228. *The Constitution of Complex Metallic Salts. Part XI. The Structure of the Tertiary Phosphine and Arsine Derivatives of Cadmium and Mercuric Halides.*

By R. C. Evans, Frederick G. Mann, H. S. Peiser, and Donald Purdie.

In order to elucidate the composition and structure of the " addition compounds " which the organic derivatives of the 3-covalent Group 5B elements form with cadmium and mercuric halides, the tertiary phosphine and arsine derivatives have been studied in detail.

These phosphines and arsines give three classes of compound with cadmium halides (CdX_2) : (1) $[\{R_3P($*or* $As)\}_2CdX_2]$, in which the 4-covalent complex is almost certainly tetrahedral; (2) $[\{R_3P(As)\}_2(CdX_2)_2]$, which has now been shown to have the *trans*-symmetric bridged structure (V); (3) $[\{R_3P(As)\}_3(CdX_2)_2]$, a novel type of derivative, of which the structure is now being investigated.

Mercuric halides give five classes of compound: (A) $[\{R_3P(As)\}_2HgX_2]$, similar in configuration to Class 1 in the cadmium series; (B) $[\{R_3P(As)\}_2(HgX_2)_2]$, which also has the *trans*-symmetric bridged structure (VII); (C) $[\{R_3P(As)\}_2(HgX_2)_3]$, which contains two distinct structural types, one of which consists essentially of molecules of Class B alternating with simple HgX_2 molecules; (D) $\{[R_3P(As)\}_2(HgX_2)_4]$, of which the detailed structure is still under investigation; (E) $\{[R_3P(As)\}_3(HgX_2)_2]$, of structure presumably closely similar to that of Class 3 in the cadmium series. The stability, structure, and inter-relationships of these compounds are discussed.

For the identification and characterisation of amines, the crystalline addition products which they and their halogen salts form with mercuric halides have frequently been employed. In the products formed by the salts, usually of type $B_2,H_2[HgX_4]$ where B represents a molecule of the base and X a halogen atom, mercury is part of a complex anion, and is co-ordinated solely to halogen atoms; such products are not considered in this paper. The addition products of free amines and mercuric halides necessarily contain, however, the amine molecules co-ordinated to the mercuric atom, and they are remarkable for the range and diversity shown in the ratio of amine molecules to mercuric halide molecules. For instance, Staronka (*Bull. Acad. Sci. Cracow*, 1910, 372) has isolated crystalline derivatives of pyridine having empirical formulæ py_2HgBr_2, $pyHgBr_2$, $py_2(HgBr_2)_3$, of m. p. 118°, 123°, and 134° respectively, and obtained some indication from solubility curves of the existence of the compounds $py_6Hg(CN)_2$, $py_3Hg(CN)_2$, $py_2Hg(CN)_2$, $py_3\{Hg(CN)_2\}_2$, and $pyHg(CN)_2$, of which series, however, he isolated in the crystalline form only the third and the fifth member. Derivatives of piperidine of formulæ $(C_5H_{11}N)_4(HgCl_2)_3$, $(C_5H_{11}N)_3(HgCl_2)_2$, $(C_5H_{11}N)_2HgCl_2$, and $C_5H_{11}N(HgCl_2)_2$ have been described by various authors (Pesci, *Z. anorg. Chem.*, 1897, **15**, 231; Varet, *Compt. rend.*, 1892, **115**, 880; Ray and Dhar, J., 1913, **103**, 6). A similar but more limited diversity in composition has been found in addition products of amines with cadmium halides, and of tertiary phosphines and arsines with both mercuric and cadmium halides. We have therefore investigated in considerable detail the composition and structure of the derivatives of the phosphines and arsines with mercuric and cadmium halides in order to clarify this subject; these compounds were chosen because they crystallise well, usually have sharp m. p.'s, and are freely soluble in many organic liquids. It was found essential to prepare a considerable number of homologous members of each series, in order both to study their comparative stability and to select suitable compounds for crystallographic investigation. The derivatives of cadmium, being the more limited in type, are discussed first; its halides form three distinct classes of non-ionic compound with tertiary phosphines and arsines:

Class 1, $[\{R_3P(As)\}_2CdX_2]$, *dihalogenobisphosphine*(or *arsine*)*cadmium*. These compounds are readily formed by shaking an aqueous or alcoholic solution of the cadmium halide with the theoretical quantity of the phosphine or arsine. They vary in stability, and some members readily discard half their phosphine or arsine content to afford the corresponding compound of Class 2. Although no detailed investigation has been made of the structure of these compounds, it is reasonably certain that the four groups are tetrahedrally arranged around the central cadmium atom (I):* there is considerable evidence for this tetrahedral configuration in the cadmium compounds of Class 2, and in other 4-covalent cadmium compounds, such as $K_2[Cd(CN)_4]$ (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 774) and $[Cd(NH_3)_4][ReO_4]$ (Pitzer, *Z. Krist.*, 1935, **92**, 131), the tetrahedral arrangement of the cadmium complex has been proved by *X*-ray analysis.

Class 2, $[\{R_3P(As)\}_2(CdX_2)_2]$, *dihalogenobisphosphine*(or *arsine*)-*μ-dihalogenodicadmium*. These compounds are readily formed by the interaction of the former compounds with 1 mol. of cadmium halide in hot alcoholic solution, and they are usually more stable than the parent compounds of Class 1. Their molecular formula has been proved by molecular-weight determinations in organic solvents. They bear an obvious resemblance to the

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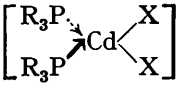
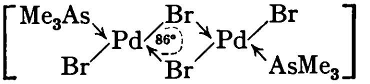
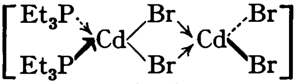
* In this and following formulæ, valency bonds in normal type are to be regarded as lying in the plane of the paper, whilst those in heavy type project tetrahedrally above, and those in dotted type tetrahedrally below, this plane.

" bridged " dipalladium compounds previously described (Mann and Purdie, J., 1936, 873; Mann and Wells, J., 1938, 702; Chatt and Mann, *ibid.*, p. 1949; Chatt, Mann, and Wells, *ibid.*, p. 2086; Chatt and Mann, J., 1939, 1622), where it was shown, for instance, that the compound $[(Me_3As)_2(PdBr_2)_2]$ was actually dibromobis(trimethylarsine)-μ-dibromodipalladium having the *trans*-symmetric structure (II), in which the molecule (excluding the alkyl groups) is flat owing to the planar distribution of the 4-covalent palladium complex. Three isomeric forms of any one of these bridged cadmium compounds

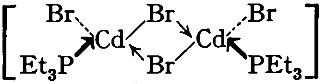
(I.) 

 (II.)

can theoretically exist; *e.g.*, *dibromobis(triethylphosphine)-μ-dibromodicadmium*, $[(Et_3P)_2(CdBr_2)_2]$, could have the unsymmetric (III), the *cis*-symmetric (IV), or the *trans*-symmetric structure (V). All the compounds of this class had, however, a sharp m. p.,



(III.)



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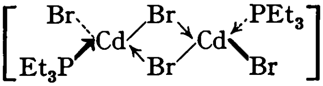


(V.)

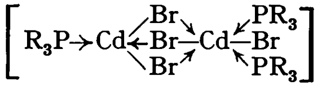
were clearly homogeneous in the crystalline state, and must therefore occur in only one of these three isomeric forms. Crystallographic analysis of the compound $[(Et_3P)_2(CdBr_2)_2]$ showed that the molecule possessed a centre of symmetry and must therefore have the *trans*-symmetric structure (V); moreover, only a tetrahedral arrangement of the four groups around each cadmium atom harmonised with the *X*-ray evidence. The compounds (II) and (V) are therefore closely similar in structure, each possessing a centre of symmetry; they differ, however, in that each palladium complex in (II) is planar whilst each cadmium complex in (V) is tetrahedral. Further evidence that the cadmium compounds of this class have the tetrahedral *trans*-symmetric structure is provided by the fact that the compound (V) is isomorphous not only with $[(Pr^a{}_3P)_2(CdI_2)_2]$ and $[(Pr^a{}_3As)_2(CdI_2)_2]$ but also with $[(Pr^a{}_3As)_2(HgI_2)_2]$, and mercuric compounds of this class are shown later by independent evidence to possess this structure.

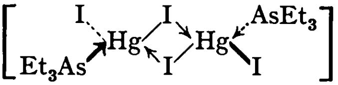
When the *compound* $[(Et_3P)_2(CdI_2)_2]$ was treated in acetone solution with αα′-dipyridyl, triethylphosphine was liberated and *di-iododipyridylcadmium*, $[dpyCdI_2]$, was deposited. This reaction cannot be accepted as evidence for the structure of the dicadmium compound (cf. Chatt and Mann, *loc. cit.*). Morgan and Burstall (J., 1930, 2594) have suggested the use of the mercuric compound $[dpyHgI_2]$ for the gravimetric estimation of dipyridyl in solution. The cadmium derivative is, however, even less soluble in water and organic solvents; *e.g.*, it is insoluble in boiling alcohol, from which the mercuric compound can be recrystallised. It is probable, therefore, that the cadmium compound could be used for the estimation of dipyridyl or of cadmium.

Class 3, $[\{R_3P(As)\}_3(CdX_2)_2]$, *tetrahalogenotrisphosphine*(or *arsine*)*dicadmium*. Members of this class can be prepared in hot alcoholic solution by the interaction (*a*) of the corresponding member of Class 1 with the theoretical quantity of cadmium halide, or (*b*) of corresponding members of Classes 1 and 2 in the correct proportion, *i.e.*, 2 mols. and 1 mol. respectively. They are crystalline compounds of sharp m. p., and, although stable in the solid state, show considerable dissociation in organic solvents, from which however they crystallise again unchanged in composition. They are often more stable than the corresponding members of Class 2; *e.g.*, the tributylphosphinecadmium bromide and iodide members of Class 2 could not be prepared, the corresponding members of Class 3 being always obtained instead.

