446. *Trimethylgallium. Part I. The Relative Stabilities of its Co-ordination Compounds with the Methyl Derivatives of Groups* VB *and* VIB, *and the Thermal Decomposition of Some Trimethylgallium–Amine Complexes.*

By G. E. Coates.

Co-ordination compounds of trimethylgallium with all the trimethyl derivatives of the Group VB elements from nitrogen to antimony have been prepared; trimethylbismuth does not react. The donor properties of the VB elements, as measured by the dissociation of these co-ordination compounds, diminish regularly in the sequence N > P > As > Sb > Bi. A similar series of compounds between trimethylgallium and the dimethyl derivatives of the Group VIB elements (from O to Te) has also been prepared; the variation of donor properties to trimethylgallium in this group is irregular, *viz.*, O > Se > S = Te. Towards trimethylaluminium the donor properties of the Group VIB elements diminish regularly from oxygen to tellurium. This contrast between trimethylgallium and trimethylaluminium, together with a review of the other co-ordination compounds of the Group VIB elements, suggests that double bonding by means of *d* orbitals plays an important part in determining the stability of the co-ordinate link. The co-ordinating properties of ethers are discussed, and some complexes between silver iodide and dimethyl selenide and telluride are described.

The elements of Group IIIB, *viz.*, boron, aluminium, gallium, indium, and thallium, show a remarkable variation in their electron-acceptor properties. Compounds of all these elements in their tervalent states tend to increase their covalency to four, or sometimes six, by co-ordination with donor molecules. Boron, aluminium, and gallium exhibit this tendency to such a degree that, in some of their compounds, the element contrives to increase its covalency above three without acquiring an electron from a donor molecule; these compounds are the well known " electron-deficient " molecules exemplified by diborane B_2H_6, trimethylaluminium Al_2Me_6, and digallane Ga_2H_6, in which the total number of valency electrons is less than twice the number of valency bonds (see Coates, *Quart. Reviews*, 1950, **4**, 217).

The co-ordination compounds of the trimethyl derivatives of these elements are particularly suitable for studies on relative electron-acceptor and -donor properties, since the trimethyl derivatives themselves are all conveniently volatile and stable, and it is frequently possible to investigate their dissociation equilibria in the gas phase. The co-ordination compounds of trimethylboron have been thoroughly examined by H. C. Brown and others, and Brown and Davidson (*J. Amer. Chem. Soc.*, 1942, **64**, 316) have studied some co-ordination compounds of trimethylaluminium (these results are reviewed by Sidgwick, " The Chemical Elements and their Compounds," Oxford, 1950). Compounds have been described between trimethylgallium and the donor molecules, ammonia and ethyl ether (Kraus and Toonder, *Proc. Nat. Acad. Sci.*, 1933, **19**, 292), trimethyl- and triethyl-amine (Wiberg, Johannsen, and Stecher, *Z. anorg. Chem.*, 1943, **251**, 114). The reactions between trimethylgallium and the methyl derivatives of the elements of Groups VB and VIB have now been studied with the object of determining the relative donor properties of these elements towards a common acceptor molecule, trimethylgallium, and of establishing the acceptor properties of the latter in relation to boron and aluminium. The methyl derivatives of the donor elements are suitable for this purpose, since there is no possibility of reaction (at the temperatures involved in this work, *viz.*, <200°) other than the formation of a co-ordination compound. Compounds containing hydrogen bonded to nitrogen or other donor atoms frequently co-ordinate to trimethylgallium and then undergo further reaction with elimination of methane. Some of these reactions, which also take place with trimethylboron and trimethylaluminium, are described.

Trimethylgallium forms 1 : 1 co-ordination compounds with the methyl derivatives of all the VB and VIB elements except bismuth; trimethylbismuth did not combine even in the liquid state, since the vapour pressure of an equimolar mixture of the components slightly exceeded that calculated for an ideal solution. The physical properties of all the other compounds are given in Table I, which also includes the compounds formed with dimethylamine,

methylamine, and ammonia. The compound, trimethylgallium–trimethylamine (Wiberg *et al., loc. cit.*) is very stable, as judged by its rather high melting point, 96·2°, and the fact that it begins to show perceptible dissociation in the gas phase only above 110°. This compound, made during the present work, exhibited dimorphism; crystals condensed from the vapour above 18—20° were quite transparent, had very rounded edges, and an almost glassy appearance but, on cooling to 10° or below, they slowly changed to a polycrystalline opaque mass. This change is reversible. The vapour pressure at these temperatures is too small to allow the detection of any change of slope in the log v.p.–T^{-1} graph.

TABLE I.

Co-ordination compounds of trimethylgallium.

Compound.	M. p.	B. p. (extrap.).	A.*	B.	L_V.†	Trouton const.	Temp. range.
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{N}Me_3}$ [a]	96·2°	164°	2226	7·947	10·19	23·3	96—107°
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{N}HMe_2}$	33·3—33·6	170	2532	8·596	11·6	26·2	50—110
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{N}H_2Me}$	37—38	169	2760	9·119	12·6	28·6	50—120
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{N}H_3}$ [b]	31—32	179	1947	7·190	8·9	19·7	20—70
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{P}Me_3}$	56·4—56·7	173	2662	8·851	12·2	27·3	60—120
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{As}Me_3}$	23·4—23·7	121	2458	9·114	11·2	28·5	25—100
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{Sb}Me_3}$	0·3—2·2	95	2105	8·591	9·6	26·1	16—40
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{O}Me_2}$	—	100	2078	8·453	9·5	25·5	20—60
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{S}Me_2}$	—	116	2580	9·516	11·8	30·4	20—60
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{Se}Me_2}$	−43° to −42°	111	2783	10·118	12·7	33·0	15—80
$\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{Te}Me_2}$	−32·5° to −32°	122	2488	9·172	11·4	28·8	20—80
($\mathrm{Me_3\overset{-}{Al}{-}\overset{+}{Se}Me_2}$ [c]	—	146	2320	8·410	10·6	25·3	20—120)
($\mathrm{Me_3\overset{-}{Al}{-}\overset{+}{Te}Me_2}$ [c]	—	146	2022	7·708	9·3	22·1	20—120)

* $\log_{10}(\text{v. p.})_{\text{mm.}} = -(A/T) + B$. † Latent heat of evaporation, kcals./g.-mol.

