514. *Trimethylgallium. Part II.* Reactions with Hydroxy- and Similar Compounds.*

By G. E. Coates and R. G. Hayter.

Trimethylgallium forms weak co-ordination compounds with acetone and methyl cyanide, but with methanol, methanethiol, methaneselenol, and acetic acid elimination of methane gives dimeric products, *e.g.*, $(Me_2Ga{\cdot}SMe)_2$. The methoxy-derivative is unaffected by trimethylamine, whereas the others are split reversibly, *e.g.*, to $MeS{\cdot}\overset{-}{Ga}Me_2{\cdot}\overset{+}{N}Me_3$. Similar dimeric compounds are obtained from phenol, *p-tert.*-butylphenol, *p*-chlorophenol, thiophenol, and selenophenol; all these products are split by trimethylamine. Acetylacetone and salicylaldehyde give monomeric products. 2-Dimethylaminoethanol gives a dimeric cyclic compound in which the oxygen atoms appear to be co-ordinated to gallium in preference to the nitrogen atoms.

Whereas the final products of the reactions of many organometallic compounds with a variety of substances have been investigated, usually after the reaction mixture has been decomposed with water, the primary reaction products have received little attention. They are the subject of the present paper for the special case of trimethylgallium, whose characteristic reaction is the expansion of the covalency of the gallium atom to four by co-ordination to a donor atom. Any subsequent reaction appears to depend on the presence of reactive hydrogen in the resulting co-ordination compound (other possibilities, such as the presence of reactive halogen, have not yet been investigated).

With methyl cyanide, a weak co-ordination compound is formed, which is fully dissociated in the vapour state at 100°/90 mm., and no further reaction occurs. On the other hand, with acetone, which is more acidic, a 1 : 1 co-ordination compound is again formed, but between 60° and 90° one mol. of methane is evolved, giving a non-volatile product $Me_2Ga{\cdot}OC_3H_5$. The latter, possibly an *iso*propenyl compound, evolves a little more methane at 170° and evidently then decomposes extensively to an involatile orange-yellow mass.

Compounds containing a still more acidic hydrogen atom give methane directly and products which usually contain two gallium atoms. In Part I* it was shown that with ammonia, methylamine, and dimethylamine, trimethylgallium forms co-ordination compounds which evolve a mol. of methane when heated, giving dimeric products, *e.g.*, $(Me_2Ga{\cdot}NH_2)_2$, to which cyclic structures were assigned. The reactions between trimethylgallium and compounds containing hydrogen bonded to oxygen, sulphur, and selenium, all weaker donor atoms (to gallium) than nitrogen, have now been studied and, although a co-ordination compound is likely to be the initial product, in all cases methane evolution occurs at or below room temperature.

Methanol, methanethiol, and methaneselenol give products which are sufficiently volatile to be vaporised completely and hence to allow their molecular weights to be determined in the gas phase. They are dimeric † like the products from ammonia and methyl- and

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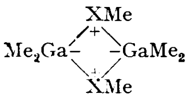
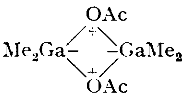
* Part I, *J.*, 1951, 2003.

† One of the corresponding aluminium compounds, $AlMe_2{\cdot}OMe$, is described as dimeric by Wiberg and Stecher (FIAT Review, 1939—46, Inorganic Chemistry, Part II, p. 160) and as trimeric by Brown and Davidson (*J. Amer. Chem. Soc.*, 1942, **64**, 316).