The ease with which members of this class can be prepared by method (*b*) and their ready dissociation in solution suggested that discrete molecules of composition $[(R_3P)_3(CdX_2)_2]$ might not exist even in the crystal, which might alternatively have a " molecular lattice " structure composed solely of $[(R_3P)_2CdX_2]$ and $[(R_3P)_2(CdX_2)_2]$ molecules. Strong evidence against this suggestion has been obtained by a crystallographic investigation of the *propyl* and *butyl* bromo-compounds; it would appear, therefore, that these compounds represent an entirely new structural type of complex metallic compounds, and their complete *X*-ray analysis is now being made. It is possible that the molecule has the structure (VI),* in which one cadmium atom is 4-covalent and at the centre of a tetrahedron, and the other is 6-covalent and at the centre of an octahedron, the two complexes having a triangular face in common bridged by three halogen atoms. In this case the first cadmium atom acquires six electrons (as in compounds of Classes 1 and 2), whilst the second acquires ten electrons as in the compound $(NH_3)_2CdCl_2$ (see p. 1216) : each bridged complex in (VI) would therefore be non-ionic and have a configuration normal to cadmium compounds. It should be noted that compounds of Class 3 are readily decomposed by dipyridyl with the precipitation of $[dpyCdX_2]$, in which respect they differ materially from the similar but more stable mercuric compounds of Class E.

(VI.)





(VII.)

Tertiary phosphines and arsines form five classes of non-ionic compounds with mercuric halides.

Class A, $[\{R_3P(As)\}_2HgX_2]$, *dihalogenobisphosphine*(or *arsine*)*mercury*. Stable compounds of this class are formed by many triaryl-phosphines and -arsines, but not apparently by trialkyl-phosphines and -arsines. There is little doubt that they have the tetrahedral structure (as I), since this configuration has been established for the mercuric complexes in the following classes B and C. Moreover, the same configuration has been determined for other derivatives of 4-covalent mercury; *e.g.*, Bijvoet, Claassen, and Karssen (*Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 529) have shown that in crystalline red mercuric iodide, each mercuric atom is tetrahedrally surrounded by four iodine atoms, and Dickinson (*loc. cit.*) has proved that $K_2[Hg(CN)_4]$ has a tetrahedral complex ion.

Class B, $[\{R_3P(As)\}_2(HgX_2)_2]$, *dihalogenobisphosphine*(or *arsine*)*-μ-dihalogenodimercury*. Many compounds have been formulated in the literature as $R_3P(As),HgX_2$; *e.g.*, $Ph_3As,HgCl_2$ (La Coste and Michaelis, *Annalcn*, 1880, **201**, 241) and $Et_3As,HgCl_2$ (Challenger and Ellis, J., 1935, 396). It is clear that satisfactory constitutional formulæ cannot be allotted to compounds of this molecular formula, and that they must possess the double " bridged " formula indicated above, and thus be analogous to the members of Class 2 of the cadmium series.

This is fully confirmed by the results of the present investigation. The dimercury compounds of Class B are formed by the interaction of the corresponding member of Class A with mercuric halide in alcoholic solution, or, if this fails, by the direct action of the free phosphine (or arsine) upon the mercuric halide dissolved either in alcohol or (in the case of the bromide or iodide) in an aqueous solution of the corresponding potassium halide. They are well-crystallised stable compounds, whose molecular weight in organic solvents fully confirms the " double " formula $[\{R_3P(As)\}_2(HgX_2)_2]$. Three *compounds* of this class have been investigated crystallographically, *viz.*, $[(Et_3As)_2(HgI_2)_2]$, $[(Pr^a{}_3P)_2(HgBr_2)_2]$, and $[(Pr^a{}_3As)_2(HgI_2)_2]$, and it is noteworthy that these three compounds are not isomorphous, unlike the three dicadmium compounds of Class 2 studied. Strong crystallographic evidence has been obtained that *di-iodobis*(*triethylarsine*)*-μ-di-iododimercury*, $[(Et_3As)_2(HgI_2)_2]$, which possesses a centre of symmetry, has the bridged *trans*-symmetric structure (VII), and that the four groups are again arranged tetrahedrally round the mercuric atoms.

A number of further points of interest have been discovered from the study of these dimercuric compounds. The *compound* $[(Et_3P)_2(HgI_2)_2]$ occurs solely as colourless crystals; but its n-*propyl* homologue occurs both as colourless (α) and yellow (β) crystals, whereas its n-*butyl* and n-*amyl* homologues occur solely as yellow crystals closely similar to the β-form of the propyl compound. The α-crystals of the propyl compound are always obtained when either form is rapidly recrystallised from organic solvents; when they are kept in the mother-liquor or exposed to the air they pass slowly into the β-crystals, which in turn on heating are reconverted into the α-form just below its m. p. It is clear, therefore,

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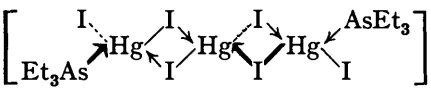
* In this formula, no differentiation between the planes of the bonds has been attempted.

that there can be only a small difference in the stability of the two interconvertible propyl derivatives: the difference in stability in the homologous compounds is, however, apparently so great that only the white form of the ethyl compound and the yellow form of the butyl and the amyl compound can be isolated. The interpretation of these experimental facts is at present uncertain, but there are two possible explanations. The white and the yellow series of crystals may represent merely dimorphous forms, or the two propyl derivatives may be true isomerides, representing possibly the *cis*- and the *trans*-symmetric forms respectively; the latter alternative is unlikely, as it would entail the existence of a series of comparatively stable *cis*-symmetric dimercury compounds, yet all the bridged dipalladium, dicadmium, and dimercury compounds whose structures have been determined crystallographically have the *trans*-symmetric structure. The true explanation can be found only by a complete *X*-ray analysis of both forms of the propylphosphine compound, which is now being attempted. It is noteworthy that in the $[(R_3As)_2(HgI_2)_2]$ compounds, this phenomenon does not occur, the *ethyl* and the n-*propyl* compound existing solely in the colourless, and the n-*butyl* compound solely in the yellow form.

The triphenylarsine derivatives of the mercuric halides show an interesting gradation in stability. When mercuric chloride is boiled in alcoholic solution with even a large excess of the arsine, only the bridged compound of Class B, $[(Ph_3As)_2(HgCl_2)_2]$, is formed. Mercuric bromide in these circumstances gives the unbridged compound of Class A, $[(Ph_3As)_2HgBr_2]$; this is stable in hot alcoholic solution, but on attempted recrystallisation from hot benzene gives the bridged derivative $[(Ph_3As)_2(HgBr_2)_2]$, which in turn is stable in hot benzene but in hot alcohol again furnishes the unbridged compound. Mercuric iodide in the above circumstances readily gives the unbridged *compound* $[(Ph_3As)_2HgI_2]$ which even with an excess of mercuric iodide will not give the unknown bridged $[(Ph_3As)_2(HgI_2)_2]$.

When $[(Bu_3P)_2(HgI_2)_2]$ was treated with $\alpha\alpha'$-dipyridyl in acetone solution, di-iododipyridylmercury, $[dpyHgI_2]$ (Morgan and Burstall, *loc. cit.*), was rapidly deposited. This instability to dipyridyl is in marked contrast to the great stability shown by members of Class E.

Class C, $[\{R_3P(As)\}_2(HgX_2)_3]$, *bisphosphine*(or *arsine*)*trismercuric halide*. These compounds were usually prepared by the interaction of the corresponding member of Class B with an excess of mercuric halide in hot alcoholic or acetone solution. They crystallise readily, and each member has a sharp m. p., no evidence of isomerism having been obtained. Crystallographic analysis shows, however, that two entirely distinct structures are present in this class. The *compound* $[(Et_3As)_2(HgI_2)_3]$ forms yellow orthorhombic crystals of which the space-group, and therefore almost certainly the constituent molecules, do not possess a centre of symmetry. It is possible that this compound has the bridged structure (VIII),



(VIII.)

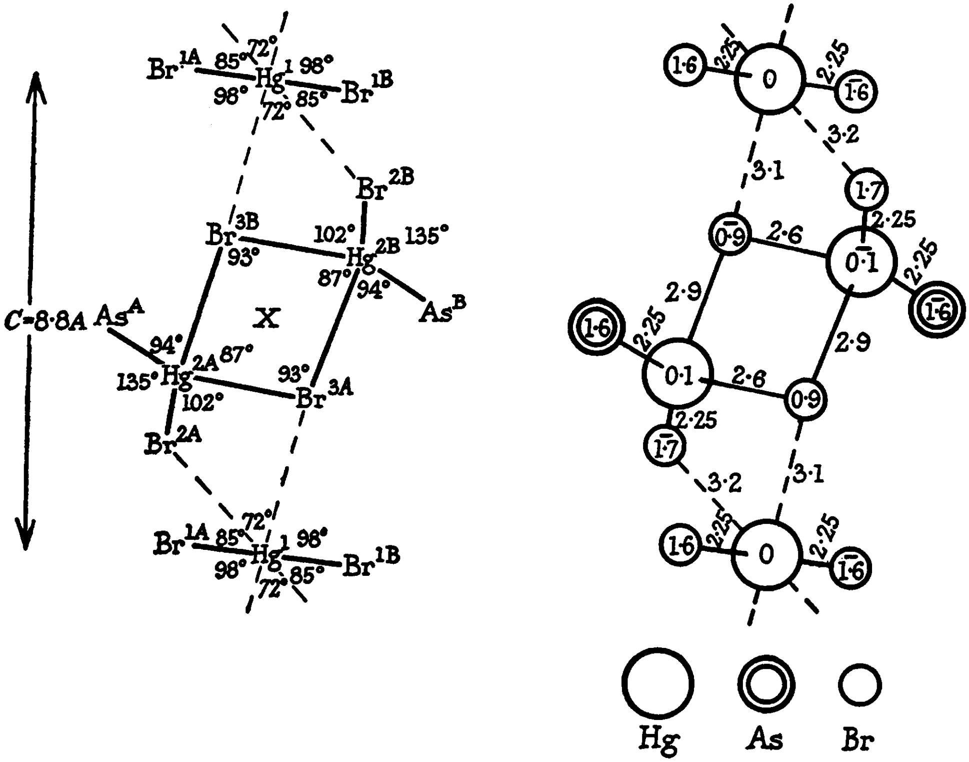
in which the alternation of the two bridged rings round the tetrahedral mercuric atoms would not allow a centre of symmetry. The structure of this compound is now being more completely investigated.

