{ kJ mol}^{-1}$), and the onset of metallic conduction is presumably due to the spreading and eventual overlap of the two bands as the atoms are forced closer together.⁽⁴⁹⁾

Several other lower halides of Tl are known: TlCl_2 and TlBr_2 are $\text{Tl}^{\text{I}}[\text{Tl}^{\text{III}}\text{X}_4]$, Tl_2Cl_3 and Tl_2Br_3 are $\text{Tl}_3^{\text{I}}[\text{Tl}^{\text{III}}\text{X}_6]$. In addition there is Tl_3I_4 , which is formed as an intermediate in the preparation of $\text{Tl}^{\text{I}}\text{I}_3$ from TlI and I_2 (p. 239).

7.3.3 Oxides and hydroxides

The structural relations between the many crystalline forms of aluminium oxide and hydroxide are exceedingly complex but they are of exceptional scientific interest and immense technological importance. The principal structural types are listed in Table 7.8 and many intermediate and related structures are also known. Al_2O_3 occurs as the mineral corundum ($\alpha\text{-Al}_2\text{O}_3$, d 4.0 g cm^{-3}) and as emery, a granular form of corundum contaminated with iron oxide and silica. Because of its great hardness (Mohs 9),[†] high mp (2045°C), involatility (10^{-6} atm at 1950°), chemical inertness and good electrical

insulating properties, it finds many applications in abrasives (including toothpaste), refractories, and ceramics, in addition to its major use in the electrolytic production of Al metal (p. 219). Larger crystals, when coloured with metal-ion impurities, are prized as gemstones, e.g. ruby (Cr^{III} red), sapphire ($\text{Fe}^{\text{II/III}}$, Ti^{IV} blue), oriental emerald (? Cr^{III} / V^{III} green), oriental amethyst (Cr^{III} / Ti^{IV} violet) and oriental topaz (Fe^{III} , yellow). Many of these gems are also made industrially on a large scale by the fusion process first developed at the turn of the century by A. Verneuil. Pure $\alpha\text{-Al}_2\text{O}_3$ is made industrially by igniting $\text{Al}(\text{OH})_3$ or $\text{AlO}(\text{OH})$ at high temperatures ($\sim 1200^\circ$); it is also formed by the combustion of Al and by calcination of various Al salts. It has a rhombohedral crystal structure comprising a hcp array of oxide ions with Al ordered on two-thirds of the octahedral interstices as shown in Fig. 7.11.⁽²⁶⁾ The same $\alpha\text{-M}_2\text{O}_3$ structure is adopted by several other elements with small M^{III} (r 62–67 pm), e.g. Ga, Ti, V, Cr, Fe and Rh.[‡]

[†] On the Mohs scale diamond is 10 and quartz 7. An alternative measure is the Knoop hardness (kg mm^{-2}) as measured with a 100-g load: typical values on this scale are diamond 7000, boron carbide 2750, corundum 2100, topaz 1340, quartz 820, hardened tool steel 740.

[‡] For somewhat larger cations (r 70–96 pm) the C-type rare-earth M_2O_3 structure (p. 1238) is adopted, e.g. for In,

⁴⁹ G. A. SAMARA and H. G. DRICKAMER, *J. Chem. Phys.* **37**, 408–10 (1962); see also E. A. PEREZ-ALBUERNE and H. G. DRICKAMER, *J. Chem. Phys.* **43**, 1381–7 (1965).

Table 7.8 The main structural types of aluminium oxides and hydroxides^(a)

Formula	Mineral name	Idealized structure
$\alpha\text{-Al}_2\text{O}_3$	Corundum	hcp O with Al in two-thirds of the octahedral sites
$\alpha\text{-AlO(OH)}$	Diaspore	hcp O (OH) with chains of octahedra stacked in layers interconnected with H bonds, and Al in certain octahedral sites
$\alpha\text{-Al(OH)}_3$	Bayerite	hcp (OH) with Al in two-thirds of the octahedral sites
$\gamma\text{-Al}_2\text{O}_3$	—	ccp O defect spinel with Al in $21\frac{1}{3}$ of the 16 octahedral and 8 tetrahedral sites
$\gamma\text{-AlO(OH)}$	Boehmite	ccp O (OH) within layers; details uncertain
$\gamma\text{-Al(OH)}_3$	Gibbsite (Hydrargillite)	ccp OH within layers of edge-shared Al(OH)_6 ; octahedra stacked vertically via H bonds