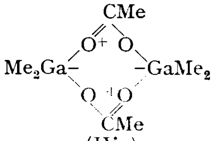
dimethyl-amine, and show no sign of dissociation at temperatures and pressures at which the simpler co-ordination compounds $Me_3\overset{-}{Ga}\cdot\overset{+}{O}Me_2$, $Me_3\overset{-}{Ga}\cdot\overset{+}{S}Me_2$, and $Me_3\overset{-}{Ga}\cdot\overset{+}{Se}Me_2$ are almost fully dissociated. They are assigned cyclic structures (I)—(III), since no other formulation appears reasonable. These cyclic structures are compatible with their high



(I; X = O) (II; X = S)
(III; X = Se)



(IV)



(IV*a*)

stability, since their dissociation would involve the breaking of two bonds, whereas the dissociation of the simple co-ordination compounds of trimethylgallium involves only one. In fact no evidence for dissociation of any of the above compounds in the gaseous phase was obtained from vapour-density measurements up to 170°. The heats of co-ordination of dimethyl ether, sulphide, and selenide with trimethylgallium are from 8 to 10 kcal./mole (Part I). Electropositive substituents such as methyl increase the donor properties of a donor atom and diminish the acceptor properties of an acceptor atom. The acceptor nature of the gallium atom in (I) should be greater than in $Me_3\overset{+}{Ga}\cdot\overset{-}{O}Me_2$, since it is bonded to two electronegative oxygen atoms and only two electropositive methyl groups instead of one and three respectively. Similarly the oxygen in (I) is bonded to two electropositive gallium atoms and one methyl group instead of one and two. Consequently the heat of dissociation of (I) should be very considerably more than twice that of $Me_3\overset{-}{Ga}\cdot\overset{+}{O}Me_2$, *i.e.*, well over 20 kcal./mole, in agreement with the observed lack of dissociation.

Acetic acid reacts vigorously with trimethylgallium giving methane and dimethylgallium acetate, which is dimeric (in acetone solution) and is therefore assigned the structure (IV). Evidently even the rather electronegative acetyl group does not sufficiently depress the donor nature of the oxygen to prevent dimerisation. An alternative structure (IV*a*) would allow resonance in the carboxy-group,* which would increase stability. The authors have no means for distinguishing between (IV) and (IV*a*) by, for example, infra-red measurements. Some of the properties of these compounds are given in Table I.

TABLE 1.

Compound	M. p.	B. p. (extrap.)	*A* *	*B*	L_v †	Trouton const.	Temp. range
$Me_3\overset{-}{Ga}\cdot\overset{+}{N}C\cdot Me$	24·8—25·2°	120°	2342	8·840	10·7	27·3	25—80°
$Me_3\overset{-}{Ga}\cdot\overset{+}{O}CMe_2$	—	104	2648	9·896	12·1	32·1	20—55
$(Me_2Ga\cdot OMe)_2$	24·5—24·7	187	2903	9·187	13·3	28·8	40—150
$(Me_2Ga\cdot SMe)_2$ (s) ...	113·3—113·7	—	5800	15·00	26·6 ‡	—	80—110
,, (l) ...	—	243	2990	8·679	13·7	26·6	115—170
$(Me_2Ga\cdot SeMe)_2$ (l) ...	119—120	—	3450	9·63	16	—	120—140
$(Me_2Ga\cdot O\cdot CO\cdot Me)_2$ ...	162·0—162·3	216	4704	12·50	21·6 ‡	—	90—162

* $\log_{10}$ (v. p.)$_{mm.}$ = − (*A*/*T*) + *B*.
† Latent heat of evaporation, kcal./mole.
‡ Latent heat of sublimation.

Phenol and *p-tert.*-butylphenol also give methane and dimeric products (V; R = H and CMe_3 respectively). The combined effect of a phenol group and a *p*-chlorine atom, however, depresses the donor character of oxygen more extensively, since molecular-weight measurements on the product from *p*-chlorophenol indicate an equilibrium between monomer and dimer. Similarly, thio- and seleno-phenol give analogous dimeric compounds. *p*-Chlorothiophenol gives a dimer $(Me_2Ga\cdot S\cdot C_6H_4Cl)_2$ with indication of partial dissociation into monomer in dilute benzene solution. Although thiols and selenols are more acidic than the corresponding alcohols and phenols in aqueous or hydroxylic media, thiophenol and selenophenol react much more slowly than phenol with trimethylgallium in ether.