The colourless isomorphous monoclinic crystals of $[(Pr^{\alpha}{}_3As)_2(HgCl_2)_3]$ and $[(Bu^{\alpha}{}_3As)_2(HgBr_2)_3]$ have, however, an entirely different structure; this was shown at once by the fact that they possess centres of symmetry, and a complete crystallographic analysis of the latter compound has consequently been made. It proves to be essentially a molecular compound of the bridged compound of Class B, $[(Bu_3As)_2(HgBr_2)_2]$, and of mercuric bromide. Fig. 1A has been drawn to differentiate between the constituent atoms and to show the intervalency angles; Fig. 1B, drawn on the same scale, shows the interatomic distances and also the height of the various atoms above the plane of the paper. It will be seen that the mercury atoms Hg^{2A} and Hg^{2B} are linked to the arsenic and bromine atoms As^{A}, Br^{2A} and As^{B}, Br^{2B} respectively, and are also bridged through the bromine atoms Br^{3A} and Br^{3B}, the whole forming the bridged molecule $[(Bu_3As)BrHgBr_2HgBr(Bu_3As)]$ Each bridged mercury atom Hg^{2A} and Hg^{2B} is linked to four groups (*e.g.*, As^{A}, Br^{2A}, Br^{3A}

Br^{3B}) but considerable distortion of the normal tetrahedral arrangement now occurs. On both sides of this bridged molecule are mercuric bromide molecules, composed of the atoms Hg^1, Br^{1A}, and Br^{1B}. Since this alternation of bridged and of $HgBr_2$ molecules continues indefinitely in the crystal, it will be seen that there are centres of symmetry at each Hg^1 atom and also at the centre of each bridged ring, *i.e.*, at the point X.

Several points of considerable interest arise from this structure. The distance between a mercury and an unbridged bromine atom (2·25 A.) is constant both in the bridged molecule (*e.g.*, Hg^{2B}–Br^{2B}) and in the $HgBr_2$ units (*e.g.*, Hg^1–Br^{1A}). On the other hand, the Hg–Br distance in the bridged ring is considerably greater and is not uniform, having the two values 2·6 A. (Hg^{2B}–Br^{3B}) and 2·9 A. (Hg^{2A}–Br^{3B}). These results are in striking contrast to those obtained in the dipalladium compound (II), where the Pd—Br link has a constant value of 2·45 A. no matter whether the bromine atom forms part of the bridged ring or not; nevertheless, the intervalency angles within the ring at the metallic atom in the two compounds are nearly identical (Br^{3A}–Hg^{2A}–Br^{3B} = 87°; Br–Pd–Br = 86°). It is to be expected that this intervalency angle in the planar dipalladium molecule would closely approach 90°, but there is a notable difference between the corresponding intervalency angle in the dimercury molecule and the natural tetrahedral angle of 109°. It will be seen, however, that the mercury atom Hg^1 lies at a distance of 3·1 A. and 3·2 A. from the bridged and unbridged bromine atoms Br^{3B} and Br^{2B}, and that the former distance is only slightly greater than the longer side of the bridged ring (Hg^{2A}–Br^{3B}, 2·9 A.). It is probable that, although no chemical links exist between the atom Hg^1 and the bridged and unbridged bromine atoms Br^{3B} and Br^{2B}, this mercury atom exerts a definite attraction on both these

FIG. 1.



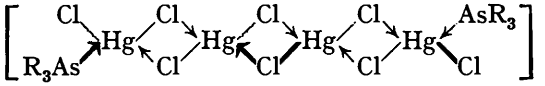
A B

[$(Bu_3As)_2(HgBr_2)_3$]. Fig. 1A *shows the intervalency and other angles.* Fig. 1B (*on the same scale*) *shows the interatomic distances, and the height of individual atoms above the plane of the paper. Atoms of the same element bearing the same number are crystallographically equivalent and related by a centre of symmetry: they are distinguished from one another where necessary by the letters* A *and* B.

atoms, and it is this attraction which distorts the tetrahedral configuration of Hg^{2A} and Hg^{2B}, and is thus responsible for the extraordinarily high value (135°) for the valency angle Br^{2B}–Hg^{2B}–As^{B} and the correspondingly low value for the ring angle Br^{3A}–Hg^{2A}–Br^{3B}; moreover, it is probably this attraction which lengthens the bridged ring and, by nearly equalising the distances Hg^{2A}–Br^{3B}, Br^{3B}–Hg^{1}, largely stabilises the whole structure, since the two molecules cannot be regarded as being absolutely independent. Incidentally, it follows for this structure that each Hg^{1} atom is surrounded by a distorted octahedron of six bromine atoms, two being directly bound to the Hg^{1} atom at 2·25 A., and the remaining four being contributed by neighbouring bridged molecules, two of these bromine atoms being at 3·1 A. and two at 3·2 A. This arrangement of halogen atoms around the Hg^{1} atoms closely resembles that found in NH_4HgCl_3 (Harmsen, *Z. Krist.*, 1939, **100**, 208), in which the mercuric atom is surrounded by a distorted octahedron of chlorine atoms, two at 2·34 A., and four at 2·96 A., and also that in mercuric bromide (Verweel and Bijvoet, *Z. Krist.*, 1931, **77**, 122), isomorphous with yellow mercuric iodide, where a similar arrangement of halogen atoms obtains, with two bromine atoms at 2·48 A., and four at 3·23 A. The Hg^{1}–Br^{1} and Hg^{2}–Br^{2} distances (2·25 A.) are, however, sensibly smaller than those found in mercuric bromide.

Class D, $[\{R_3P(As)\}_2(HgX_2)_4]$, *bisphosphine*(or *arsine*)*tetrakismercuric halide*. Many references also occur in the literature to compounds formulated as $R_3As,2HgX_2$; *e.g.*, Challenger, Higginbottom, and Ellis (J., 1933, 95) isolated compounds formulated as $Me_3As,2HgCl_2$ and $Me_2EtAs,2HgCl_2$. Here again, it is very difficult to allot satisfactory constitutional formulæ on this molecular basis, and it is almost certain that the double formula $[(R_3As)_2(HgCl_2)_4]$ is correct. Such compounds might have molecules of structure (IX), where the mercuric complexes are again tetrahedral, and the molecule in consequence

(IX.)



possesses a centre of symmetry. Alternatively, they might consist of a molecular lattice of bridged $[(R_3As)_2(HgCl_2)_2] + 2HgCl_2$ molecules somewhat similar in general type to the compounds of Class C shown in Fig. 1. The low solubility of these compounds in cold solvents prevents satisfactory molecular-weight determinations being carried out; in any case, both the above alternative structures might allow considerable dissociation in solution, and such determinations would probably not distinguish between the structures.

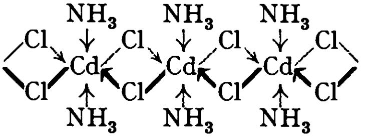
The *compounds* $[(Et_3P)_2(HgBr_2)_4]$ and $[(Et_3As)_2(HgCl_2)_4]$ have been studied in some detail. The latter is readily formed when the bridged compound $[(Et_3As)_2(HgCl_2)_2]$ is dissolved in hot acetone; half the arsine is discarded, and the octachloro-compound separates with a molecule of acetone in monoclinic crystals of m. p. 112—114°. This solvated *compound* is surprisingly stable, and lost very little acetone even when heated at 80° for 20 hours at atmospheric pressure or for 3 hours at 20 mm. The mother-liquor on long standing deposits acetone-free monoclinic crystals of the pure octachloro-compound, m. p. 138°. A preliminary crystallographic examination of these compounds indicates that a fully bridged structure such as (IX) is unlikely, and their detailed structure is now under investigation.

Class E, $[\{R_3P(As)\}_3(HgX_2)_2]$, *tetrahalogenotrisphosphine*(or *arsine*)*dimercury*. This class of compound is apparently strictly analogous to Class 3 of the cadmium compounds, but in the mercuric compounds only iodo-derivatives appeared to be formed. These were usually prepared by shaking a solution of mercuric iodide in aqueous potassium iodide with an excess of the free phosphine or arsine. They possess sharp m. p.'s, and although on boiling in alcoholic solution they are often converted into the corresponding member of Class B, they show a remarkable stability to αα′-dipyridyl; *e.g.*, the *compound* $[(Bu^{a}_3As)_3(HgI_2)_2]$ in cold acetone solution was unaffected by dipyridyl even after 3 weeks, an inertness in striking contrast to the rapid decomposition of the Class B analogues in similar circumstances.

It would be expected that zinc halides would form with phosphines and arsines similar compounds to those obtained with cadmium and mercuric halides, but we failed to detect any such reaction in aqueous solution, although some reaction occurs in alcoholic solution. Burrows and Lench (*J. Proc. Roy. Soc. N.S.W.*, 1936, **70**, 63) have shown, however, that phenyldimethylarsine and diphenylmethylarsine give a number of derivatives of type $[(R_3As)_2ZnX_2]$, where X = Cl or Br, which are clearly similar to the cadmium and mercuric compounds of Classes 1 and A respectively; moreover, the former arsine gives a compound formulated as $Me_2PhAs,ZnCl_2$, which is almost certainly a bridged compound $[(Me_2PhAs)_2(ZnCl_2)_2]$ similar to the cadmium and mercuric compounds of Classes 2 and B.