^(a)The Greek prefixes α - and γ - are not used consistently in the literature, e.g. bayerite is sometimes designated as $\beta\text{-Al(OH)}_3$ and gibbsite as $\alpha\text{-Al(OH)}_3$. The UK usage adopted here is consistent with Wells⁽²⁶⁾ and emphasizes the structural relations between the hcp α -series and the ccp γ -series. Numerous other intermediate crystalline phases have been characterized during partial dehydration and designated as γ' , δ , ζ , η , θ , κ , κ' , ρ , χ , etc.

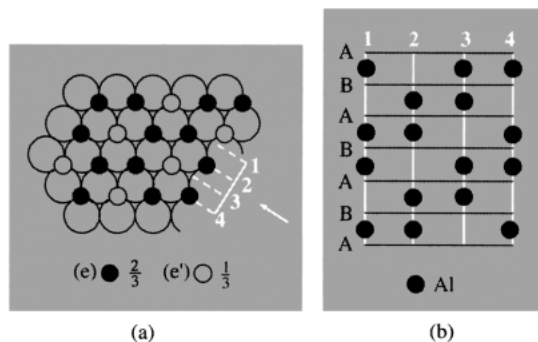


Figure 7.11 Schematic representation of the structure of $\alpha\text{-Al}_2\text{O}_3$. (a) pattern of occupancy by Al (●) of the octahedral sites between hcp layers of oxide ion (○), and (b) stacking sequence of successive planes of Al atoms viewed in the direction of the arrow in (a).

The second modification of alumina is the less compact cubic $\gamma\text{-Al}_2\text{O}_3$ (d 3.4 g cm⁻³); it is formed by the low-temperature dehydration (<450°) of gibbsite, $\gamma\text{-Al(OH)}_3$, or boehmite, $\gamma\text{-AlO(OH)}$. It has a defect spinel-type structure (p. 248) comprising a face-centred cubic (fcc) arrangement of 32 oxide ions and a random occupation of $21\frac{1}{3}$ of the 24 available cation

sites (16 octahedral, 8 tetrahedral). This structure forms the basis of the so-called “activated aluminas” and progressive dehydration in the γ -series leads to open-structured materials of great value as catalysts, catalyst-supports, ion exchangers and chromatographic media. Calcination of $\gamma\text{-Al}_2\text{O}_3$ above 1000° converts it irreversibly to the more stable and compact α -form ($\Delta H_{\text{trans}} - 20 \text{ kJ mol}^{-1}$). Yet another form of Al_2O_3 occurs as the protective surface layer on the metal: it has a defect NaCl-type structure with Al occupying two-thirds of the octahedral (Na) interstices in the fcc oxide lattice. Perhaps the most ingenious and sophisticated development in aluminium technology has been the recent production of Al_2O_3 fibres which can be fabricated into a variety of textile forms, blankets, papers, and boards. Some idea of the many possibilities of such high-temperature inert fabrics is indicated in the Panel on p. 244.

Diaspore, $\alpha\text{-AlO(OH)}$ occurs in some types of clay and bauxite; it is stable in the range 280–450° and can be made by hydrothermal treatment of boehmite, $\gamma\text{-AlO(OH)}$, in 0.4% aqueous NaOH at 380° and 500 atm. Crystalline boehmite is readily prepared by warming the amorphous, gelatinous white precipitate which first forms when aqueous NH_3 is added to cold solutions of Al salts. In $\alpha\text{-AlO(OH)}$ the O atoms are arranged in hcp; continuous chains of edge-shared octahedra are stacked in layers

Tl, Sc, Y, Sm and the subsequent lanthanoids, and perhaps surprisingly for Mn^{III} (r 65 pm); the largest lanthanoids La, Ce, Pr and Nd (r 106–100 pm) adopt the A-type rare-earth M_2O_3 structure (p. 1238).