[a] Data from Wiberg, Johannsen, and Stecher, *loc. cit.* [b] Kraus and Toonder, *loc. cit.*, give m. p. 31°. [c] These aluminium compounds are discussed later, but are included in this Table for convenience.

New compounds are listed only in this Table; they are not mentioned again in the Experimental section.

All these compounds, except trimethylgallium–ammonia, have unusually large Trouton constants, rising to the remarkable value 33 for the dimethyl selenide complex. Brown and Davidson (*loc. cit.*) record large Trouton constants for some of the corresponding trimethylaluminium compounds, *e.g.*, 27·2 for $\mathrm{Me_3\overset{-}{Al}{-}\overset{+}{S}Me_2}$. In these instances high Trouton constants are probably largely caused by dipole association, since co-ordination compounds of this type generally have large dipole moments. For example, Laubengayer and Finlay (*J. Amer. Chem. Soc.*, 1943, **65**, 884) report Trouton constants of 33·0 and 32·8 for $\mathrm{MeEt\overset{+}{O}{-}\overset{-}{B}F_3}$ and $\mathrm{Et_2\overset{+}{O}{-}\overset{-}{B}F_3}$ respectively (dipole moments 5·07 and 4·92 D.). The effect may in some cases be enhanced when the process of evaporation is accompanied by partial or complete dissociation of the complex. The compounds of trimethylgallium with the trimethyls of the VB elements from nitrogen to antimony must have a high degree of molecular symmetry (like hexamethylethane), and are all solid at room temperature with the exception of $\mathrm{Me_3\overset{-}{Ga}{-}\overset{+}{S}bMe_3}$, which is the least stable, being wholly dissociated as vapour. Its melting range +0·3—2·2° may be caused by some dissociation in the liquid (a slight excess of the more volatile component, trimethylgallium, may be present in the vapour above the melting solid). The less symmetrical compounds with dimethyl ether, and dimethyl sulphide, selenide, and telluride are all liquids of fairly low freezing point.

With the exception of the compounds with dimethylamine, methylamine, and ammonia, which decompose when heated (see below), relative stabilities were determined by dissociation measurements in the vapour phase. Heats of dissociation, derived from the slope of the log K_p (dissociation constant)–T^{-1} graph, were also measured in favourable cases; when the dissociation is of the order of 90% or more the values for ΔH are only approximate. The uncertainty in ΔH is probably about ± 1 kcal./g.-mol. in the case of $Me_3\overset{-}{Ga}-\overset{+}{P}Me_3$ and rather greater for the others; the order of stability is more reliable. These measurements are summarised in Table II.

TABLE II.

Relative stability of the co-ordination compounds of trimethylgallium.

Donor molecule.	Dissociation (100°), %.	K_p (atm.) at 100°.†	$-\Delta H$.*
NMe_3	~0	Very small	—
PMe_3	<10 (22% at 130°)	0·03 (at 130°)	18
$AsMe_3$	75	1·34	10
$SbMe_3$	100	(∞)	—
$BiMe_3$	No compound formed even in liquid.		
OMe_2	70	1·07	9·$_5$
SMe_2	~90	~2·5	~8
$SeMe_2$	78	1·52	10
$TeMe_2$	~90	~2·5	~8

* Heat of dissociation, kcals./g.-mol. † Dissociation constant.

The order of decreasing donor properties, from Table II, is :

Group VB : >N >P >As >Sb >Bi
Group VIB : >O >Se >S = Te

Relative Acceptor Properties : Group IIIB.—These results, in addition to showing the relative donor properties of the methyls of the VB and VIB elements, which are further discussed below, enable the acceptor properties of trimethylgallium to be compared with those of trimethylboron and trimethylaluminium. Trimethylboron–trimethylamine is 92% dissociated at 100° (Brown and Gerstein, *ibid.*, 1950, **72**, 2923), and trimethylboron forms a compound with trimethylphosphine of as yet unknown heat of dissociation (Brown and Harris, *ibid.*, 1949, **71**, 2751). Trimethylboron does not react with dialkyl ethers. Brown and Davidson (*loc. cit.*) obtained an order of stability N > P > O > S for the corresponding compounds of trimethylaluminium (other donor elements were not investigated, but methyl chloride did not react), all of which are much more stable than their gallium analogues. Hence trimethylgallium, though a stronger acceptor than trimethylboron, is weaker than trimethylaluminium. Trimethylindium is evidently practically devoid of acceptor properties since it forms no ammines or ether complexes even at −35° (Dennis, Work, and Rochow, *J. Amer. Chem. Soc.*, 1934, **56**, 1047), while trimethylthallium may be separated from its very unstable ether complex $Me_3\overset{-}{Tl}-\overset{+}{O}Et_2$ by distillation under reduced pressure (Gilman and Jones, *ibid.*, 1946, **68**, 517). Thus, in the absence of any quantitative measurements on indium and thallium alkyls, the relative acceptor properties of the trimethyls of the Group IIIB elements may provisionally be written :

$$Al > Ga\ (>Tl\,?) > B > In.$$

The position of aluminium at the head of this somewhat irregular series is in agreement with the fact that only trimethylaluminium is dimeric in the vapour phase [trimethylthallium (*idem, ibid.*), which is liable to explode on heating, is monomeric in benzene solution]. Only in aluminium is the tendency to form four covalent bonds sufficiently strong to stabilise the type of electron-deficient ring structure probably present in Al_2Me_6; the hydrides of boron and gallium are, however, dimeric (B_2H_6, Ga_2H_6), while aluminium hydride is polymeric $(AlH_3)_n$.