It is noteworthy, however, that an identity in chemical composition between the derivatives of these three metals does not necessarily entail an identity in constitution; for instance, MacGillavry and Bijvoet (*Z. Krist.*, 1936, **94**, 231, 249), investigating the six compounds of composition $[(NH_3)_2MX_2]$, where M = Zn, Cd, or Hg, and X = Cl or Br, found that the zinc compounds consist of discrete molecules of formula $[(NH_3)_2ZnX_2]$, having the four groups tetrahedrally arranged around the zinc atom, but that the cadmium compounds have an entirely different structure, consisting of chains of octahedra each having two ammonia radicals in the 1 : 6 position and four chlorine atoms in the square cross-section, neighbouring octahedra showing two chlorine atoms at an octahedral edge. It follows that the cadmium atoms are bridged through two chlorine atoms and have two ammonia radicals directly co-ordinated to them (X). The cadmium atoms in these compounds will thus acquire in all 10 electrons by this linkage, in contrast to the cadmium atoms in Classes 1 and 2 and the mercury atoms in Classes A and B, which acquire throughout only 6 electrons by their method of linkage. The compounds of formula $[(NH_3)_2HgX_2]$, in which X = Cl or Br, have yet another structure, one ammonia radical being at the centre of the cubic cell having 8 halogen atoms at its corners; since each cube has all its faces held in common with neighbouring cubes, each halogen atom is thus common to eight cubes. Further, each cube has one mercury atom in the centre of one face; the mercury atoms have, however, otherwise random distribution in the crystal, and so do not necessarily occupy the corresponding faces in neighbouring cubes. It is obviously difficult to give a precise chemical structure to such compounds.

(X.)



EXPERIMENTAL.

CHEMICAL DATA.

In view of the number of compounds isolated, the general name of each group is given, followed by details of the individual members prepared. In the following formulæ, R indicates an alkyl or aryl radical, and X a halogen atom. The names of the solvents used are given in parentheses immediately after the names of the compounds concerned or after their m. p.'s. All the derivatives of cadmium and mercury prepared in this investigation, unless otherwise stated, were colourless.

Cadmium Compounds.

Class 1 $[\{R_3P(As)\}_2CdX_2]$, *Dihalogenobisphosphine*(or *arsine*)*cadmium* (as I).—Most of the members in the alkyl-phosphine and -arsine series were unstable, and the higher members (*e.g.*, *n*-butyl) were oils at room temperature. The triarylphosphine members were stable, crystalline compounds.

Phosphine compounds. Triethylphosphine (10 g., 2 mols.) and a solution of cadmium iodide (15 g., 1 mol.) in water (50 c.c.) were vigorously shaken together, and the crystalline precipitate was collected, drained, and thrice recrystallised (alcohol); the *di-iodo*-compound $[(Et_3P)_2CdI_2]$ had m. p. 132—134° (Found: C, 23·7; H, 5·0; I, 42·2. $C_{12}H_{30}I_2P_2Cd$ requires C, 23·9; H, 5·0; I, 42·2%). The dibromo-compound was similarly obtained as crystals, m. p. 103—104°, too unstable for analysis. Tripropylphosphine gave with an aqueous solution of cadmium chloride only an unstable oil which did not apparently react with a further quantity of cadmium chloride.

Tripropylphosphine (2 mols.) and cadmium bromide (1 mol.) in aqueous solution similarly afforded the *dibromo*-compound $[(\text{Pr}^{\alpha}{}_3\text{P})_2\text{CdBr}_2]$; crystallisation (alcohol) gave needles, m. p. 75—77°, having an odour of free phosphine (Found : C, 35·9; H, 7·1; Br, 27·1. $C_{18}H_{42}Br_2P_2Cd$ requires C, 36·5; H, 7·1; Br, 27·0%). The *di-iodo*-compound (alcohol) formed needles, m. p. 72—73°, easily soluble in acetone and benzene (Found : C, 31·5; H, 6·4; *M*, cryoscopic in 2·914% benzene solution, 754; in 5·511% solution, 862. $C_{18}H_{42}I_2P_2Cd$ requires C, 31·5; H, 6·2%; *M*, 686).

The compounds $[(\text{Bu}^{\alpha}{}_3\text{P})_2\text{CdBr}_2]$ and $[(\text{Bu}^{\alpha}{}_3\text{P})_2\text{CdI}_2]$ were obtained only as oils.

Triphenylphosphine and an alcoholic solution of cadmium bromide afforded the *dibromo*-compound $[(\text{Ph}_3\text{P})_2\text{CdBr}_2]$; this (benzene) had m. p. 225—226° (Found : C, 54·3; H, 4·0. $C_{36}H_{30}Br_2P_2Cd$ requires C, 54·25; H, 3·8%). Similarly prepared, the *di-iodo*-compound had m. p. 243° with preliminary softening, and was only slightly soluble in benzene, alcohol, and chloroform (Found : C, 48·7; H, 3·6. $C_{36}H_{30}I_2P_2Cd$ requires C, 48·5; H, 3·4%).

Arsine compounds. $[(\text{Et}_3\text{As})_2\text{CdBr}_2]$ was not apparently formed in either aqueous or alcoholic solution, only the bridged dicadmium compound (see below) being obtained. The action of free triethylarsine (2 mols.) on a cold aqueous solution of cadmium iodide (1 mol.) afforded the *di-iodo*-compound, which had m. p. 79—81° (alcohol) and smelt markedly of the free arsine (Found : C, 20·8; H, 4·7; I, 37·0. $C_{12}H_{30}I_2As_2Cd$ requires C, 20·9; H, 4·4; I, 36·8%). Similarly prepared, the recrystallised n-*propyl di-iodo*-compound (alcohol) was collected in a chilled filter-funnel; it had m. p. 27—29°, and on exposure to air slowly lost free arsine and formed the bridged dicadmium compound (see below) (Found : C, 27·1; H, 4·8. $C_{18}H_{42}I_2As_2Cd$ requires C, 27·9; H, 5·3%).

Class 2, $[\text{R}_3\text{P(As)XCdX}_2\text{CdXR}_3\text{P(As)}]$, *Dihalogenobisphosphine*(or *arsine*)-μ-*dihalogenodicadmium* (as V).—In the alkylphosphine series, the chloro-derivatives are either not formed or exist only as oils; among the bromo- and iodo-derivatives, the methyl, ethyl, and *n*-propyl members are formed, but higher members apparently do not exist, since all attempts to prepare the *n*-butyl members gave solely the " sesqui "-compounds of type $[(\text{Bu}_3\text{P})_3(\text{CdX}_2)_2]$ (see below). In the alkylarsine series, the chloro-derivatives again were not formed, but the ethyl and *n*-propyl members of the bromo- and iodo-derivatives were readily obtained.

Phosphine compounds. Trimethylphosphine was prepared by thermal decomposition of its silver iodide compound, $[\text{Me}_3\text{P,AgI}]_4$ (Purdie's method; J., 1938, 708), the phosphine being then passed directly into the cadmium halide solution. When an aqueous solution of cadmium bromide was thus treated with an excess of the phosphine, the *tetrabromo*-compound $[(\text{Me}_3\text{P})_2(\text{CdBr}_2)_2]$ rapidly separated, m. p. 195—198° (alcohol) (Found : C, 10·75; H, 3·0. $C_6H_{18}Br_4P_2Cd_2$ requires C, 10·3; H, 2·6%); it smells of free phosphine and decomposes slowly on standing and rapidly when heated with acetone. Similarly prepared, the *tetraiodo*-compound, twice recrystallised (alcohol), had m. p. 174—176° (decomp.) (Found : C, 8·45; H, 1·8. $C_6H_{18}I_4P_2Cd_2$ requires C, 8·1; H, 2·0%) and was similarly unstable. It is noteworthy that in spite of the use of an excess of phosphine in these two preparations, the unbridged compounds, $[(\text{Me}_3\text{P})_2\text{CdX}_2]$, were not obtained.

When an aqueous solution of cadmium bromide was shaken with 2 equivs. of triethylphosphine, the unstable unbridged compound, $[(\text{Et}_3\text{P})_2\text{CdBr}_2]$, was obtained. This was therefore treated in boiling alcoholic solution with 1 equiv. of cadmium bromide, and the *tetrabromo*-compound (V) separated in fine needles, m. p. 163—164° (alcohol) (Found : C, 18·7; H, 3·7; Br, 41·0. $C_{12}H_{30}Br_4P_2Cd_2$ requires C, 18·45; H, 3·9; Br, 41·0%). This is only slightly soluble, but is quite stable, in boiling alcohol; it dissolves readily in warm acetone and benzene, but undergoes partial decomposition, giving a turbid solution.

The analogous *tetraiodo*-compound was best prepared by the interaction of $[(\text{Et}_3\text{P})_2\text{CdI}_2]$ and 1 equiv. of cadmium iodide in *cold* alcoholic solution, m. p. 141° (alcohol) (Found : C, 14·9; H, 3·2. $C_{12}H_{30}I_4P_2Cd_2$ requires C, 14·9; H, 3·1%). Experiments showed that in alcohol an equilibrium $[(\text{Et}_3\text{P})_2(\text{CdI}_2)_2] \rightleftarrows [(\text{Et}_3\text{P})_2\text{CdI}_2] + \text{CdI}_2$ exists, the equilibrium point lying to the left in cold, and to the right in hot, solution; on cooling a hot solution, fine needles of the unbridged compound always separated first, and were later entirely replaced by the prisms of the bridged form.