Fibrous Alumina and Zirconia^(50,51)

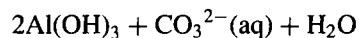
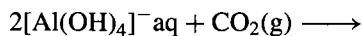
A new family of lightweight inorganic fibres made its commercial debut in 1974 when ICI announced the production of "Saffil", fibrous Al_2O_3 and ZrO_2 on an initial scale of 100 tonnes pa. Du Pont also has a process for $\alpha\text{-Al}_2\text{O}_3$ fibres and the current world production of fibrous Al_2O_3 is of the order of 1000 tonnes per annum. The price is about \$60/kg (1986). The fibres, which have no demonstrable toxic effects (cf. asbestos), have a diameter of $\sim 3\ \mu\text{m}$ (cf. human hair $\sim 70\ \mu\text{m}$), and each fibre is extremely uniform along its length (2–5 cm). The fibres are microcrystalline (5–50 μm diam) and are both flexible and resilient with a high tensile strength. They have a soft, silky feel and can be made into rope, yarn, cloth, blankets, fibre matts, paper of various thickness, semi-rigid and rigid boards, and vacuum-formed objects of any required shape. The surface area of Saffil alumina is 100–150 $\text{m}^2\ \text{g}^{-1}$ due to the presence of small pores 2–10 μm diameter between the microcrystals, and this enhances its properties as an insulator, filtration medium, and catalyst support. The fibres withstand extended heating to 1400° (Al_2O_3) or 1600°C (ZrO_2) and are impervious to attack by hot concentrated alkalis and most hot acids except conc H_2SO_4 , conc H_3PO_4 and aq HF. This unique combination of properties provides the basis for their use in high-temperature insulation, heat shields, thermal barriers, and expansion joints and seals. Fibrous alumina and zirconia are also valuable in thermocouple protection, electric-cable sheathing, and heating-element supports in addition to their use in the high-temperature filtration of corrosive liquids. Both oxides are stabilized by incorporation of small amounts of other inorganic oxides which inhibit disruptive transformation to other crystalline forms.

Alumina fibres can also be used to strengthen metals. Molten metals (e.g. Al, Mg, Pb) or their alloys are forced into moulds containing up to 70% by volume of $\alpha\text{-Al}_2\text{O}_3$ fibre. For example, fibre-reinforced Al containing 55% fibre by volume is 4–6 times stiffer than unreinforced Al even up to 370°C and has 2–4 times the fatigue strength. Potential applications for which high structural stiffness, heat resistance, and low weight are required include helicopter housings, automotive and jet engines, aerospace structures and lead-acid batteries. For example, fibre reinforced composites of Al or Mg could eventually replace much of the steel used in car bodies without decreasing safety, since the composite has the stiffness of steel but only one-third of its density.

In addition to the production of stabilized Al_2O_3 fibres there is also a huge production of melt-spun glassy fibres containing approximately equal proportions by weight of Al_2O_3 and SiO_2 . This is used mainly for thermal insulation at temperatures up to 1400°C and current world production exceeds 20 000 tonnes per annum.

and are further interconnected by H bonds. The underlying hcp structure ensures that diaspore dehydrates directly to $\alpha\text{-Al}_2\text{O}_3$ (corundum) which has the same basic hcp arrangement of O atoms. The structure is also adopted by several other $\alpha\text{-MO(OH)}$ ($M = \text{Ga}, \text{V}, \text{Mn}$ and Fe); this contrasts with the structure of boehmite, $\gamma\text{-AlO(OH)}$, which as a whole is not close-packed, though within each layer the O atoms are arranged in cubic close packing. Dehydration at temperatures up to 450° proceeds via a succession of phases to the cubic $\gamma\text{-Al}_2\text{O}_3$ and the α (hexagonal) structure cannot be attained without much more reconstruction of the lattice at 1100–1200° as noted above [and of $\gamma\text{-ScO(OH)}$ and $\gamma\text{-FeO(OH)}$].

