651. *Co-ordination Complexes of Methyl Derivatives of Indium and Thallium.*

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Trimethylindium forms 1 : 1 co-ordination complexes with ammonia, trimethylamine, and some methyl derivatives of Group VB and VIB elements. The heat of co-ordination to trimethylamine and to trimethylphosphine is a little less than that of trimethylgallium. The co-ordination of trimethylthallium was studied qualitatively and the greatest co-ordination affinity appears to be shown to trimethylamine, trimethylphosphine, and dimethyl sulphide and selenide. Trimethylthallium is a weaker acceptor than trimethylindium, hence the order of acceptor character to trimethylamine among the Group III and IIIB trimethyls is B $<$ Al $>$ Ga $>$ In $>$ Tl. Some dimethylamino-, methoxy-, methylthio-, and methylseleno-derivatives of the dimethylindium and dimethylthallium radicals have been prepared; the greater thermal stability, lower sensitivity to hydrolysis, and absence of reaction with trimethylamine of the S and the Se compounds suggest that thallium and possibly indium might form dative π bonds to S and Se.

Since various co-ordination complexes are formed by trimethylaluminium [1] and trimethylgallium,[2] the reported inability of trimethylindium [3] to form complexes, even with ammonia, appeared worthy of further investigation. Another reason for examining the co-ordination of derivatives of indium(III) and thallium(III) was to obtain evidence about the possibility of the occurrence of dative π bonding to donors such as sulphur or phosphorus. Much evidence from the chemistry of the Group IIB and the Group VIII elements suggests that such bonds are more likely to be formed by the heavier than by the lighter members of a group. Since the inorganic compounds of thallium(III) are reduced by the donor substances of interest in this connection, it is necessary to use an organic derivative such as trimethylthallium.

Trimethylindium forms the complexes listed in the Table.

Complex	M. p.	B. p. (extrap.)	*A* *	*B* *	L_v †	Temp. range
Me_3In,NMe_3(s)	66·2—66·4°	—	2590	8·802	11·9 ‡	30—65°
Me_3In,NMe_3(l)	—	171°	2460	8·402	11·3	70—100
Me_3In,PMe_3	46·5	189	2832	9·015	13·0	50—110
$Me_3In,AsMe_3$	28·2—28·8	155	2590	8·925	11·9	30—95
Me_3In,OEt_2	—	147	2175	8·066	10·0	20—60
Me_3In,SMe_2	19·0—19·5	185	1808	6·825	8·3	30—85
Me_3In,NH_3	28·5—29·0	—	—	—	—	—
$(Me_2In{\cdot}NMe_2)_2$	—	—	1890	5·61	8·6	30—75
	—	—	3018	8·861	13·8	75—140

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

Heats of dissociation in the gas phase were measured by the vapour-density method used in previous studies;[2] that of the trimethylamine complex is 19·9 ± 0·5 kcal./mole, and that of the trimethylphosphine complex 17·1 ± 0·8 kcal./mole. The other complexes (trimethylarsine, dimethyl ether, and dimethyl sulphide) were so extensively dissociated that no useful equilibrium measurements could be made. The ammine, Me_3In,NH_3, evolved methane very slowly even at room temperature; at 70—80° methane evolution was rapid and amounted to one mole per g.-atom of indium. The resulting amide, $(Me_2In{\cdot}NH_2)_x$, melted at 120—124° to a thick syrup which underwent further decomposition; it was not appreciably volatile, unlike its gallium analogue,[2a] $(Me_2Ga{\cdot}NH_2)_2$.

Trimethylindium forms a 1 : 1 co-ordination compound with dimethylamine, $Me_3In,NHMe_2$, liquid at room temperature, which also evolves a mol. of methane when heated to 140—160°. The product is sufficiently stable and volatile to allow its vapour

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[1] H. C. Brown and Davidson, *J. Amer. Chem. Soc.*, 1942, **64**, 316.
[2] (*a*) Coates, *J.*, 1951, 2003; (*b*) Coates and Hayter, *J.*, 1953, 2519.
[3] Dennis, Work, and Rochow, *J. Amer. Chem. Soc.*, 1934, **56**, 1047.