When solutions of the tetraiodo-compound (0·48 g.; 2 mols.) and αα′-dipyridyl (0·16 g.; 1 mol.) in acetone (20 c.c. and 5 c.c.) were mixed, free triethylphosphine was liberated and a white precipitate of *di-iododipyridylcadmium* rapidly separated (Found : C, 23·0; H, 1·8. $C_{10}H_8N_2I_2Cd$ requires C, 23·0; H, 1·5%); this was collected, washed with alcohol and dried. It is insoluble in water, alcohol, acetone, and acetic acid and could not be recrystallised; on heating it decomposed at 350—360° with evolution of dipyridyl. The same compound was formed in theoretical yield when alcoholic solutions of cadmium iodide and dipyridyl (1 mol.) were mixed.

When either $[(\mathrm{Pr_3P})_2\mathrm{CdBr_2}]$ or $[(\mathrm{Pr_3P})_3(\mathrm{CdBr_2})_2]$ was treated with cadmium bromide (1 mol.) in boiling alcoholic solution, the *tetrabromo*-compound $[(\mathrm{Pr^{\alpha}_3P})_2(\mathrm{CdBr_2})_2]$ was obtained; m. p. 105—106° (alcohol) (Found: C, 25·0; H, 5·1. $\mathrm{C_{18}H_{42}Br_4P_2Cd_2}$ requires C, 25·0; H, 4·9%). The analogous *tetraiodo*-compound, prepared from the unbridged compound and cadmium iodide, had m. p. 123—125° (alcohol) (Found: C, 20·5; H, 4·1. $\mathrm{C_{18}H_{42}I_4P_2Cd_2}$ requires C, 20·5; H, 4·0%).

The *n*-butyl tetrabromo-compound could not be prepared. When the oily $[(\mathrm{Bu_3P})_2\mathrm{CdBr_2}]$ was boiled with cadmium bromide (1 mol.) in alcoholic solution, only the "sesqui"-compound, $[(\mathrm{Bu_3P})_3(\mathrm{CdBr_2})_2]$ (see below), was isolated, and this was unaffected by further boiling with cadmium bromide. Similar results were obtained with the iodo-compounds.

Arsine compounds. When cadmium bromide in cold aqueous or warm alcoholic solution was treated even with an excess (2 mols.) of triethylarsine, the *tetrabromo*-compound $[(\mathrm{Et_3As})_2(\mathrm{CdBr_2})_2]$ alone was precipitated, and when rapidly crystallised (alcohol) it had m. p. 175—178° (decomp.) (Found: Br, 37·0. $\mathrm{C_{12}H_{30}Br_4As_2Cd_2}$ requires Br, 36·8%); it decomposes when warmed with acetone, benzene, or chloroform.

The *tetraiodo*-compound was too unstable to be prepared by the above method, but was obtained by keeping $[(\mathrm{Et_3As})_2\mathrm{CdI_2}]$ in a vacuum over sulphuric acid until loss of arsine ceased; the residue had m. p. 80—81° (decomp.), but underwent partial decomposition on recrystallisation from alcohol (Found: I, 48·4. $\mathrm{C_{12}H_{30}I_4As_2Cd_2}$ requires I, 48·1%).

The unbridged $[(\mathrm{Pr^{\alpha}_3As})_2\mathrm{CdI_2}]$ (1 mol.) and cadmium iodide (1 mol.) were boiled together in alcoholic solution, and on cooling the *tetraiodo*-compound $[(\mathrm{Pr^{\alpha}_3As})_2(\mathrm{CdI_2})_2]$ separated in fine needles, m. p. 114—116·5° (Found: C, 19·2; H, 3·6; *M*, cryoscopic in 1·281% ethylene dibromide solution, 1170. $\mathrm{C_{18}H_{42}I_4As_2Cd_2}$ requires C, 18·9; H, 3·7%; *M*, 1140); this compound withstands long boiling in alcoholic solution without decomposition.

Class 3, $[(\mathrm{R_3P})_3(\mathrm{CdX_2})_2]$, *Tetrahalogenotrisphosphinedicadmium.*—In the alkylphosphine series, the *n*-butyl members of the bromo- and iodo-derivatives were readily prepared, and were formed to the exclusion of the corresponding bridged derivatives of Class 2.

All attempts to prepare $[(\mathrm{Et_3P})_3(\mathrm{CdBr_2})_2]$ by the union of $[(\mathrm{Et_3P})_2\mathrm{CdBr_2}]$ and cadmium bromide failed, but the *n-propyl* homologue was formed when $[(\mathrm{Pr_3P})_2\mathrm{CdBr_2}]$ was boiled in alcoholic solution either with cadmium bromide (0·33 mol.) or with $[(\mathrm{Pr_3P})_2(\mathrm{CdBr_2})_2]$ (0·5 mol.) for a few minutes; it separated in beautiful prisms, m. p. 126—128° (alcohol) (Found: C, 31·75; H, 6·0; Br, 31·2. $\mathrm{C_{27}H_{63}Br_4P_3Cd_2}$ requires C, 31·6; H, 6·2; Br, 31·25%).

The *n-butyl* compound $[(\mathrm{Bu^{\alpha}_3P})_3(\mathrm{CdBr_2})_2]$ was formed when an alcoholic solution of tri-*n*-butylphosphine (1·5 mols.) and cadmium bromide (1 mol.) or of the oily $[(\mathrm{Bu_3P})_2\mathrm{CdBr_2}]$ and cadmium bromide (1 mol.) was boiled for ½ hour; it had m. p. 93—94·5° (alcohol) (Found: C, 37·6; H, 7·0; Br, 27·8; *M*, cryoscopic in 0·941% benzene solution, 839; in 2·549% solution, 918; in 3·550% solution, 930. $\mathrm{C_{36}H_{81}Br_4P_3Cd_2}$ requires C, 37·5; H, 7·1; Br, 27·8%; *M*, 1151). When solutions of this compound (0·51 g.) and dipyridyl (0·156 g., 1 mol.) in acetone (20 c.c. and 5 c.c.) were mixed, a white amorphous precipitate of *dibromodipyridylcadmium*, $[\mathrm{dpyCdBr_2}]$, immediately separated; on heating, this compound softens between 350° and 400° and loses dipyridyl, but the residue does not melt below 400° (Found: C, 28·3; H, 2·05. $\mathrm{C_{10}H_8N_2Br_2Cd}$ requires C, 28·0; H, 1·9%).

The *compound* $[(\mathrm{Bu^{\alpha}_3P})_3(\mathrm{CdI_2})_2]$ was prepared similarly, and had m. p. 100—101° (alcohol) (Found: C, 31·4; H, 6·1; Cd, 16·4; *M*, cryoscopic in 2·112% benzene solution, 975; in 4·899% solution, 1050. $\mathrm{C_{36}H_{81}I_4P_3Cd_2}$ requires C, 32·3; H, 6·1; Cd, 16·8%; *M*, 1338). It was readily soluble in cold acetone and benzene.

Mercury Compounds.

Class A, $[\{\mathrm{R_3P(As)}\}_2\mathrm{HgX_2}]$, *Dihalogenobisphosphine*(or *arsine*)*mercury* (as I).—Stable compounds of this type do not appear to be formed with aliphatic phosphines or arsines; many of the aryl derivatives are quite stable.

Phosphine compounds. Solutions of triphenylphosphine (1·1 g., 2 mols.) and of mercuric chloride (0·5 g., 1 mol.) both in hot alcohol (50 c.c. and 25 c.c.) were rapidly mixed and allowed to cool. White crystals of the *dichloro*-compound $[(\mathrm{Ph_3P})_2\mathrm{HgCl_2}]$, m. p. 273° (followed by decomp.), separated (Found: C, 54·4; H, 4·0. $\mathrm{C_{36}H_{30}Cl_2P_2Hg}$ requires C, 54·3; H, 3·8%). Similarly prepared, the *di-iodo*-compound separates as pale cream-coloured crystals, m. p. *ca.* 250° (ethylene dibromide) (Found: C, 44·1; H, 3·15. $\mathrm{C_{36}H_{30}I_2P_2Hg}$ requires C, 44·15; H, 3·1%).

Arsine compounds. The triphenyl dichloro-compound was not formed when an alcoholic solution of mercuric chloride and excess of the arsine was boiled, only the tetrachloro-compound (see below) separating on cooling; but when solutions of triphenylarsine (1·5 g., 2 mols.) and mercuric bromide (0·9 g., 1 mol.), each in hot alcohol (25 c.c.), were mixed, boiled for ½ hour, and cooled, the *dibromo*-compound $[(Ph_3As)_2HgBr_2]$ separated as leaflets, m. p. 182—212° (Found: C, 43·9; H, 3·2. $C_{36}H_{30}Br_2As_2Hg$ requires C, 44·4; H, 3·1%). These could be recrystallised unchanged from alcohol, but dissociated in hot benzene, which deposited the tetrabromo-compound (see below); the wide range of the m. p. indicates that similar dissociation occurs on heating.

Similarly prepared, the *di-iodo*-compound formed crystals, m. p. 197° (benzene) (Found: C, 40·65; H, 3·0. $C_{36}H_{30}I_2As_2Hg$ requires C, 40·5; H, 2·8%). The considerable stability of this compound, when heated alone or in benzene solution, is in marked contrast to that of the preceding dibromo-compound.

Class B, $[R_3P(As)XHgX_2HgXR_3P(As)]$, *Dihalogenobisphosphine*(or *arsine*)-*μ-dihalogenodimercury*.—This represents the best known and, in general, the most frequently occurring class of mercuric derivative.