The high stability of the trimethylaluminium compounds investigated by Davidson and Brown (*loc. cit.*) prevented the measurement of heats of dissociation, except in the case of the dimethyl sulphide complex $Me_3\overset{-}{Al}-\overset{+}{S}Me_2$ ($\Delta H = -19 \pm 2$ kcals./g.-mol., 27% dissociated at 100°). The comparative stabilities of the other compounds with NMe_3, PMe_3, and Me_2O, which did not dissociate perceptibly in the temperature range investigated, were determined by displacement reactions. Trimethylaluminium–trimethylphosphine ($Me_3\overset{-}{Al}-\overset{+}{P}Me_3$) gave trimethylaluminium–trimethylamine ($Me_3\overset{-}{Al}-\overset{+}{N}Me_3$) and trimethylphosphine quantitatively when heated with trimethylamine, showing that trimethylamine is a stronger donor molecule than trimethylphosphine. In the present work trimethylphosphine similarly displaced trimethylarsine quantitatively from its trimethylgallium complex, and trimethylamine quantitatively displaced trimethylphosphine :

$$Me_3\overset{-}{Ga}-\overset{+}{As}Me_3 + PMe_3 \longrightarrow Me_3\overset{-}{Ga}-\overset{+}{P}Me_3 + AsMe_3$$

and

$$Me_3\overset{-}{Ga}-\overset{+}{P}Me_3 + NMe_3 \longrightarrow Me_3\overset{-}{Ga}-\overset{+}{N}Me_3 + PMe_3$$

Similarly, as expected, trimethylamine displaced trimethylarsine. This method of investigating comparative stabilities is not suitable when the dissociation of the complex is appreciable at or a little below room temperature. For example, when trimethylgallium–trimethylarsine was heated with one molar equivalent of methyl ether (which forms a more stable complex, see Table II), until all was gaseous, the mixture then being cooled and subjected to fractional condensation, methyl ether was recovered quantitatively. In this instance methyl ether was by far the most volatile component present and its removal from the mixture by fractional condensation doubtless resulted in a displacement of the equilibrium :

$$Me_3\overset{-}{Ga}-\overset{+}{As}Me_3 + OMe_2\uparrow \rightleftharpoons Me_3\overset{-}{Ga}-\overset{+}{O}Me_2 + AsMe_3$$

Relative Donor Properties : Group Vb.—Towards a constant acceptor molecule, trimethylgallium, the donor properties of the Group Vb trimethyls diminish steadily from nitrogen to bismuth. Since the formation of a co-ordination compound by a donor molecule consists essentially of the process, $Me_3M \longrightarrow Me_3\overset{+}{M}- + e^-$, relative donor properties should be directly related to the first ionisation potentials, which are not known for the methyl derivatives concerned here. Three types of reaction may, however, be compared with the formation of a co-ordination compound. These are : (*a*) Reaction as a base, $Me_3M + HX \rightleftharpoons Me_3HM^+ + X^-$. Only the amines and the much weaker trialkylphosphines are basic in this direct sense, so the comparison cannot be carried far. (*b*) Reaction with methyl iodide, $Me_3M + MeI = Me_4M^+ + I^-$. Here it may be noted that trimethylbismuth alone of the series does not form a quaternary compound with methyl iodide. The comparative stabilities of the others are not known quantitatively; the greater *rate* of reaction of trimethylphosphine than of trimethylamine (Davies and Evans, *J.*, 1934, 244) is probably due to differences in the degree of steric hindrance since the C–N–C angle in NMe_3 (108° ± 4°; Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036) is greater than the C–P–C angle in PMe_3 (100° ± 4°; Springall and Brockway, *ibid.*, 1938, **60**, 996). (*c*) Reaction with oxygen, $2Me_3M + O_2 = 2Me_3\overset{+}{M}-\overset{-}{O}$. Here there is an apparent discrepancy, in the contrast between the difficulty of oxidation of trimethylamine, which requires hydrogen peroxide, and the extreme ease of oxidation (sometimes amounting to spontaneous inflammability) of all the other members of the series. This, however, is almost certainly due to the possibility of quinquevalency in all the elements except nitrogen. The trialkyl oxides, except $R_3\overset{+}{N}-\overset{-}{O}$, are probably mesomeric between $R_3\overset{+}{M}-\overset{-}{O}$ and $R_3M{=}O$, in which case the very easy reaction with molecular oxygen would proceed through the formation of an intermediate compound, for example :

$$Me_3M + O_2 \longrightarrow Me_3M{=}\overset{+}{O}-\overset{-}{O} \xrightarrow{Me_3M} 2Me_3M{=}O$$

(M = P, As, Sb, Bi, but *not* N.)

Reaction with a suitable acceptor molecule such as the trialkyls of some of the Group III elements appears to be the most reliable way of investigating relative donor properties. Stability comparisons, with transition metal halides as acceptor molecules, are complicated by the influence of solubility, since in a competition (or displacement) reaction between two donor molecules for a given acceptor the least soluble co-ordination compound is likely to separate irrespective of relative stabilities unless the equilibrium is very strongly in favour of the more soluble compound. However, the steady gradation in donor properties from nitrogen to bismuth found in the present work is entirely in agreement with the known properties of transition-metal and other co-ordination compounds. Nitrogen (tervalent) forms complexes with a very large number of salts, and is generally regarded as the strongest donor atom. Phosphorus, in the alkyl- and aryl-phosphines, combines with many of the transition metals, also with the Group IB and IIB elements. Similar arsenic compounds combine with the same elements, but it may be significant that fewer of these compounds have been described, while antimony and bismuth act as donor atoms only to very powerful acceptors such as platinum and palladium. It is important that the donor properties of these elements are greatly influenced by the groups to which they are attached.* While ammonia forms so many metal complexes, triphenylamine does not combine even with platinum. The apparently more powerful donor properties of the trialkyl- and triaryl-phosphines and -arsines would seem to be in disagreement with the above generalisation. This is to be attributed to the possibility of π-bonding between donor and acceptor in the case of complexes between donor elements with vacant low-energy d orbitals (*i.e.*, excluding nitrogen) and transition elements with d orbitals which are partly or just completely filled, as suggested by Chatt (*J.*, 1949, 3340; 1950, 2301; *Nature*, 1950, **165**, 637). This aspect is more fully discussed in the next section.