density to be measured in the temperature range 130—180°, and it is dimeric like the gallium compound [2a] $(Me_2Ga{\cdot}NMe_2)_2$. Again like the gallium analogue, it is dimorphic and has the curious property that the low-temperature form (below 70°) appears to have a *lower* latent heat of sublimation ($\Delta H_s \gtrsim 9$ kcal./mole) than the high-temperature form (above 80°, $\Delta H_s = 13{\cdot}8$ kcal./mole). The difference in latent heat is similar to that observed for the gallium compound ($\Delta H_s = 6{\cdot}6$ kcal./mole below 55° and 12·5 kcal. above 80°). Crystals of $Me_2In{\cdot}NMe_2$ formed by condensation from the vapour at or near room temperature are well formed and have sharply defined faces and angles, but those condensing above about 80° are of quite different appearance and have a strong tendency to form rounded edges. Crystals of the second type may persist below 50—80° for several minutes, but suddenly change from a transparent to an opaque polycrystalline mass if slight local cooling is applied.

FIG. 1.

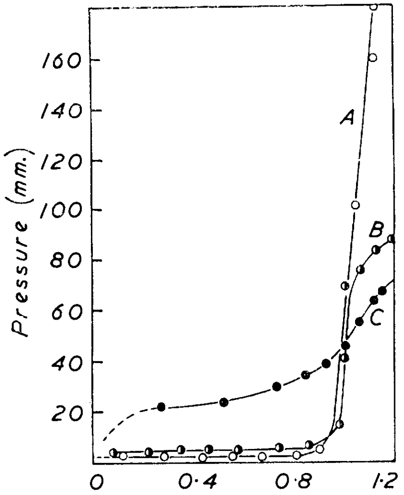

FIG. 2.

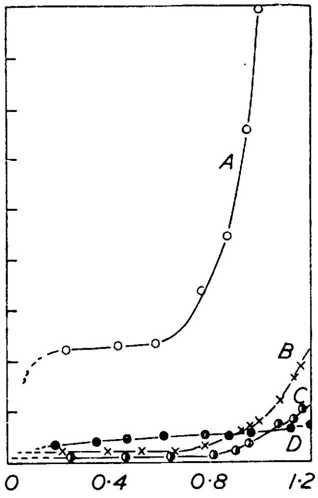

FIG. 1. *A, Trimethylamine* (○). *B, Trimethylphosphine* (◑). *C, Trimethylarsine* (●).
FIG. 2. *A, Dimethyl ether* (○). *B, Dimethyl sulphide* (×). *C, Dimethyl selenide* (◑). *D, Dimethyl telluride* (●).

Dimethylindium methoxide results from the reaction, vigorous at —98° (m. p. of methanol), between trimethylindium and methanol. It is a colourless viscous liquid, whose molecular weight (ebullioscopically in benzene) varies with concentration but indicates a degree of association of about three. Though very sensitive to hydrolysis, it is stable to dry air. The initial product from trimethylaluminium [1] and methanol is a mixture of liquid and solid, but this becomes a homogeneous crystalline substance when heated at 90°; no crystalline material could be obtained from the indium product by similar treatment. In contrast, the methylthio-derivative, obtained from trimethylindium and methanethiol in ether solution, is a colourless crystalline solid which can be sublimed in a vacuum and is dimeric in benzene solution. It is far less sensitive to hydrolysis than the methoxide, but is decomposed rapidly by dilute acids. Neither compound reacts with trimethylamine.

The reported ease with which trimethylthallium can be separated from ether by vacuum-distillation [4] indicates a low co-ordination affinity. Since trimethylthallium explodes with violence when heated to about 100°, no attempts were made to study gas dissociation equilibria. Instead some qualitative information was obtained by measuring the vapour pressure of various ligands in equilibrium with trimethylthallium at 0° (Figs. 1 and 2). The vapour pressure of trimethylthallium is 2 mm. at 0° C.

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[4] Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 1946, **68**, 517.

Trimethylamine, trimethylphosphine, dimethyl sulphide, and dimethyl selenide all appear to form 1 : 1 complexes with trimethylthallium. Dimethyl ether, dimethyl telluride, and trimethylarsine are all evidently very weak donors and in the case of dimethyl telluride there is scarcely evidence for any reaction (v. p. of pure dimethyl telluride is 15 mm. at 0°). Only the trimethylphosphine and the dimethyl sulphide complexes had nearly sharp melting points (27—28° and $-0{\cdot}5°$ respectively), the others melting over a range usually a little below 0°. It should be noted that for all complexes studied between any given Group III trimethyl and the various Group VB trimethyls the melting point of the complex increases with its stability. The data of Fig. 1 merely indicate that trimethylamine and trimethylphosphine are donors of comparable strength, both being much stronger than trimethylarsine, but the significantly higher melting point of the phosphine complex is some slight evidence for an order $Me_3P > Me_3N \gg Me_3As$. Such an order, or even if the amine and the phosphine were equivalent, would be evidence for the strengthening of the co-ordinate bond in the phosphine complex by a dative π bond. In the absence of such double bonding trimethylamine always appears to co-ordinate more strongly than trimethylphosphine.