Phosphine compounds. A solution of triethylphosphine (1 g., 1 mol.) in a small quantity of alcohol was added to one of mercuric bromide (3·0 g., 1 mol.) in alcohol (25 c.c.); the rather sticky product which separated became crystalline when the mixture was boiled and cooled. The *tetrabromo*-compound $[(Et_3P)_2(HgBr_2)_2]$ after four rapid recrystallisations from alcohol separated as hairy needles, m. p. 106° (Found: C, 14·8; H, 3·2. $C_{12}H_{30}Br_4P_2Hg_2$ requires C, 15·0; H, 3·1%). Rapid recrystallisation is essential, since the hot alcoholic solution soon deposits mercurous bromide.

Similarly prepared, the *tetraiodo*-compound separated in crystals, m. p. 121—123° (acetone) (Found: C, 12·5; H, 2·8. $C_{12}H_{30}I_4P_2Hg_2$ requires C, 12·6; H, 2·6%). Rapid recrystallisation was necessary for the purification of this compound: longer boiling of the solution caused loss of free phosphine and formation of $[(Et_3P)_2(HgI_2)_3]$.

Similarly prepared by the action of an alcoholic solution of tri-*n*-propylphosphine (1 mol.) on mercuric bromide dissolved either in 4% aqueous potassium bromide solution or in alcohol, the *tetrabromo*-compound $[(Pr^{\alpha}{}_3P)_2(HgBr_2)_2]$ has m. p. 133° (alcohol or benzene) (Found: C, 20·95; H, 4·0; Br, 30·4; Hg, 39·0. $C_{18}H_{42}Br_4P_2Hg_2$ requires C, 20·8; H, 4·0; Br, 30·8; Hg, 38·5%).

Tri-*n*-propylphosphine (4·0 g., 1 mol.) and a solution of excess mercuric iodide (22·7 g., 2 mols.) in 10% aqueous potassium iodide solution (150 c.c.) were vigorously shaken together; a pale yellow product separated as a sticky mass which subsequently solidified completely (*ca.* 16 g.), and recrystallisation from alcohol–acetone (4 : 1 by vol.) gave the *α-form* of the *tetraiodo*-compound as white blunt-ended needles, m. p. 114—115°. The mother-liquor on standing deposited the *β-form* as yellow crystals, which on heating turned white at 104—107° with conversion into the α-form, and then had m. p. 113—115°, either alone or when mixed with a sample of the α-form [Found, for the α-form: C, 17·6; H, 3·5; Hg, 32·2; *M*, cryoscopic in 2·643% benzene solution, 1260; in 5·139% solution (almost saturated), 1335; for the β-form: C, 17·4; H, 3·4; *M*, cryoscopic in 2·359% benzene solution, 1220; in 3·582% solution, 1120. $C_{18}H_{42}I_4P_2Hg_2$ requires C, 17·6; H, 3·4; Hg, 32·6%; *M*, 1229]. These compounds can also be prepared by the interaction of their generators in alcoholic or acetone solution.

Crystals of the α-form when kept at room temperatures are slowly converted into the β-form, becoming opaque and yellow. When the α-crystals are left in contact with the saturated organic mother-liquor at room temperature, they are ultimately entirely replaced by the yellow β-crystals. Quick recrystallisation of either form from alcohol gives solely the white α-form however.

Prepared by the action of the free phosphine on alcoholic mercuric bromide solution, the *tetrabromo*-compound $[(Bu^{\alpha}{}_3P)_2(HgBr_2)_2]$ separated as crystals, easily soluble in hot alcohol and benzene, m. p. 116° (alcohol) (Found: C, 25·5; H, 4·8; Hg, 35·6. $C_{24}H_{54}Br_4P_2Hg_2$ requires C, 25·6; H, 4·8; Hg, 35·65%). Similarly prepared in warm alcoholic solution, the *tetraiodo*-compound $[(Bu^{\alpha}{}_3P)_2(HgI_2)_2]$ was purified by adding alcohol to a cold concentrated acetone solution and chilling in ice–salt; the pale yellow crystals which separated had m. p. 84—85° (Found: C, 21·8; H, 4·4; I, 38·9; Hg, 30·7. $C_{24}H_{54}I_4P_2Hg_2$ requires C, 21·9; H, 4·1; I, 38·7; Hg, 30·55%). No indication of a colourless form was detected. Solutions of this compound (1·32 g., 1 mol.) and of dipyridyl (0·31 g., 2 mols.) in acetone (20 c.c. and 10 c.c.) were mixed; crystals of di-iododipyridylmercury, $[dpyHgI_2]$, slowly separated, m. p. 242—244° (Found: C, 19·7; H, 1·5. Calc. for $C_{10}H_8N_2I_2Hg$: C, 19·6; H, 1·3%). The same compound was formed when mercuric iodide was treated in acetone solution with 1 or 2 mols. of dipyridyl.

Prepared as for the butyl compound, the n-*amyl tetraiodo*-compound separated from alcohol as an oil which later solidified; slow recrystallisation from alcohol gave yellow crystals, m. p. 54—55° (Found : C, 25·9; H, 4·9; Hg, 26·5; *M*, ebullioscopic in 2·677% acetone solution, 851; in 5·326% solution, 894; in 8·067% solution, 913. $C_{30}H_{66}I_4P_2Hg_2$ requires C, 25·8; H, 4·8; Hg, 26·5%; *M*, 1397).

A solution of triphenylphosphine (0·52 g., 1 mol.) in alcohol (25 c.c.) was added to one of mercuric chloride (0·54 g., 1 mol.) in hot alcohol (25 c.c.); glistening white scales of the *tetrachloro*-compound $[(Ph_3P)_2(HgCl_2)_2]$ rapidly separated, and when collected and dried had m. p. 306—309° (Found : C, 40·7; H, 2·95. $C_{36}H_{30}Cl_4P_2Hg_2$ requires C, 40·5; H, 2·8%). Michaelis and von Soden (*Annalen*, 1885, **229**, 298) apparently prepared this substance; they stated that it melts above 300°, but gave no analyses.

The analogous *tetrabromo*-compound, similarly prepared, had m. p. 240—250° (decomp.) (chloroform) (Found : C, 34·95; H, 2·4. $C_{36}H_{30}Br_4P_2Hg_2$ requires C, 34·7; H, 2·4%).

Arsine compounds. Triethylarsine (4·65 g.) was shaken with a solution of mercuric chloride (15·6 g., 2 mols.) in water (500 c.c.), and the flocculent precipitate of the tetrachloro-compound, $[(Et_3As)_2(HgCl_2)_2]$, which separated was collected and dried (18 g.); very fine needles (alcohol), *d ca.* 3·2 (determined by flotation in ethylene dibromide), m. p. 162—163° (Found : C, 16·4; H, 3·6. Calc. for $C_{12}H_{30}Cl_4As_2Hg_2$: C, 16·6; H, 3·4%). Challenger and Ellis (*loc. cit.*) give m. p. 162°.

The corresponding *tetraiodo*-compound (VII) was produced when triethylarsine (4·8 g.) was added with shaking to a solution of mercuric iodide (27·0 g., 2 mols.) in 12% potassium iodide solution (150 c.c.). The yellow viscous oil which separated slowly solidified, and was purified by dissolution in warm acetone followed by dilution with alcohol. Large white prisms of the compound (VII) slowly separated, m. p. 87—88° (Found : C, 11·9; H, 2·55; I, 40·95; *M*, cryoscopic in 1·70% ethylene dibromide solution, 1260. $C_{12}H_{30}I_4As_2Hg_2$ requires C, 11·7; H, 2·4; I, 41·2%; *M*, 1233). The substance is unstable in presence of excess of solvent and readily passes over into $[(Et_3As)_2(HgI_2)_3]$.

Prepared in warm alcoholic solution, the *tetrabromo*-compound $[(Pr^{a}{}_3As)_2(HgBr_2)_2]$ had m. p. 91—92° (alcohol) (Found : C, 18·9; H, 3·7; Hg, 36·1. $C_{18}H_{42}Br_4As_2Hg_2$ requires C, 19·1; H, 3·75; Hg, 35·5%); it is very soluble in acetone and benzene, sparingly so in hot alcohol, acetic acid, and carbon tetrachloride. The corresponding *tetraiodo*-compound, prepared by the interaction of equimolecular quantities of the arsine and the iodide in warm alcoholic solution, had m. p. 107—108° (alcohol) (Found : C, 16·2; H, 3·1; As, 11·6; *M*, cryoscopic in 2·965% benzene solution, 1300. $C_{18}H_{42}I_4As_2Hg_2$ requires C, 16·4; H, 3·2; As, 11·4%; *M*, 1316); it forms beautiful long white needles similar to the α-form of the phosphine analogue. When the arsine was added to a solution of the iodide in aqueous potassium iodide solution, the compound $[(Pr_3As)_3(HgI_2)_2]$ was always formed, but when this was boiled with much alcohol, it decomposed with the formation of the bisarsine derivative.

Prepared in warm alcoholic solution, the *tetrabromo*-compound $[(Bu^{a}{}_3As)_2(HgBr_2)_2]$ had m. p. 86—87° (alcohol) (Found : C, 24·0; H, 4·5; Br, 26·5. $C_{24}H_{54}Br_4As_2Hg_2$ requires C, 23·8; H, 4·5; Br, 26·4%); it crystallised well from alcohol or ether. The corresponding *tetraiodo*-compound was prepared by mixing equimolecular quantities of the sesqui-derivative $[(Bu_3As)_3(HgI_2)_2]$ (see later) and mercuric iodide in warm alcoholic solution; the yellow oil which separated solidified on standing and then gave yellow crystals when crystallised from much alcohol; m. p. 55—56° (Found : C, 20·7; H, 4·2. $C_{24}H_{54}I_4As_2Hg_2$ requires C, 20·5; H, 3·9%).