Relative Donor Properties: Group VIB.—To trimethylgallium dimethyl ether, sulphide, selenide, and telluride are much weaker donors than trialkylamines or trialkylphosphines. The order within the group is rather peculiar, $O > Se > S = Te$. Again, the ionisation potentials of these compounds are not known, but applying the comparisons made in the previous section, it is found that: (*a*) Only the ethers show any basic properties, in accordance with the position of oxygen at the head of the donor series given above.

(*b*) In contrast to the ethers, dialkyl sulphides, selenides, and tellurides readily combine with methyl iodide, forming stable 'onium salts. The only known trialkyloxonium salts have to be prepared by other means; they are highly reactive, alkylating agents, and usually unstable to heat.

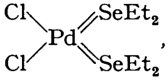
(*c*) Doubtless for the same reasons as apply to Group VB, the sulphides, selenides, and tellurides are readily oxidised; indeed, the ease of oxidation increases with atomic weight.

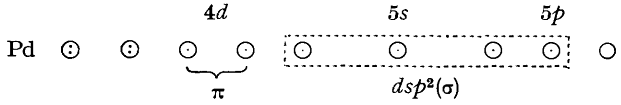
There are two striking features in the above order, (1) that selenium appears out of place, (2) that oxygen heads the order. It is difficult to comment on the former in relation to the known co-ordination compounds of this group, since there is no information allowing a comparison between the stabilities of the complexes formed by sulphides, selenides, and tellurides. The position of oxygen merits some consideration. With boron, aluminium, gallium, and possibly tin and titanium, oxygen co-ordinates more readily than sulphur (there is practically no information about selenium and tellurium in relation to some of these acceptor atoms other than that contained in this work). On the other hand, whereas sulphides, selenides, and tellurides co-ordinate with mercuric, palladous, and platinous halides, ethers do not. Considering how oxygen differs from the other elements of its group one finds (i) that its electronegativity is larger than that of any of the other donor atoms under discussion, and (ii) having no stable d orbital it cannot form double bonds of the type $R_2O{=}O$, unlike, for example, $R_2Se{=}O$.

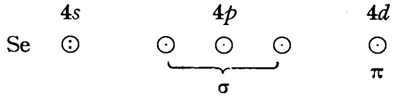
With regard to (i), in the trialkyloxonium salts, which are less stable than the 'onium salts of sulphur, selenium, and tellurium, a formal positive charge is imposed on the oxygen atom. This is doubtless reduced somewhat by polarisation of the three C–O bonds in the sense $\overset{\delta+}{C}{-}\overset{\delta-}{O}$, but a positive charge on a highly electronegative atom is likely to cause some instability. In its co-ordination complexes, on the other hand, the oxygen atom may be held to the acceptor atom by electrostatic attraction between the negatively charged lone pairs of the oxygen and the positive centre of the acceptor. This would be the type of bonding described by Lennard-Jones and Pople (*Proc. Roy. Soc.*, 1951, *A*, **205**, 155) in their discussion of hydrogen bonding, the formation of many salt hydrates, and some co-ordination compounds. It is possible that the co-ordination compounds of oxygen differ from those of other donor atoms in that their bonding is predominantly electrostatic in nature rather than covalent. With regard to the covalency limit of three [see (ii) above], one finds that all the stable complexes containing sulphur, selenium, or tellurium as donor atoms involve acceptor atoms with incomplete or just completed d groups, *e.g.*, palladium, silver, and mercury; in all these instances no corresponding oxygen compounds have been described. It seems very likely that the former have not the true co-ordination structure, but are mesomeric between the latter and a formulation in which the donor atom is bound to the metal by a double bond, for which the d orbital of the metal

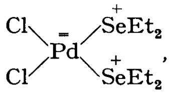
---

* The author is indebted to a Referee for drawing his attention to this point.

contributes the π-component. For example, the compound $PdCl_2,2SeEt_2$ (m. p. 45°; Fritzmann, *Z. anorg. Chem.*, 1924, **133**, 119) may be formulated as  , with the following atomic orbital configurations:



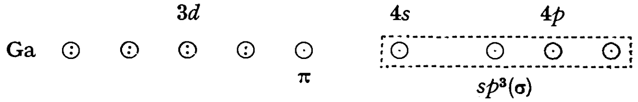


In this formulation, in contrast to the true co-ordination structure,  , the electropositive metal atom is not loaded with a double negative charge. That the co-ordination structure of these compounds contributes largely to the mesomeric form follows from the high diple moments of their *cis*-forms (for examples see "Tables of Electric Dipole Moments," L. G. Wesson, Massachusetts Inst. Technology, 1948; the moment of the compound quoted is not known, but that of the *cis*-form of its platinum analogue is 9·1 D.). The non-combination of ethers with such strong acceptor molecules as the halides of palladium, platinum, and mercury may thus be due in part to the impossibility of this type of mesomeric stabilisation when oxygen is the donor atom. This type of stabilisation will be more pronounced, the greater the tendency of the donor atom to assume a quadricovalent configuration. This tendency, judged by the relative ease of oxidation of sulphides, selenides, and tellurides, increases with atomic weight in that order. It is not therefore surprising to find that the stability of the complexes between mercuric halides and dimethyl sulphide, selenide, and telluride increases in the order, S, Se, Te, the evidence for this being the relative ease with which the complexes lose the donor molecule when heated or exposed to the air (Coates and Miss V. Hodson, unpublished observations). Similarly, two compounds $AgI(TeMe_2)_2$ and $(AgI)_2TeMe_2$ have been isolated by the addition of an acetone solution of dimethyl telluride to a solution of silver iodide in concentrated aqueous potassium iodide; these are unstable and smell strongly of dimethyl telluride. Dimethyl selenide gives a colourless compound $(AgI)_2SeMe_2$, which is so unstable that it quickly shows the yellow colour of silver iodide when exposed to air, while dimethyl sulphide and diethyl ether show no sign of combining with a solution of silver iodide.