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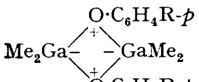
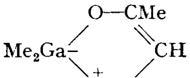
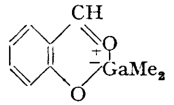
* The authors are indebted to a referee for suggesting this point.

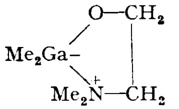
Monomeric compounds (VI) and (VII) are obtained from trimethylgallium and acetylacetone and salicylaldehyde. The former is volatile and similar to the thallium compound $Me_3Tl{\cdot}C_5H_7O_2$ (Menzies, Sidgwick, Cutcliffe, and Fox, *J.*, 1928, 1288). These compounds

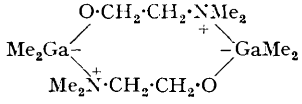

(V)

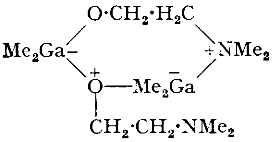

(VI)

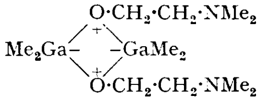

(VII)

may be monomeric because two donor atoms are available in the reacting molecule, or because a conjugated system is formed (VII is bright yellow). The latter effect is probably the more important since 2-dimethylaminoethanol does not give the expected monomeric product (VIII) but a dimer, for which structures (IX)—(XI) are feasible. This


(VIII)


(IX)


(X)


(XI)

compound immediately forms a methiodide on addition of methyl iodide to its benzene solution, suggesting the presence of tercovalent nitrogen; thus the ten-membered ring structure (IX) is improbable. The methiodide is very hygroscopic, easily hydrolysed, and not easy to purify and analyse. The iodine content, however, was a few units per cent. short of that calculated for a dimethiodide and far too large for a monomethiodide; hence the four-membered ring structure (XI) is preferred. The formation of (XI) rather than (VIII) is remarkable since nitrogen is a considerably stronger donor than oxygen, and suggests that gallium has a particularly high tendency to form four-membered rings with oxygen.

Although no direct measurement of the heats of dissociation of these compounds into monomers has been possible, on account of their high stability, some information about relative stabilities is provided by their reaction with trimethylamine. Thus, one of the most stable compounds, the methoxide (I), does not react with trimethylamine, whereas the monomeric *p*-chlorophenoxide forms a 1 : 1 co-ordination compound whose dissociation pressure is only about 1 mm. at 20°. The dissociation pressure at 20° of the trimethylamine adducts of most of the compounds prepared are given in Table 2. A low dissociation

TABLE 2. *Dissociation pressures at* 20° *of* $Me_2\overset{-}{Ga}R{\cdot}\overset{+}{N}Me_3$.

R	*P* (mm.)	R	*P* (mm.)	R	*P* (mm.)
OMe	No adduct	$O{\cdot}C_6H_4Bu^t$-*p*	14	SPh [c]	0·4 (m. p. 51°)
SMe [a]	10·3—10·4 (m. p. 26·0—26·2°)	OPh	6·1 (m. p. 39—40°)	SePh	0·1—0·2 (m. p. 48—50°)
		$O{\cdot}C_6H_4Cl$-*p*	1·5		
SeMe [b]	4·5 (m. p. 29·8—30·0°)			$O{\cdot}C_6H_4{\cdot}CHO$-*o*	11

ΔH (dissociation): *a* = 7·5; *b* = 6·6; *c* = 9·3 kcal./mole.

pressure indicates that trimethylamine successfully competes with R as a donor to gallium; thus, for a group of similar compounds in which entropy changes would be alike, the donor properties of the group R should be in the same order as the dissociation pressures. Table 2 thus indicates that: (*a*) the order of donor character is O > S > Se, a result in contrast to that found in Part I (O > Se > S), for co-ordination between Me_3Ga and OMe_2, SMe_2, and $SeMe_2$ (the difference between S and Se is small and may easily be due to entropy effects);

(*b*) substitution of phenyl for methyl diminishes the dissociation pressure and thus also diminishes the donor nature of the atom concerned, *e.g.*, R = SMe, p = 10 mm., while for R = SPh, p = 0·4 mm.; and (*c*) substitution of an electropositive radical (Bu^t) in a phenoxy-group increases the donor character of the oxygen, while an electronegative radical (Cl) decreases it. Effects (*b*) and (*c*) illustrate the well-known effect of the electronegativity of substituents bonded to a donor atom on its donor character.