When solutions of mercuric chloride (0·66 g., 1 mol.) and triphenylarsine (1·5 g., 2 mols.), each in hot alcohol (15 c.c.), were mixed, the tetrachloro-compound rapidly separated as crystals, m. p. 251—253° with softening at 245° (alcohol) (Found : C, 37·8; H, 2·8. Calc. for $C_{36}H_{30}Cl_4As_2Hg_2$: C, 37·4; H, 2·6%). The corresponding *tetrabromo*-compound, prepared by the direct union of equimolar proportions of its generators or by dissolving the unbridged $[(Ph_3As)_2HgBr_2]$ in boiling benzene and cooling, had m. p. 219° (benzene) (Found : C, 32·8; H, 2·5. $C_{36}H_{30}Br_4As_2Hg_2$ requires C, 32·4; H, 2·25%). When this compound was boiled with 2 equivs. of the arsine in benzene solution, it crystallised unchanged on cooling; in alcoholic solution, however, the unbridged dibromo-compound separated.

The analogous iodide was not formed when $[(Ph_3As)_2HgI_2]$ was boiled with a considerable excess of mercuric iodide in alcoholic solution.

Class C, $[\{R_3P(As)\}_2(HgX_2)_3]$, *Bisphosphine*(or *arsine*)*trismercuric Halides*.—Compounds of this class were usually prepared by the interaction of the bridged compound of Class B and mercuric halide in an organic solvent.

Phosphine compounds. When hot solutions of the cadmium derivative $[(Et_3P)_2(CdBr_2)_2]$ (1·10 g., 1 mol.) and of mercuric bromide (2·1 g., 3 mols.) in alcohol (40 c.c. and 20 c.c.) were mixed, the *hexabromo*-compound $[(Et_3P)_2(HgBr_2)_3]$ separated as a powder, which crystallised when the solution was boiled; m. p. 130° (alcohol or acetone) (Found: C, 10·9; H, 2·3. $C_{12}H_{30}Br_6P_2Hg_3$ requires C, 10·9; H, 2·25%). The *hexaiodo*-compound, prepared by the action of the phosphine (2 mols.) on a cold alcoholic solution of mercuric iodide (3 mols.), formed yellow tablets (acetone), m. p. 109—110° (Found: C, 9·0; H, 1·95; I, 47·9. $C_{12}H_{30}I_6P_2Hg_3$ requires C, 9·0; H, 1·9; I, 47·8%). This compound, which is almost insoluble in alcohol, is also formed when an alcoholic solution of $[(Et_3P)_2(HgI_2)_2]$ is boiled for some time.

When hot alcoholic solutions of $[(Pr_3P)_2PdCl_2]$ (1 mol.) and mercuric chloride (3 mols.) were mixed, crystals of the *compound* $[(Pr^{\alpha}_3P)_2(HgCl_2)_3]$ separated at first, but were later contaminated with orange crystals of $[(Pr_3P)_2(PdCl_2)_2]$. These were separated by fractional crystallisation from alcohol, and the hexachloro-compound then further crystallised from benzene; m. p. 113—114° (Found: C, 19·3; H, 3·9. $C_{18}H_{42}Cl_6P_2Hg_3$ requires C, 19·1; H, 3·7%). The tetrachloropalladium compound had m. p. 187°, alone and when mixed with an authentic sample, and the reaction is therefore $2[(R_3P)_2PdCl_2] + 3HgCl_2 = [(R_3P)_2(HgCl_2)_3] + [(R_3P)_2(PdCl_2)_2]$.

When solutions of tri-*n*-butylphosphine (1·5 g.) and mercuric chloride (4·03 g., 2 mols.) in alcohol (50 c.c. and 200 c.c. respectively) were mixed, a small quantity of mercurous chloride first separated (Found: Cl, 15·0. Calc. for Hg_2Cl_2: Cl, 15·0%), followed by large crystals of the *butyl hexachloro*-compound; these, after careful crystallisation from alcohol, had m. p. 72—74° (Found: C, 23·7; H, 4·4; Cl, 17·7. $C_{24}H_{54}Cl_6P_2Hg_3$ requires C, 23·7; H, 4·4; Cl, 17·5%). This compound, when heated above its m. p., or when vigorously boiled with alcohol, gives a white turbidity of mercurous chloride.

Arsine compounds. When solutions of $[(Et_3As)_2(HgI_2)_2]$ (1·23 g., 1 mol.) and mercuric iodide (0·45 g., 1 mol.) in acetone (20 c.c. and 30 c.c.) were mixed, a yellow colour rapidly developed. The mixture, when boiled for 1 min. and cooled, deposited the *compound* $[(Et_3As)_2(HgI_2)_3]$ (VIII) as yellow crystals, m. p. 114—115° (acetone) (Found: C, 8·7; H, 1·9; I, 45·4. $C_{12}H_{30}I_6As_2Hg_3$ requires C, 8·5; H, 1·8; I, 45·1%). The tetraiodo-compound, when boiled with much alcohol, loses free arsine and gives this compound.

Prepared by the interaction of the arsine (1 mol.) and excess mercuric chloride (3 mols.) in aqueous solution, the *hexachloro*-compound $[(Pr^{\alpha}_3As)_2(HgCl_2)_3]$ has m. p. 105° (alcohol) (Found: C, 17·9; H, 3·5. $C_{18}H_{42}Cl_6As_2Hg_3$ requires C, 17·7; H, 3·5%). The corresponding bromide and iodide could not be prepared, only the tetrahalogen compounds of Class B being obtained.

The *hexabromo*-compound $[(Bu^{\alpha}_3As)_2(HgBr_2)_3]$, prepared by the interaction of warm alcoholic solutions of $[(Bu_3As)_2(HgBr_2)_2]$ (1 mol.) and mercuric bromide (2 mols.), had m. p. 62—64° (alcohol) (Found: C, 18·5; H, 3·4. $C_{24}H_{54}Br_6As_2Hg_3$ requires C, 18·3; H, 3·5%). Even when a large excess of mercuric bromide was used, the same product was obtained.

The *butyl hexaiodo*-compound crystallised from the alcoholic mother-liquor obtained from the interaction of the arsine (1 mol.) and mercuric iodide (1 mol.); it was also prepared by the interaction of the sesqui-compound, $[(Bu_3As)_3(HgI_2)_2]$, and mercuric iodide (4 mols.) in warm alcoholic solution. It separated as bright yellow crystals when an acetone solution was diluted with alcohol and set aside; m. p. 63—65° (Found: C, 15·4; H, 2·9; Hg, 32·8. $C_{24}H_{54}I_6As_2Hg_3$ requires C, 15·5; H, 2·9; Hg, 32·4%); it slowly decomposes with liberation of mercuric iodide on long standing, or more rapidly in benzene solution at room temperature.

Class D, $[\{R_3P(As)\}_2(HgX_2)_4]$, *Bisphosphine*(or *arsine*)*tetrakismercuric Halides*.—Iodo-compounds of this class do not appear to be formed.

Phosphine compounds. The *bistriethylphosphine octachloro*-compound was obtained indirectly by the interaction of solutions of the dichloropalladium compound $[(Et_3P)_2PdCl_2]$ (0·41 g., 1 mol.) and of mercuric chloride (0·27 g., 1 mol.) in warm alcohol (15 c.c. and 10 c.c.); it separated as crystals after a few minutes; m. p. 163—164° (alcohol) (Found: C, 10·8; H, 2·35. $C_{12}H_{30}Cl_8P_2Hg_4$ requires C, 10·9; H, 2·3%). From the mother-liquor, the tetrachloropalladium compound, $[(Et_3P)_2(PdCl_2)_2]$, m. p. 230°, and unchanged $[(Et_3P)_2PdCl_2]$ were isolated; the reaction is therefore $2[(Et_3P)_2PdCl_2] + 4HgCl_2 = [(Et_3P)_2(PdCl_2)_2] + [(Et_3P)_2(HgCl_2)_4]$.

The corresponding *octabromo*-compound was obtained from the alcoholic mother-liquors from the preparation of $[(Et_3P)_2(HgBr_2)_2]$ as large prisms, m. p. 149—151° (Found: C, 8·85; H, 2·05. $C_{12}H_{30}Br_8P_2Hg_4$ requires C, 8·6; H, 1·8%).

Arsine compounds. When the compound $[(Et_3As)_2(HgCl_2)_2]$ was dissolved in hot acetone, it lost half the arsine, and the solution on cooling deposited large blunt-ended needles of the *acetone-addition product* of the octachloro-compound; these had $d < 3{\cdot}2$ (flotation in ethylene dibromide), and m. p. 112—114° to a turbid liquid (Found: C, 12·45; H, 2·7; Cl, 18·3. $C_{12}H_{30}Cl_8As_2Hg_4,COMe_2$ requires C, 12·3; H, 2·5; Cl, 18·6%). The acetone is very tenaciously held by these crystals: the loss in weight after 20 hours' heating at 80° was 0·50% (Calc. for $1COMe_2$: 4·12%). The acetone mother-liquors on long standing gave large prisms of the acetone-free *octachloro*-compound; these had $d > 3{\cdot}2$ and m. p. 138° to a turbid liquid (Found: C, 10·2; H, 2·15. $C_{12}H_{30}Cl_8As_2Hg_4$ requires C, 10·6; H, 2·1%). When these crystals were dissolved in hot acetone, the solution on cooling deposited the above acetone addition product; when, however, they were boiled with alcohol, they decrepitated to a powder and then gave a clear solution, which on cooling gave $[(Et_3As)_2(HgCl_2)_2]$, half the mercuric chloride having been lost.

Class E, $[\{(R_3P(As)\}_3(HgX_2)_2]$, *Tetrahalogenotrisphosphine*(or *arsine*)*dimercury*.—Only iodo-compounds of this series appeared to be formed. They were usually obtained by the action of excess of phosphine or arsine on a solution of mercuric iodide in aqueous potassium iodide.