The increase in the stability of trimethylgallium co-ordination compounds as one passes from dimethyl sulphide to dimethyl selenide may be explained in a similar way, *viz.*, by the increased mesomeric contribution of the double bonded structure (*b*):

$$(a.)\quad Me_3\overset{-}{Ga}-\overset{+}{Se}Me_2 \qquad\qquad Me_3Ga{=}SeMe_2\quad (b.)$$

The electronic configuration of the gallium atom in structure (*b*) is:



The donor properties of the Group VIB elements, *i.e.*, the tendency to form true co-ordination compounds with the structure of type (*a*), diminish with increasing atomic weight. This is evident from their behaviour, described below, towards trimethylaluminium, and also by analogy with Group VB elements. It is suggested that the ability of the Group VIB elements to form double-bonded structures of type (*b*) increases with atomic weight. Since the stability of the mesomer must depend on a balance between both these tendencies, the irregularity O > Se > S = Te in the observed stability series may be at least qualitatively accounted for.

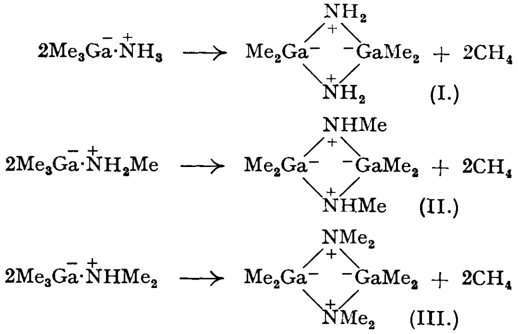
These suggestions can be tested by reference to aluminium which, having no *d* group, cannot form (*b*)-type double-bonded structures. In contrast to trimethylgallium, trimethylaluminium should form a *weaker* compound with dimethyl selenide than with dimethyl sulphide and a still weaker compound with dimethyl telluride. The compound trimethylaluminium–dimethyl selenide (which was not mentioned by Brown and Davidson, *loc. cit.*) was therefore prepared and its stability measured by gas-phase dissociation; from the slope of the $\log_{10} K_p$–T^{-1} graph, ΔH, the heat of the reaction $\mathrm{Me_3\overset{-}{Al}{-}\overset{+}{Se}Me_2} \rightleftharpoons \frac{1}{2}\mathrm{Me_6Al_2} + \mathrm{SeMe_2}$, is 6 kcals./g.-mol. Since the heat of the reaction $\frac{1}{2}\mathrm{Me_6Al_2} \rightleftharpoons \mathrm{Me_3Al}$, $\Delta H'$, is $-10{\cdot}1$ kcals./g.-mol. (Laubengayer and Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477), the heat of the dissociation $\mathrm{Me_3\overset{-}{Al}{-}\overset{+}{Se}Me_2} \rightleftharpoons \mathrm{Me_3Al} + \mathrm{SeMe_2}$ is 16 kcals./g.-mol. The compound is 40% dissociated at 100° and 54% at 130°, whereas Brown and Davidson found that the heat of dissociation of $\mathrm{Me_3\overset{-}{Al}{-}\overset{+}{S}Me_2}$ is 19 kcals./g.-mol. and the extent of dissociation is 27% at 100°. Trimethylaluminium–dimethyl telluride was also prepared; its dissociation in the temperature range 100—150° was so great (approaching 100% at 140°) that the heat of dissociation could not be measured. The vapour-pressure constants of these compounds are given in Table I. It is clear that to aluminium, with no possibility of double bonding by means of a *d* orbital, the donor properties of the Group VIB elements decrease with increasing atomic weight in the normal way, O > S > Se > Te.

It is, of course, probable that the co-ordination compounds of the Group VB elements with acceptor atoms with suitable *d* orbitals are also stabilised by partial double bonding. In this series, however, as far as gallium is concerned, any such effect would appear to be subordinated to the decrease of true donor tendency with increasing atomic weight. That some double bonding by *d* orbitals contributes to the structure of various platinum compounds with phosphines and with olefins has already been indicated by Chatt (*loc. cit.*). The dipole moments of the *cis*-series of complexes between platinous chloride and trimethyl-phosphine, -arsine, and -stibine decrease in the order 10·7, 10·5, 9·2 (Jensen, *Z. anorg. Chem.*, 1936, **229**, 225), although the lengths of the co-ordinate bonds must increase with the atomic weight of the donor atom. It is probable that increasing contribution of type-(*b*) double-bonded structures more than offsets the increase of bond length and causes the net decrease of dipole moment.

The relative importance of π-bonding by *d* orbitals is clearly much greater with platinum than with gallium, since Chatt (*J.*, 1951, 652) has recently shown that the co-ordinating affinity of the *n*-propyl derivatives of the Group VB elements towards platinous chloride is in the order P > As > Sb > N > Bi. The possible stabilisation of co-ordination compounds by mesomerism involving VB elements in the quinquecovalent state is at present being studied in this laboratory.

In general, it would appear very likely that mesomerism between the true co-ordination structure $\overset{-}{\mathrm{A}}{-}\overset{+}{\mathrm{B}}$ and the double-bonded structure A=B (involving *d* orbitals in the π-component) plays an important part in stabilising all co-ordination compounds in which the donor and acceptor atoms have appropriate *d* groups.

Decomposition of the Compounds between Trimethylgallium and Ammonia, Methylamine, and Dimethylamine.—Each of these compounds decomposed when heated, with the loss of one molecule of methane per gallium atom. The products are dimeric in the gas phase and probably have the four-membered ring structure * already assigned to some similar compounds of boron and aluminium (*e.g.*, Brown and Davidson, *loc. cit.*).


$2\mathrm{Me_3\overset{-}{Ga}{\cdot}\overset{+}{N}H_3} \longrightarrow$ (I.) $+ 2\mathrm{CH_4}$

$2\mathrm{Me_3\overset{-}{Ga}{\cdot}\overset{+}{N}H_2Me} \longrightarrow$ (II.) $+ 2\mathrm{CH_4}$

$2\mathrm{Me_3\overset{-}{Ga}{\cdot}\overset{+}{N}HMe_2} \longrightarrow$ (III.) $+ 2\mathrm{CH_4}$

Some properties of these compounds are given in Table III.

---

* The names, (I) *cyclo*(bisammonium bisdimethylgallide), (II) *cyclo*(bismethylammonium bisdimethylgallide), and (III) *cyclo*(bisdimethylammonium bisdimethylgallide), are tentatively suggested for this novel type of compound. ED.