Neither the acetylacetone derivative (VI) nor the dimethylaminoethanol derivative (XI) reacts with trimethylamine, but the salicylaldehyde derivative (VII) forms an unstable adduct (dissociation pressure 11 mm. at 20°; m. p. 56—67° with decomp.).

EXPERIMENTAL

All the compounds described were prepared in a vacuum-apparatus, but the less volatile ones were purified by crystallisation in normal apparatus with care to exclude water. Trimethylgallium was prepared as described in Part I. The other reagents were prepared and purified by established methods, except 2-dimethylaminoethanol, which required careful drying by three distillations over barium oxide, and methaneselenol, which was prepared by the reduction (by sodium in liquid ammonia) of dimethyl diselenide (Coates, this vol., paper no. 575) and was purified by fractionation in the vacuum-apparatus.

Trimethylgallium–Methyl Cyanide.—Trimethylgallium (17·7 N-c.c.) and methyl cyanide (17·7 N-c.c.) were condensed in the high-temperature bulb (see Part I). A mild reaction occurred when the former melted, and the addition compound, m. p. 24·8—25·2°, crystallised. No methane was formed. The v. p. was measured from 20° to 80°. Above 85° the bulb contained gas only. The vapour volume was 33·0, 33·5, 33·8, and 34·0 N-c.c. at 90°, 100°, 110°, and 120°, indicating almost complete dissociation. No methane was formed even at 100°, the compound being unchanged on cooling to room temperature.

Trimethylgallium–Acetone.—The components (17·5 N-c.c. of each) gave a liquid, v. p. 8 mm./22°, with no evolution of methane. The *product* froze to a homogeneous crystalline mass below room temperature. The v. p. was measured between 20° and 55°. It was not possible to measure the density of the vapour since reaction occurred at an appreciable rate at 50° and above, with deposition of a white solid and formation of methane. The bulb was heated to 90° for 10 min., then cooled to room temperature, and methane (17·8 N-c.c.) was removed. The residue, which must have the composition $Me_2Ga{\cdot}OC_3H_5$, was non-volatile at room temperature. Further heating at 170° (10 min.) gave a further 5·7 N-c.c. of methane (0·33 mole per g.-atom of gallium), and the solid became orange-yellow.

Tetramethyl-μμ′-dimethoxydigallium * (I).—Trimethylgallium (28·2 N-c.c.) and methanol (28·2 N-c.c.) were condensed in the high-temperature bulb at −183°. Warming caused vigorous gas evolution as soon as the trimethylgallium melted; a colourless liquid was formed, which later crystallised. The vessel was again cooled in liquid oxygen, and the gas, identified as methane (v. p. at −183°), was quantitatively pumped into a gas burette (28·1 N-c.c.). The composition of the residue was therefore $Me_2Ga{\cdot}OMe$ (which requires CH_4 28·2 N-c.c.). The compound melted at 24·5—24·7° and became entirely gaseous at 128°. Between 140° and 150° the volume of the vapour (reduced to N.T.P.) was 13·9 N-c.c.; hence the vapour is dimeric, *i.e.*, $(Me_2Ga{\cdot}OMe)_2$. For the measurement of v. p. a larger quantity was prepared by a similar method. The compound was stable to dry air and did not react with an excess of methanol.

Tetramethyl-μμ′-dimethoxydigallium did not react with trimethylamine.