Since information is now available about the co-ordination complexes of all the trimethyl derivatives of the Group III and IIIB elements, it is apparent that the order of acceptor character to a constant donor such as trimethylamine is $B < Al > Ga > In > Tl$. The heats of co-ordination to trimethylamine are: Me_3B [5] 17·6, Me_3Al [1,6] > 21, Me_3Ga [6] 21·0, Me_3In 19·9 kcal./mole, Me_3Tl unknown, but there is appreciable dissociation at 0°.

Certain thallium compounds were prepared, in which the dimethylthallium group is bound to a donor atom, for purposes of comparison with aluminium, gallium, and indium analogues. Dimethylthallium methoxide [7] and ethoxide [8] have already been described and are reactive and very easily hydrolysed. A specimen of the methoxide was prepared in the course of this investigation and was found not to react with trimethylamine in common with all the other dimethylmetal methoxides of Group III.

An attempt at the preparation of dimethyl-thallium dimethylamide, $Me_2Tl{\cdot}NMe_2$, by thermal decomposition of the dimethylamine adduct of trimethylthallium failed because general decomposition with deposition of thallium took place simultaneously with evolution of methane. The compound was, however, prepared from dimethylthallium bromide and dimethylaminolithium, and can be purified quite easily by sublimation. It is dimeric in benzene, very sensitive to hydrolysis, and, like the methoxide, decomposes at 120—130°. It does not absorb trimethylamine.

The sulphur and selenium derivatives $(Me_2Tl{\cdot}SMe)_2$ and $(Me_2Tl{\cdot}SeMe)_2$, obtained from dimethylthallium fluoride and sodium methyl sulphide (or selenide) in methanol, are, in contrast, much more stable thermally and are relatively insensitive to hydrolysis. Like the indium compound $(Me_2In{\cdot}SMe)_2$ neither absorbed trimethylamine; this contrasts with the reaction of $(Me_2Al{\cdot}SMe)_2$,[1] $(Me_2Ga{\cdot}SMe)_2$, and $(Me_2Ga{\cdot}SeMe)_2$ [2b] with trimethylamine. The sulphur and selenium compounds appear to be generally rather more stable than the corresponding oxygen compounds, and this might well be due to some strengthening of the bonds between thallium (or even indium) and sulphur or selenium by the formation of a dative π bond.

EXPERIMENTAL

Most of the compounds described were prepared and studied in a vacuum-apparatus. Trimethylindium,[3] trimethylthallium,[4] and the various donor substances [2a] were prepared as previously described. All experiments with trimethylthallium took place in a darkened room, and care was taken to reduce exposure of the substance to mercury with which it slowly reacts with formation of thallium amalgam and dimethylmercury.

Trimethylindium–Ammonia.—Trimethylindium (0·5813 g., *i.e.*, 81·4 N-c.c.) and ammonia (81·4 N-c.c.) were condensed in the " high-temperature bulb." [2a] Reaction occurred as the

[5] H. C. Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2923.
[6] Coates and Huck, *J.*, 1952, 4511.
[7] Menzies and Walker, *J.*, 1934, 1131.
[8] Menzies, *J.*, 1930, 1571.

ammonia melted, giving colourless acicular crystals of the *adduct*, m.p. 28·5—29·5°. Methane, identified by its vapour pressure at —196°, was slowly evolved at room temperature at the rate of about 1 c.c. a day. When the adduct was heated to 70—80° methane was rapidly evolved and the total quantity collected (by Töpler pump) was 81·35 N-c.c. (1 mol. = 81·4 N-c.c.). The white residue, which was involatile at room temperature, was therefore *aminodimethylindium*, $Me_2In{\cdot}NH_2$, and melted with decomposition at 120—124° to a thick syrup.