TABLE III.

Associated condensation compounds derived from trimethylgallium.

Compound.	M. p.	B. p. (extrap.).	*A*.*	*B*.*	L_V.†	Trouton const.	Temp. range.
(III)	—	—	1450	4·850	6·63 ‡	—	30— 55°
(III)	—	—	2712	12·652	12·46 ‡	—	80—150
(II)	—	—	2666	8·656	12·2	—	30— 90
(II)	—	226°	2078	7·045	9·5	19·1	90—140
(I)	97·2—97·5°	—	3940	11·72	18·0 ‡	—	50— 90
(I)	—	212	2800	8·648	12·8	26·4	100—140

* $\log_{10}$ (v. p.)$_{mm.}$ = − (*A*/*T*) + *B*.

† Latent heat of evaporation, kcals./g.-mol.

‡ Latent heat of sublimation.

FIG. 1.

Vapour pressure of ($Me_2Ga{-}NHMe)_2$ (II), *liquid.*

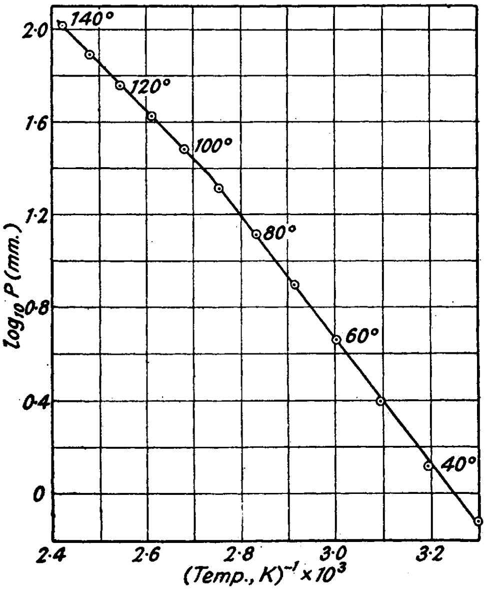
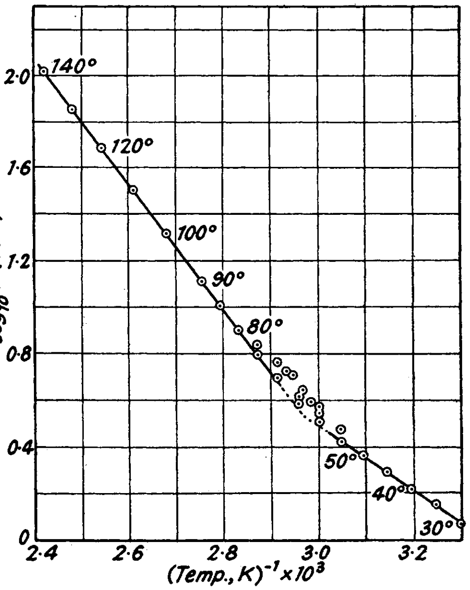


FIG. 2.

Vapour pressure of ($Me_2Ga{-}NMe_2)_2$ (III), *solid.*



Trimethylgallium–ammonia begins to evolve methane at 70° and decomposes into (I) and methane quite rapidly at 90°. On further heating above 140° (I) begins to form more methane and a white non-volatile substance of amorphous appearance, almost certainly polymeric :

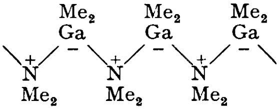
$$(Me_2Ga{-}NH_2)_2 \xrightarrow{>140^\circ} [\cdot MeGa{-}NH\cdot]_n + CH_4$$

Trimethylgallium–methylamine is more stable, since it begins to split off methane only at 120—130°. The product (II) is stable at least to 180° without further methane evolution, although one hydrogen atom is still bonded to each nitrogen. Trimethylgallium–dimethylamine begins to decompose into (III) and methane at 115—130°, so it is of comparable stability to the methylamine compound; (III) is stable at least to 180°.

Similar compounds of boron and aluminium have been described [boron : Wiberg, " F.I.A.T. review of German Science, 1939—1946," published 1949, Inorganic Chemistry, Part I, pp. 129—137; Goubeau, *ibid.*, pp. 228—234; aluminium : Bähr, *ibid.*, Part II, pp. 159—160; the aluminium analogue of (III) : Brown and Davidson, *loc. cit.*]. The loss of methane from the co-ordination compounds of trimethylboron with ammonia, methylamine, and dimethylamine requires much higher temperatures than are necessary to decompose those of aluminium and gallium. The boron compounds decompose at 280—330°, while those of aluminium appear to be somewhat less stable than their gallium analogues, their decomposition temperatures being 57—70° (NH_3), 55—57° (NH_2Me), and 90—120° ($NHMe_2$), in contrast to 70°, 120—130°, and 115—130°. The molecular weights of the boron analogues of (I) and (II) indicate a reversible equilibrium between the mono- and di-meric (ring) forms, while $Me_2B{-}NMe_2$ is monomeric

(Goubeau, *loc. cit.*; Coates, *J.*, 1950, 3481). Like (I), $Me_2Al–NH_2$ (m. p. 134·2°) was found to be dimeric (cryoscopically in liquid ammonia). The aluminium analogue of (III), *viz.*, $Me_2Al{\cdot}NHMe$, is much less stable than (II), since it loses methane even at its melting point ~110°, giving a polymeric product, and its molecular complexity was not determined.