Bayerite, $\alpha\text{-Al(OH)}_3$, does not occur in nature but can be made by rapid precipitation from alkaline solutions in the cold:



Gibbsite (or hydrargillite), $\gamma\text{-Al(OH)}_3$, is a more stable form and can be prepared by slow precipitation from warm alkaline solutions or by digesting the α -form in aqueous sodium aluminate solution at 80°. In both bayerite (α) and gibbsite (γ) there are layers of composition Al(OH)_3 built up by the edge sharing of Al(OH)_6 octahedra to give a pair of approximately close-packed OH layers with Al atoms in two-thirds of the octahedral interstices (Fig. 7.12a). The two crystalline modifications differ in the way this layer is stacked: it is approximately hcp in $\alpha\text{-Al(OH)}_3$ but in the γ -form the OH groups on the under side of one layer rest directly above the OH groups of the layer below as shown in Fig. 7.12b. A third form of Al(OH)_3 , nordstrandite, is obtained from the gelatinous

⁵⁰ J. D. BIRCHALL, J. A. A. BRADBURY and J. DINWOODIE, Chap IV in W. WATT and B. V. PEROV (eds.), *Handbook of Composites, Vol. 1, Strong Fibres*, Elsevier, Amsterdam, 1985, pp. 115–54. J. D. BIRCHALL, in M. B. BEVER (ed.) *Encyclopedia of Materials Science and Engineering*, Pergamon Press, Oxford, 1986, pp. 2333–5.

⁵¹ W. BÜCHNER, R. SCHLIEBS, G. WINTER and K. H. BÜCHEL, *Industrial Inorganic Chemistry*, VCH, Weinheim, 1989, pp. 362–4.

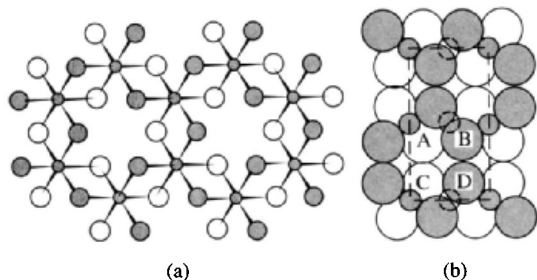


Figure 7.12 (a) Part of a layer of $\text{Al}(\text{OH})_3$ (idealized); the heavy and light open circles represent OH groups above and below the plane of the Al atoms. In $\alpha\text{-Al}(\text{OH})_3$ the layers are stacked to give approximately hcp. (b) Structure of $\gamma\text{-Al}(\text{OH})_3$ viewed in a direction parallel to the layers; the OH groups labelled C and D are stacked directly beneath A and B. The six OH groups A, B, C, D and B', D' (behind B and D), form a distorted H-bonded trigonal prism.

hydroxide by ageing it in the presence of a chelating agent such as ethylenediamine, ethylene glycol, or edta; this aligns the OH to give a stacking arrangement which is intermediate between those of the α - and γ -forms.

As expected from the foregoing structural discussion, gibbsite can be dehydrated to boehmite at 100° and to anhydrous $\gamma\text{-Al}_2\text{O}_3$ at 150° , but ignition above 800° is required to form $\alpha\text{-Al}_2\text{O}_3$. Numerous recipes have been devised for preparing catalysts of differing reactivity and absorptive power, based on the partial dehydration and progressive reconstitution of the Al/O/OH system.⁽¹⁾ In addition to pore size, surface area and general reactivity, the basic character of the surface diminishes (and its acidic character increases) in the following series as indicated by the pH of the isoelectric point:

(amorph. Al oxide hydrate)	$>\gamma\text{-AlO}(\text{OH})$	$>\alpha\text{-Al}(\text{OH})_3$	$>\gamma\text{-Al}(\text{OH})_3$	$>\gamma\text{-Al}_2\text{O}_3$
	boehmite	bayerite	gibbsite	
pH: 9.45	9.45–9.40	9.20	–	8.00
(isoelec. pt.)				