Dimethylindium Methoxide.—Anhydrous methanol (27·4 N-c.c.) was condensed on trimethylindium (0·1958 g., 27·4 N-c.c.) at —183°. Reaction was apparent as soon as the methanol melted, and was completed by gentle warming. Methane (27·3 N-c.c.) was collected. The *product* is a colourless rather viscous liquid, very easily hydrolysed by moist air. It could not be made to crystallise as it always formed a clear glass. A larger quantity was prepared for molecular-weight measurement (Found: *M*, ebullioscopically in benzene: 1·4% solution, 623; 2·5%, 586; 4·0%, 548. $C_9H_{27}O_3In_3$ requires *M*, 528).

Tetramethyl-μμ'-bismethylthiodi-indium.—Trimethylindium (2·972 g., 18·58 mmoles), methanethiol (416·1 N-c.c., 18·58 mmoles), and dry ether (5 c.c.) were condensed in an ampoule connected to a ½-l. bulb. Methane was rapidly evolved when the ampoule was allowed to warm. The mixture was cooled in liquid nitrogen, and the methane pumped away. The remaining volatile matter (mainly ether) was then removed, and the colourless solid residue was sublimed in a vacuum; it then had m. p. 122—124° (decomp.) (Found: C, 18·6; H, 4·6; In, 60·0%; *M*, ebullioscopic in benzene, 370, 354, 346. $C_6H_{18}S_2In_2$ requires C, 18·75; H, 4·7; In, 59·9%; *M*, 384). The compound is freely soluble in benzene.

Tetramethyl-μμ'-bisdimethylaminodi-indium.—Trimethylindium (0·0723 g., 10·1 N-c.c.) and dimethylamine (10·1 N-c.c.) were condensed in the high-temperature bulb and formed a liquid adduct. The bulb was heated at 160° until no further pressure change was noted (½ hr.), and methane (10·1 N-c.c.) was subsequently collected by Töpler pump from the cooled bulb. The product was then heated until it had all become gaseous and the volume (5·1—5·2 N-c.c. from 140° to 160°) indicated the dimeric constitution.

Dimethylindium–acetylacetone, from trimethylindium and acetylacetone, sublimed in a vacuum, and decomposed at 118° (Found: C, 34·75; H, 5·8; In, 56·9. $C_7H_{13}O_2In$ requires C, 34·4; H, 5·3; In, 56·6%).

Tetramethyl-μμ'-bisdimethylaminodithallium.—Dimethylthallium bromide (31·4 g., 0·1 mole) was added with continuous stirring to a solution of lithium dimethylamide obtained from phenyllithium (120 c.c. of 0·84M-solution in ether) and a slight excess of dimethylamine (30 c.c. of 4·1M-solution in ethylene glycol dimethyl ether). The greater part of the solid dissolved during ½ hr. at room temperature. The solvent was evaporated and the *product* (19·5 g., 70%) separated by high-vacuum sublimation, which was rapid at 110°. The substance was exceedingly sensitive to moisture and was analysed by alkaline hydrolysis (Found: NMe_2, 15·6; Me_2Tl, as Me_2TlI, 84·3%; *M*, ebullioscopic in benzene, 541, 560, 545. $C_8H_{24}N_2Tl_2$ requires NMe_2, 15·8; Me_2Tl, 84·2%; *M*, 557).

Tetramethyl-μμ'-bismethylthiodithallium, was obtained from the sodium salt of methanethiol and dimethylthallium fluoride in methanol as a very pale yellow precipitate and was separated from sodium fluoride by crystallisation from benzene, or, in some instances, by vacuum-sublimation. It forms colourless crystals, m. p. 207—208° (decomp. with darkening at 190°) (Found: C, 12·86; H, 3·4; Tl, 72·25%; *M*, ebullioscopic in benzene, 544, 609, 600. $C_6H_{18}S_2Tl_2$ requires C, 12·81; H, 3·2; Tl, 72·6%; *M*, 563).

Tetramethyl-μμ'-bismethylselenodithallium, similarly prepared from dimethylthallium fluoride and sodium methyl selenide (from methaneselenol[9] and sodium methoxide) in methanol, was purified by vacuum-sublimation and formed colourless crystals, m. p. 210° (decomp. with darkening at ~170°) (Found: C, 11·3; H, 2·9; Tl, 61·9%; *M*, ebullioscopic in benzene, 684, 671, 689. $C_6H_{18}Se_2Tl_2$ requires C, 11·0; H, 2·7; Tl, 62·2%; *M*, 657).

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[9] Coates, *J.*, 1953, 2839.