Some of the physical properties of compounds (II) and (III) are rather peculiar. The vapour pressures of these compounds are plotted in Figs. 1 and 2; (II) shows a discontinuity at 90°, latent heats of evaporation above and below this temperature being 9·5 and 12·2 kcals./g.-mol. respectively, with, however, no apparent phase change since the compound is liquid throughout the measured temperature range 30—140°. The latent heat from 90° to 140° is unusually low for this class of compound, the Trouton constants of which are generally rather high. The compound (III) derived from dimethylamine is solid at least up to 150° and appears to have a remarkably low latent heat of sublimation from 30° to about 55°, *viz.*, 6·6 kcals./g.-mol. Between 55° and 80° the vapour pressure was erratic and the various points in Fig. 2 shown for this region were obtained in several independent experiments. The remainder of the graph was reproducible. In the 55—80° range the higher vapour pressures were obtained on cooling from a higher temperature, and the lower points on heating. The most extraordinary feature is the apparent *increase* of latent heat of sublimation in this temperature range, amounting to 5·9 kcals./g.-mol., which suggests that the high-temperature form has a lower energy than the low-temperature form. Crystals condensing at or near room temperature are very well formed, with sharply defined faces and angles, but those condensing above about 80° are of dendritic habit, with a strong tendency to form rounded edges. It is possible that the low- and high-temperature forms differ in chemical bonding, *e.g.*, the former might be a molecular crystal consisting of four-membered cyclic molecules, while the latter might perhaps have a linear polymeric structure :



EXPERIMENTAL.

All the compounds described were prepared and studied in a vacuum apparatus of the type described by Stock (" The Hydrides of Boron and Silicon," Cornell, 1933) and by Sanderson (" The Vacuum Manipulation of Volatile Compounds," Wiley, 1948). In general, weighed quantities of the two components were condensed in the " high-temperature bulb " (Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780; Sanderson, *op. cit.*), and vapour pressures and thermal dissociations were measured in this. All the compounds were sufficiently volatile at room temperature to allow of their weights being checked directly after these measurements. The methane evolved in the decomposition of compounds containing active hydrogen was identified by its vapour pressure at −183° and transferred to a gas burette by a Töpler pump.

Preparation of Materials.—Trimethylgallium was prepared by a modification of Wiberg, Johannsen, and Stecher's method (*Z. anorg. Chem.*, 1943, **251**, 114). Metallic gallium (6·75 g.) and dimethylmercury (37 g.), with a trace of mercuric chloride, were heated to boiling in a bulb sealed to a 20-cm. fractionating column packed with Fenske helices, in an atmosphere of dry nitrogen (1 atm. pressure). After 2 hours the temperature of reflux at the top of the column began to fall from 92° (b. p. of $HgMe_2$), and after 5 hours became steady at 55—56° (b. p. of $GaMe_3$). From time to time during the next 3 days small amounts of pure trimethylgallium were taken off from the top of the column until a residue of mercury and about 1 c.c. of liquid, consisting mainly of trimethylgallium, were left. The conversion was virtually complete and no decomposition occurred. The distillate of trimethylgallium was frozen and transferred in a nitrogen atmosphere to the vacuum apparatus, where it was stored under its own vapour pressure.

Trimethylamine was purified by treatment with phosphoric anhydride, which removes primary and secondary amines (Brown, Taylor, and Gerstein, *J. Amer. Chem. Soc.*, 1944, **66**, 431); dimethylamine was prepared from *N*-nitrosodimethylamine and dried by shaking with a liquid sodium–potassium alloy. Methylamine was purified by boiling a 90% neutralised solution, which expels practically all ammonia present, followed by recrystallisation of the picrate. The free base was then dried with potassium, which dissolves to give a blue solution in the anhydrous amine, followed by fractional distillation in a 30-cm. low-temperature fractionating column. Ammonia from a cylinder was dried by sodium and used without further purification.

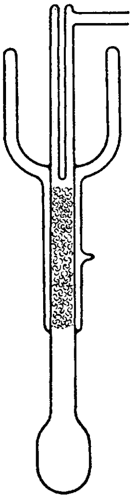
Trimethylphosphine was obtained by the action of methylmagnesium iodide on phosphorus trichloride; it was separated as the silver iodide complex $(Me_3P,AgI)_4$, which was dried and heated in a vacuum, giving pure trimethylphosphine (Mann and Wells, *J.*, 1938, 702). Trimethylarsine was prepared similarly by thermal decomposition in a vacuum of the palladium compound $(Me_3As)_2PdCl_2$ (*idem, ibid.*). Trimethyl-stibine and -bismuth were prepared by the Grignard reaction from the chlorides, and were purified by fractionation in a nitrogen atmosphere at low pressure in the vacuum apparatus.

Methyl ether, from sodium methoxide and methyl iodide in methanol, was purified by means of the low-temperature fractionating column. Methyl sulphide was purified by fractionation of the commercial product. Methyl selenide, prepared by the method of Bird and Challenger (*J.*, 1942, 570), and methyl telluride (*idem, ibid.*, 1939, 166) were purified by fractionation in the vacuum apparatus.

Analysis.—The compounds described were not subjected to analysis, since they were all prepared in the vacuum apparatus from materials of known purity, and as nothing is lost by this (quantitative) technique, the method of preparation itself constitutes an analysis. In decompositions involving the formation of methane, the latter was always measured in a gas burette.

Fractionation in the vacuum apparatus by the method of fractional condensation was greatly facilitated by use of the unit shown in Fig. 3. The substance was evaporated from the bulb and was condensed in the low-temperature bath at the top of the column held at such a temperature that the gas pressure was 1—2 mm. Fractionation took place in the vacuum-jacketed column packing (Fenske helices); gas was slowly taken off from the top, and either transferred directly to a vapour-pressure bulb or passed through the usual set of three or four fractional condensation U-tubes.

FIG. 3.



To illustrate the experimental methods used, the preparation of two compounds is described, *viz.*, trimethylgallium–dimethyl ether and the compound $(Me_2Ga{-}NMe_2)_2$ obtained by heating trimethyl-gallium–dimethylamine.