The aqueous solution chemistry of Al and the other group 13 metals is rather complicated. The aquo ions are acidic with

$\text{p}K_{\text{A}} \approx 10^{-5}, 10^{-3}, 10^{-4}$ and 10^{-1} , respectively, for $[\text{M}(\text{H}_2\text{O})_6]^{3+} \rightleftharpoons [\text{M}(\text{OH})(\text{H}_2\text{O})_5]^{2+} + \text{H}^+$ ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}$). The solution chemistry of Al in particular has been extensively investigated because of its industrial importance in water treatment plants, its use in many toiletry formulations, its possible implication in both Alzheimer's disease and the deleterious effects of acid rain, and the ubiquity of Al cooking utensils.^(52–54) For example, hydrated aluminium sulphate ($10\text{--}30 \text{ g m}^{-3}$) can be added to turbid water supplies at pH 6.5–7.5 to flocculate the colloids, some 3 million tonnes per annum being used worldwide for this application alone. Likewise kilotonne amounts of “ $\text{Al}(\text{OH})_{2.5}\text{Cl}_{0.5}$ ” in concentrated (6M) aqueous solution are used in the manufacture of deodorants and antiperspirants.

The use of ^{27}Al nmr (see Panel) has been particularly valuable in characterizing the species present in aqueous solution of Al salts.⁽⁵⁵⁾ These depend very much on both concentration and pH and include the mononuclear ions $[\text{Al}(\text{OH})_4]^-$, $[\text{Al}(\text{H}_2\text{O}_6)]^{3+}$ and $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. This latter species can deprotonate further to $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ and readily dimerizes via hydroxyl bridges to $[(\text{H}_2\text{O})_4\text{Al}(\mu\text{-OH})_2\text{Al}(\text{H}_2\text{O})_4]^{4+}$, i.e. $[\text{H}_{18}\text{Al}_2\text{O}_{10}]^{4+}$, which has also been found in several crystalline salts. Higher oligomers probably include appropriately hydrated forms of $[\text{Al}_3(\text{OH})_{11}]^{2-}$, $[\text{Al}_6(\text{OH})_{15}]^{3+}$ and $[\text{Al}_8(\text{OH})_{22}]^{2+}$. A particularly important species is the well-characterized tridecameric cation $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ which has the well-known Keggin structure (p. 1014),

⁵² H. SIGEL and A. SIGEL (eds), *Metal Ions in Biological Systems*, Vol. 24, *Aluminium and its Role in Biology*, Marcel Dekker, New York, 1988, 440 pp.

⁵³ R. C. MASSEY and D. TAYLOR (eds.), *Aluminium in Food and the Environment*. Royal Society of Chemistry (London) Special Publ. No. 73, 1989, 116 pp.

⁵⁴ G. H. ROBINSON (ed.), *Coordination Chemistry of Aluminium*, VCH, Cambridge, 1993, 234 pp.

⁵⁵ J. W. AKITT, *Prog. NMR Spectroscopy* **21**, 1–149 (1989). See also J. W. AKITT, Chap 9 in J. MASON (ed.), *Multinuclear NMR*, Plenum Press, New York, 1987, pp. 259–92, which also includes nmr of Ga, In and Tl isotopes.

²⁷Al in Nuclear Magnetic Resonance Spectroscopy

Aluminium is a very convenient element for nmr spectroscopy because ²⁷Al is 100% abundant and has a high nmr sensitivity, its receptivity being 0.206 when compared to ¹H and 1170 when compared to ¹³C. It also has a high operating frequency (26.077 MHz when scaled to 100 MHz for ¹H) and a wide range of chemical shifts, δ (>300 ppm). The nuclear spin quantum number is 5/2 and the magnetogyric ratio γ is 6.9763 rad s⁻¹T⁻¹. The only disadvantage is the presence of a nuclear quadrupole moment ($Q = 0.149 \times 10^{-28}$ m²) which leads to substantial line broadening for many species. The narrowest lines ($\omega_{1/2} \sim 2$ Hz) are obtained for highly symmetrical species such as [Al(H₂O)₆]³⁺ and [Al(OH)₄]⁻, but line widths of 1000 Hz or more are not uncommon and the use of special curve-analysis techniques is needed to extract the required parameters.