Tetramethyl-μμ′-bismethylthiodigallium (II).—Trimethylgallium (27·1 N-c.c.) and methanethiol (27·1 N-c.c.) were condensed in the high-temperature bulb at −183°. Rapid gas evolution was observed as soon as the trimethylgallium melted, but the reaction (unlike that with methanol) could be stopped by cooling in liquid oxygen. Methane (27·0 N-c.c.; identified by v. p.) was pumped from the colourless solid product (non-volatile at room temperature), which therefore had the composition $Me_2Ga{\cdot}SMe$. The v. p. was measured and is given above; at 175° the compound had entirely volatilised and at 180° and 190° its volume was 13·5 and 13·7 N-c.c. respectively, indicating a dimeric structure.

Reaction with trimethylamine. When the high-temperature bulb was cooled after the v.-p. measurement, the compound crystallised fairly uniformly over the glass surface. Trimethylamine (27·1 N-c.c.; 1 mole per g.-atom of gallium) was then condensed in the bulb. On warming

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* On the basis of the nomenclature used in Part I, this compound could be called *cyclo*(bismethyloxonium bisdimethylgallide) (cf. *J.*, 1951, 3515).

to room temperature, the gas occupied 24·2 N-c.c.; thus only a little trimethylamine had reacted. When the bulb was warmed with the hand, the pressure rapidly decreased to 12 mm., and the white deposit liquefied and soon (at room temperature) crystallised to long needles (often 4—5 cm.) of *dimethyl(methylthio)gallium–trimethylamine*, m. p. 26·0—26·2°. When the bottom of the bulb was cooled with liquid oxygen, these needles broke into minute crystals of (II), since 27·1 N-c.c. of trimethylamine were recovered by pumping as it warmed to room temperature. The trimethylamine was replaced, the addition compound formed again, and dissociation pressures were measured up to 160°.

Tetramethyl-μμ′-bismethylselenodigallium (III).—Trimethylgallium (10·6 N-c.c.) and methaneselenol (10·6 N-c.c.) gave methane (10·5 N-c.c.) and a white relatively non-volatile solid. The v. p. of the latter was measured over a rather short temperature range since a little non-condensable gas was formed at > 160°; the constants given in Table I are therefore only approximate. At 155° and 160° the material had volatilised and its volume was 5·1 and 5·4 N-c.c. respectively; a very small quantity of white deposit separated during these measurements. As vapour the substance was therefore dimeric $(Me_2Ga{\cdot}SeMe)_2$.

Reaction with trimethylamine. Addition of trimethylamine (10·6 N-c.c.) gave results very similar to those observed with the analogous sulphur compound, but the amine was absorbed more rapidly. The addition compound, *dimethyl(methylseleno)gallium–trimethylamine*, again formed long needles, m. p. 29·8—30·0°, which lost trimethylamine when the bottom of the bulb was cooled with liquid oxygen. On pumping at room temperature, 10·4 N-c.c. of trimethylamine were recovered. The trimethylamine was replaced and the dissociation pressure measured between 30° and 90°.

Tetramethyl-μμ′-diacetoxydigallium (IV).—This *product*, prepared from the trimethylgallium–ether complex and acetic acid, was purified by vacuum-sublimation at 135°, forming colourless crystals, m. p. 162·0—162·3° (Found: C, 30·2; H, 5·63; Ga, 43·8%; *M*, ebullioscopic in acetone, 325, 308. $C_8H_{18}O_4Ga_2$ requires C, 30·2; H, 5·65; Ga, 44·0%; *M*, 318). It absorbs trimethylamine at room temperature forming an unstable adduct from which all the trimethylamine can be removed by pumping at room temperature.