Trimethylgallium–Dimethyl Ether.—20·4N-c.c. (*i.e.*, c.c. at N.T.P.) of methyl ether (0·911 millimol.) were measured at a pressure of 47 mm. in a gas-volume-measuring apparatus (see Sanderson, *op. cit.*) and transferred to the high-temperature bulb (164-c.c. volume); the same volume of trimethylgallium was measured and condensed in the same high-temperature bulb. These two components were isolated from the remainder of the apparatus by raising mercury in the manometer tube which formed the connection between the high-temperature bulb and the vacuum apparatus, and the contents of the bulb were allowed to warm to room temperature. The bulb was then surrounded by an oil-bath (thermostat), and vapour pressures were measured at 5° intervals. When the compound was entirely gaseous (65°), the temperature was raised a further 10° and then pressures were measured at 5° intervals up to 120°, a similar series of pressures being measured at decreasing temperatures. From the known volume, temperature, and pressure, the total number of moles of gas was obtained. From this and the number of moles (0·911) of complex introduced into the bulb, the amount of dissociation and the equilibrium constant (K_p) were calculated for each temperature. The slope of the log K_p–T^{-1} plot gave the heat of dissociation. After the experiment the compound was transferred to a weighing tube, attached to the vacuum apparatus by a ground joint and in which the greased tap could be protected from the vapour of the compound by a mercury seal (Stock, Sanderson, *opp. cit.*), and weighed (145·9 mg.; 0·911 millimol. = 146·6 mg.). Its composition is thus settled.

cyclo-(1 : 3-*Bisdimethylammonium* 2 : 4-*Bisdimethylgallide*).—Trimethylgallium (0·3662 g.), equivalent to 71·5N-c.c., was transferred to the high-temperature bulb and kept at −183° while 71·5N-c.c. of dimethylamine were measured by volume and condensed on the trimethylgallium. On warming to room temperature the mixture partly melted and then solidified. When the high-temperature bulb was heated in the thermostat for vapour-pressure measurements, the solid *compound* was observed to melt over the range 33·3—33·6° and then pressures were measured up to 110°. Above this temperature the pressure slowly increased when the temperature was held constant. The bulb was then heated to 170° and kept at that temperature until no further pressure change occurred. On cooling, white crystals were deposited on the walls of the bulb. The pressure was 83 mm. when the bulb was cooled in liquid oxygen (v. p. of methane = 81·1 mm. at −183°), showing that the gas present was methane. The latter was pumped into the gas burette by means of a Töpler pump and measured 71·2N-c.c.; thus one mole of methane was formed from one mole of trimethylgallium; the residue therefore had the composition $(Me_2Ga{\cdot}NMe_2)_x$. After removal of the methane the vapour pressure of the residue was determined, followed by measurements of temperature and pressure when all the solid had vaporised. From the latter the volume corresponded to 35·7 c.c. at 170°, 35·8 at 175°, and 35·8 at 180° (Calc. for $x = 2$, 35·75 c.c.).

These methods were used to prepare and characterise the *compounds* listed in Tables I and III.

Some Co-ordination Compounds of Dimethyl Telluride.—Silver iodide–bis(dimethyl telluride). Dimethyl telluride (3·05 g., 0·02 mol.) in acetone (20 c.c.) was added to a solution of silver iodide (2·35 g., 0·01 mol.) in nearly saturated aqueous potassium iodide (10 c.c.). A white precipitate appeared which dissolved on warming; on cooling, the long colourless needles (4·2 g., 78%) which separated were collected and washed with a little acetone. Recrystallisation from acetone was accompanied by some decomposition and deposition of a little white insoluble matter which was removed before crystallisation of the product, m. p. 73—74° (corr.) with softening at 60—62° (sealed m. p. tube). The product, which smells strongly of dimethyl telluride, loses the latter quantitatively when heated in a vacuum at 180° (yellow silver iodide begins to appear at 90°); it was analysed by means of this decomposition, 0·1744 g. giving 0·0778 g. of silver iodide (completely soluble in concentrated aqueous potassium iodide). Thus the compound contained 20·4% of silver [$AgI(TeMe_2)_2$ requires Ag, 19·6%]. A somewhat high silver content would be expected since the compound so easily loses dimethyl telluride. An acetone solution gives a heavy yellow precipitate of silver iodide with a solution of silver nitrate; this points to a constitution $[Me_2Te{-}Ag{-}TeMe_2]^+ I^-$.

Dimethyl telluride–bis(silver iodide). Dimethyl telluride (6·1 g., 0·04 mol.) in acetone (35 c.c.) was added to a solution of silver iodide (18·8 g., 0·08 mol.) in concentrated aqueous potassium iodide (80 c.c.). A white precipitate appeared together with a heavy yellowish oil. When heated for a short time the oil dissolved and a thick white precipitate appeared. This was collected and washed with acetone, concentrated aqueous potassium iodide, and finally acetone. This product (22 g., 88%) was insoluble in water, alcohol, acetone, or benzene; when it was heated with alcohol or benzene, the yellow colour of silver iodide appeared, but vanished again on cooling. It melted at 137—138° (corr., sealed tube) with decomposition to a black liquid [Found : Ag, 34·3%, by conversion into silver iodide by 1 hour's heating at 180° in high vacuum. $TeMe_2(AgI)_2$ requires Ag, 34·4%].

Dimethyl Selenide-Bis(silver Iodide).—Dimethyl selenide (3 c.c., slightly more than one molar equivalent) in acetone (20 c.c.) was added to silver iodide (8·5 g.) in saturated aqueous potassium iodide (15 c.c.). Distilled water was added gradually to the warmed solution until precipitation began. The small colourless plates (7·5 g., 71%) which separated were filtered off, and washed first with a little acetone containing some dimethyl selenide, then with pentane also containing dimethyl selenide. Passage of air through the crystals on a filter plate caused dissociation, and appearance of the yellow colour of silver iodide {Found (as above) : Ag, 37·8%. $[Me_2Se(AgI)_2]_n$ requires Ag, 37·3%}. The compound did not melt when heated in a sealed tube, but softened at 84—85° and then gradually became yellow and evolved dimethyl selenide. The compound, which had a strong odour of dimethyl selenide, did not dissolve in any of the usual solvents, and it is probable that both it and the tellurium compound of similar composition have polymeric structures.

Dimethyl telluride forms a compound with cadmium iodide, which was not analysed, but does not combine with anhydrous nickel bromide dissolved in ethanol. Work on dimethyl telluride was abandoned at this stage on account of its rather uncongenial properties.

The author thanks the Director of the Chemical Research Laboratory, Teddington, for the kind loan of the gallium used in this work, and Mr. N. D. Huck of this Department for providing a specimen of pure trimethylaluminium.

The University, Bristol. [*Received, March* 13*th*, 1951.]