As expected, chemical shifts depend on coordination number (CN) and also on the nature of the atoms directly bonded to Al. Organometallic species, i.e. those with Al-C bonds, resonate at low field (high frequency): those with CN 3 have δ in the range 275–220 ppm, those with CN 4 have δ 220–140 ppm and those with CN 5 have δ 140–110 ppm. Tetrahalogenoaluminates, AlX₄⁻, AlX_nY_{4-n}⁻, and 4-coordinate ligand adducts in general have δ in the range 120–50 ppm with the curious exception of AlI₄⁻ which shows a resonance at a higher field than for any other Al species so far, δ being –26.7 ppm. Five-coordinate adducts have δ in the range 65–25 ppm and octahedral species have δ in the range +40 to –25 ppm. Typical parameters for some of the species mentioned in the main text are:

Species	[Al(OH) ₄] ⁻	[Al(H ₂ O) ₆] ³⁺	[Al ₂ (OH) ₂ (H ₂ O) ₈] ⁴⁺	[Al ₁₃ O ₄ (OH) ₂₄ (H ₂ O) ₁₂] ⁷⁺
δ /ppm	80	0.00 (std)	4	12Al @ ~12, 1Al @ 625
$\omega_{1/2}$ /Hz	10	2	500	8000, 25

These values show some dependence on concentration, pH and temperature. Note also the much smaller linewidth for the central, symmetrically 4-coordinated Al atom of the tridecameric Al₁₃ species when compared with that of the twelve less symmetrically coordinated octahedral Al atoms, and the possibility of extracting a reasonably precise value of δ for this latter resonance which has a linewidth of some 8000 Hz.

Solid-state ²⁷Al nmr spectroscopy has been much used in recent years to study the composition and structure of aluminosilicates (pp. 351–9) and other crystalline or amorphous Al compounds. The technique of magic angle spinning (MAS) must be used in such cases.⁽⁵⁵⁾

[AlO₄{Al(OH)₂(H₂O)}₁₂]⁷⁺, in which the central tetrahedral AlO₄ group is surrounded by corner- and edge-shared AlO₆ octahedra. The ion, which is almost spherical, has been further characterized by an X-ray diffraction study of crystalline Na[Al₁₃O₄(OH)₂₄(H₂O)₁₂](SO₄)₄·13H₂O.

The binary oxides and hydroxides of Ga, In and Tl have been much less extensively studied. The Ga system is somewhat similar to the Al system and a diagram summarizing the transformations in the systems is in Fig. 7.13. In general the α - and γ -series have the same structure as their Al counterparts. β -Ga₂O₃ is the most stable crystalline modification (mp 1740°); it has a unique crystal structure with the oxide ions in distorted ccp and Ga^{III} in distorted tetrahedral and octahedral sites. The structure appears to owe its stability to these distortions and, because of the lower coordination of half the Ga^{III}, the density is ~10% less than for the α - (corundum-type) form. This preference of Ga^{III}

for fourfold coordination despite the fact that it is larger than Al^{III} may again indicate the polarizing influence of the d¹⁰ core; a similar tetrahedral site preference is observed for Fe^{III}.

In₂O₃ has the C-type M₂O₃ structure (p. 1238) and InO(OH) (prepared hydrothermally from In(OH)₃ at 250–400°C and 100–1500 atm) has a deformed rutile structure (p. 961) rather than the layer lattice structure of AlO(OH) and GaO(OH). Crystalline In(OH)₃ is best prepared by addition of NH₃ to aqueous InCl₃ at 100° and ageing the precipitate for a few hours at this temperature; it has the simple ReO₃-type structure distorted somewhat by multiple H bonds.⁽²⁶⁾

Thallium is notably different. Tl₂O forms as black platelets when Tl₂CO₃ is heated in N₂ at 700° (mp 596°, d 10.36 g cm⁻³); it is hygroscopic and gives TlOH with water. Tl₂^{III}O₃ is brown-black (mp 716°, d 10.04 g cm⁻³) and can be made by oxidation of aqueous TlNO₃ with Cl₂ or Br₂ followed by precipitation