Tetramethyl-μμ′-diphenoxydigallium (V; R = H).—Trimethylgallium (22 millimoles, 10% excess) was combined with a slight excess of ether and then condensed (as ether complex) on a frozen solution of phenol (19·4 millimoles) in ether (10 c.c.). Gas evolution began as the mixture warmed to about 0° and became vigorous near room temperature. The solution was removed from the vacuum-apparatus, light petroleum (b. p. 60—80°; 30 c.c.) added, and most of the ether distilled away. By next morning *tetramethyl-μμ′-diphenoxydigallium* (1·91 g., 52%) had separated as large colourless plates, m. p. 132° (Found: C, 49·8; H, 5·7; Ga, 36·0%; *M*, cryoscopic in benzene, 388, 389, 381. $C_{16}H_{22}O_2Ga_2$ requires C, 49·7; H, 5·7; Ga, 36·3%; *M*, 386). The compound is very soluble in most organic solvents. It dissolves with hydrolysis (smell of phenol) in cold water, and the solution evolves gas (probably methane) with precipitation of a white solid when heated. The solid sublimes slowly in *vacuo* at 100°.

Reaction with trimethylamine. Trimethylamine (24·8 N-c.c.) was condensed on tetramethyl-μμ′-diphenoxydigallium (0·161 g.). Some gas was absorbed after warming to room temperature, and considerably more at 30—40°. By a few seconds' pumping at 0°, trimethylamine (5·4 N-c.c.) was recovered; thus 19·4 N-c.c. (just under one mole per g.-atom of gallium) had reacted, forming *dimethylphenoxygallium–trimethylamine*, colourless needles, m. p. 39—40°. The dissociation pressure is 6 mm. at 20°, and 38 at 50°. All the trimethylamine could be removed by pumping, slowly at room temperature, and quickly above the m. p. of the adduct.

The following preparations were carried out by essentially the same method.

*Tetramethyl-μμ′-bis-*p-tert.*-butylphenoxydigallium* (V; R = Bu^t) from *p-tert.*-butylphenol, needles (from light petroleum), m. p. 92° (Found: C, 57·8; H, 7·5; Ga, 28·0%; *M*, ebullioscopic in benzene, 447. $C_{24}H_{38}O_2Ga_2$ requires C, 57·9; H, 7·6; Ga, 28·1%; *M*, 498).

*Tetramethyl-μμ′-bis-*p*-chlorophenoxydigallium*, from *p*-chlorophenol, colourless needles (from ether), m. p. 147° (Found: C, 42·5; H, 4·5; Ga, 31·1. $C_{16}H_{20}O_2Cl_2Ga_2$ requires C, 42·3; H, 4·4; Ga, 30·8%). The molecular weight, measured ebullioscopically in benzene, increased with concentration: Found: *M*, 335 (0·55% solution), 374 (1·0%), 386 (1·4%), 394 (2·0%), 399 (2·5%), 432 (3·4%). $C_{16}H_{20}O_2Cl_2Ga_2$ requires *M*, 455.

Tetramethyl-μμ′-bisphenylthiodigallium from thiophenol, which reacted with trimethylgallium (in ether) markedly more slowly than the phenols, colourless crystals (from light petroleum), purified by sublimation in a high vacuum at 120—125°, m. p. 143—145° (Found: Ga, 33·2%; *M*, ebullioscopic in benzene, 410, 401, 419, 420, 414. $C_{16}H_{22}S_2Ga_2$ requires Ga, 33·4%; *M*, 418). This compound was also prepared and identified by quantitative synthesis in the high-vacuum apparatus: thiophenol (0·0715 g., *i.e.* 14·5 N-c.c.) and trimethylgallium (14·5 N-c.c.) were condensed in the "high-temperature bulb." Vigorous gas evolution was observed on warming to room temperature. Next morning methane (14·4 N-c.c.; identified by v. p. at −183°) was pumped off; the composition of the residue was thus established as $C_6H_5{\cdot}SH + Me_3Ga - CH_4$, *i.e.*, $(C_8H_{11}SGa)_x$. The product sublimed in the high-temperature bulb at 110—120°, but was not sufficiently volatile for v. p. measurements by simple methods; it absorbed trimethylamine (14·4 N-c.c.), giving *dimethylphenylthiogallium–trimethylamine*, m. p. 51°, whose dissociation pressure was measured between room temperature and 100°.

Tetramethyl-μμ′-bisphenylselenodigallium, from selenophenol, colourless crystals (from benzene), m. p. 136°, becoming yellow on exposure to air (hydrolysis and subsequent oxidation of selenophenol to diphenyl diselenide) (Found: Ga, 27·1%; *M*, ebullioscopic in benzene, 520, 518, 478, 491, 482, 497. $C_{16}H_{22}Ga_2Se_2$ requires Ga, 27·3%; *M*, 512).

*Tetramethyl-μμ′-bis-*p*-chlorphenylthiogallium*, from *p*-chlorothiophenol, small colourless needles (from benzene and light petroleum), m. p. 187—188° [Found: Ga, 28·4%; *M*, ebullioscopic in benzene, 396 (0·4% solution), 445 (0·79%), 467 (0·96%), 457 (1·26%), 486 (1·53%) 467 (1·73%). $C_{16}H_{20}Cl_2S_2Ga_2$ requires Ga, 28·8%; *M*, 487].

Dimethylgallium–acetylacetone (VI), from acetylacetone, colourless prisms, purified by sublimation at room temperature (v. p. 1·1 mm. at 20°), m. p. 21·8—22·0° (Found: Ga, 34·9, 35·2%; *M*, from vapour density, 203. $C_7H_{13}O_2Ga$ requires Ga, 35·1%; *M*, 199). The v. p. was measured between 32° and 130°: below 65°, $\log_{10} p_{\text{mm.}} = 9{\cdot}333 - 2722/T$; above 65°, $\log_{10} p_{\text{mm.}} = 8{\cdot}226 - 2348/T$; whence the b. p. is 166°, and the Trouton constant 24·4. This complex did not combine with trimethylamine.

Salicylaldehyde–dimethylgallium complex (VII) from salicylaldehyde, bright yellow deliquescent needles (from ether), purified by vacuum-sublimation at 50°, m. p. 79° (Found: Ga, 31·4%; *M*, ebullioscopic in benzene, 221, 216, 221. $C_9H_{11}O_2Ga$ requires Ga, 31·7%; *M*, 221). With trimethylamine an unstable adduct was formed, dissociation pressure 11 mm. at 20°, which melted between 56° and 67° with evolution of trimethylamine. All the latter could easily be removed by pumping at room temperature.

Tetramethyl-μμ′-bis-2-dimethylaminoethoxydigallium (XI), from 2-dimethylaminoethanol, colourless crystals, purified by vacuum-sublimation at 45°, m. p. 81·4° (Found: C, 38·3; H, 8·4; Ga, 36·9%; *M*, ebullioscopic in benzene, 350, 378, 349, 362, 360. $C_{12}H_{32}O_2N_2Ga_2$ requires C, 38·3; H, 8·5; Ga, 37·1%; *M*, 376). Addition of methyl iodide to its benzene solution gave a very hygroscopic white precipitate, m. p. 264—266° (decomp. with darkening above 220°). Crystallisation of the latter from moist acetone gave 2-hydroxyethyltrimethylammonium iodide, m. p. 266° (not depressed by mixture with a specimen prepared from 2-dimethylaminoethanol and methyl iodide) (Found: C, 26·0; H, 5·8; I, 54·8. Calc. for $C_4H_{14}ONI$: C, 26·0; H, 6·0; I, 55·0%). Owing to the high sensitivity of the methiodide to moisture direct analysis was difficult (Found: I, 34·9. Calc. for dimethiodide $C_{14}H_{38}O_2N_2I_2Ga_2$: I, 38·5; for the monomethiodide $C_{13}H_{35}O_2IGa_2$: I, 24·7%).

The compound (XI) did not react with trimethylamine.

One of us (R. G. H.) thanks the Department of Scientific and Industrial Research for a grant.

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