Phosphine compounds. The propyl iodo-compound was prepared indirectly, $[Pr_3P,AgI]_4$ (Mann, Purdie, and Wells, J., 1936, 1507) being used as a source of additional phosphine. When the compound $[(Pr_3P)_2(HgI_2)_2]$ (1 mol.) and the silver compound (1 mol.) were mixed in warm acetone solution, silver iodide was immediately precipitated, and evaporation of the filtrate gave the *trisphosphine* compound, m. p. 124—125° (alcohol) (Found: C, 23·2; H, 4·5; Hg, 28·7. $C_{27}H_{63}I_4P_3Hg_2$ requires C, 23·3; H, 4·6; Hg, 28·9%). The n-*butyl* analogue, prepared by the action of tri-*n*-butylphosphine on mercuric iodide dissolved in aqueous potassium iodide, separated as prisms, m. p. 102° (alcohol) (Found: C, 29·6; H, 5·6. $C_{36}H_{81}I_4P_3Hg_2$ requires C, 29·2; H, 5·5%). On repeated crystallisation or prolonged boiling it dissociates, giving $[(Bu_3P)_2(HgI_2)_2]$.

Arsine compounds. The *tristriethylarsine tetraiodo*-compound was obtained by shaking triethylarsine (2·5 g., 1·5 mols.) with mercuric iodide (4·5 g., 1 mol.) dissolved in a solution of potassium iodide (10 g.) in water (50 c.c.) at *ca.* 10°. The white precipitate was purified by diluting a warm alcoholic solution with acetone, and separated in long needles, m. p. 58—70°, free arsine being apparently liberated during fusion (Found: C, 15·7; H, 3·3. $C_{18}H_{45}I_4As_3Hg_2$ requires C, 15·5; H, 3·2%).

The n-*propyl* homologue was obtained as pale yellow (almost white) leaflets, m. p. 84—85·5°, when (i) a solution of mercuric iodide in aqueous potassium iodide was shaken with an excess of tri-*n*-propylarsine, and the product recrystallised from alcohol containing free arsine to suppress dissociation; or when (ii) a warm alcoholic solution of $[(Pr_3As)_2(HgI_2)_2]$ was treated with free arsine and allowed to cool (Found: C, 21·2; H, 4·3; As, 14·7. $C_{27}H_{63}I_4As_3Hg_2$ requires C, 21·8; H, 4·2; As, 14·4%). When boiled with alcohol it readily dissociates to regenerate $[(Pr_3As)_2(HgI_2)_2]$.

When tri-*n*-butylarsine (4·9 g., 1 mol.) was shaken with a solution of mercuric iodide (9·1 g., 1 mol.) in cold aqueous 5% potassium iodide solution (200 c.c.), the sticky deposit which initially formed slowly solidified. Crystallisation from alcohol or *cyclo*hexane gave the n-*butyl* compound $[(Bu_3As)_3(HgI_2)_2]$ in small plates or massive crystals, according to the speed of crystallisation; m. p. 74—75° (Found: C, 26·4; H, 4·9; Hg, 24·8; *M*, cryoscopic in 2·565% benzene solution, 1100; in 1·268% ethylene bromide solution, 1070. $C_{36}H_{81}I_4As_3Hg_2$ requires C, 26·2; H, 4·95; Hg, 24·4%; *M*, 1646). The alcoholic mother-liquor from the above crystallisations on standing slowly deposited yellow crystals of the tetraiodo-compound, $[(Bu_3As)_2(HgI_2)_2]$.

Solutions of this compound (0·823 g., 1 mol.) and of dipyridyl (0·078 g., 0·5 mol.) in acetone (10 c.c. and 5 c.c.) were mixed and set aside for six weeks; no apparent action had then occurred, and the unchanged mercury compound was recovered in high yield.

All attempts to prepare the bromo-compound $[(Bu_3As)_3(HgBr_2)_2]$ by mixing correct proportions of the components in alcoholic solution gave the tetrabromo-compound, $[(Bu_3As)_2(HgBr_2)_2]$.

Analytical.—Halogen. In the above complex cadmium and mercury compounds halogen was estimated by dissolving the compound (0·2—0·3 g.) in pure acetone (10 c.c.), adding an approximately 50% excess of 1% aqueous silver nitrate solution, and then boiling the mixture gently with 5% aqueous nitric acid (200 c.c.) until the silver halide had coagulated and the supernatant liquid was clear. The silver halide was collected and weighed as usual.

Cadmium. A mixture of the complex compound with excess fuming nitric acid was gently boiled for a few minutes, then diluted and cooled, and the cadmium estimated as the double salt with phenyltrimethylammonium iodide.

Mercury (except in the presence of chlorine). A mixture of the compound (0·4—0·7 g.), fuming nitric acid (5 c.c.), and concentrated sulphuric acid (10 c.c.) was gently warmed until solution was complete. After cooling, water (100 c.c.) was added, and the solution evaporated on a hot plate until white fumes of sulphur trioxide were evolved; the nitric acid was thus removed first, and then at *ca.* 200° the mercuric iodate decomposed with evolution of iodine. The evaporation was repeated after a further addition of water, the residue diluted with water (200 c.c.), and the mercury estimated by titration with standard potassium thiocyanate solution.

Arsenic. The compound was decomposed as in the estimation of cadmium, and the arsenic reduced as usual with sulphur dioxide and finally estimated volumetrically with standard iodine solution.

CRYSTALLOGRAPHIC DATA.

Cadmium Compounds.—Class 2. The following compounds have been investigated by crystallographic, optical, and *X*-ray examinations: $[(Et_3P)_2(CdBr_2)_2]$, $[(Pr^a{}_3P)_2(CdI_2)_2]$, and $[(Pr^a{}_3As)_2(CdI_2)_2]$. The morphological results are summarised in Table I. The three compounds are monoclinic and are clearly isomorphous. They must therefore have very similar structures, and a detailed *X*-ray examination was consequently confined to $[(Et_3P)_2(CdBr_2)_2]$ (V), which was most suitable for this purpose. This occurs in colourless crystals of very simple prismatic habit. Only the forms {110} and {001} were ever observed, so that only the axial ratio $a : b$ and the angle β could be determined goniometrically. These constants, as well as the cell dimensions determined by *X*-rays, confirmed isomorphism with the following two compounds. An optical examination showed a large optic axial angle with the optic axial plane very nearly parallel to {001}. The acute bisectrix is [010]. The crystals are optically negative and γ—β for sodium light is about 0·01. The crystals show no appreciable cleavage and form irregularly shaped fragments when broken.

TABLE I.

Compound.	Crystallographic constants by goniometric measurements.	Cell dimensions, A.
$[(Et_3P)_2(CdBr_2)_2]$	$a : b : c = [1·39] : 1 : ?;\ \beta = 130°$	$a = 17·5,\ b = 12·2,\ c = 7·4$; whence $a : b : c = 1·43 : 1 : 0·61$
$[(Pr_3P)_2(CdI_2)_2]$	$a : b : c = 1·421 : 1 : 0·631;\ \beta = 132°\ 42'$	Not investigated
$[(Pr_3As)_2(CdI_2)_2]$	$a : b : c = 1·42 : 1 : [0·6];\ \beta = 131°$	$a = 18·8,\ b = 13·2,\ c = 8·6$; whence $a : b : c = 1·42 : 1 : 0·65$

The cell dimensions were determined from oscillation photographs about the three axes, and Weissenberg photographs about the [010] and [001] axes. For the Weissenberg photographs the crystals were selected as nearly cylindrical as possible about the axis of rotation. The density was found to be less than that of bromoform (2·85 g./c.c.), whence the number of molecules of composition $[(Et_3P)_2(CdBr_2)_2]$ per unit cell is < 2·7 and must therefore be 2. The calculated density is then 2·13 g./c.c. The photographs showed only the following absent reflections: (*h0l*) when *h* is odd; (*0k0*) when *k* is odd. The space-group is therefore $P2_1/a$, and the crystals belong to the holohedral class $2/m$ of the monoclinic system. The number of equivalent general positions in this space-group is 4, and since there are only 2 molecules in the unit cell they must occupy special positions. The only special positions are centres of symmetry, and we may therefore conclude that the molecules themselves must be centrosymmetrical and possess the *trans*-symmetric structure (V) and not the structure (III) or (IV). The detailed form of the molecule may be assumed to be based on an arrangement of the four cadmium valency bonds, which is either planar (as in the analogous dipalladium compounds) or tetrahedral. The former of these arrangements, which is intrinsically most unlikely in the case of cadmium, is not compatible with the optical properties, for in the monoclinic system a molecule containing a planar arrangement of atoms of such high refractivity as bromine would necessarily show a large birefringence whatever the orientation of the molecules.

More direct evidence for a tetrahedral configuration of bonds round the two cadmium atoms is provided by the preliminary stages of the detailed structure analysis. Patterson F^2 projections were made on planes perpendicular to [010] and [001] from intensities visually estimated on the Weissenberg photographs. These projections showed conspicuous peaks which enabled approximate cadmium positions to be determined, and on the basis of these positions an elegant structure suggests itself in which the cadmium atoms are tetrahedrally co-ordinated and the molecule centred about the point (0, 0, 0) is so disposed that its alkyl groups are directed towards the molecules at ± (½, ½, 1). Such an arrangement is in conformity with the observed changes in cell dimensions as between the ethyl and the propyl compound, and also explains the general features of the F^2 syntheses; the detailed features of this structure are now being established.

$[(Pr_3P)_2(CdI_2)_2]$ was available in small colourless crystals of simple prismatic habit. The faces were very well developed and enabled accurate goniometric measurements to be made. The crystallographic constants (Table I) establish isomorphism with the following compound and no X-ray observations were made.

$[(Pr_3As)_2(CdI_2)_2]$ crystallises in small colourless prisms elongated along [001], the forms {110}, {010}, $\{\bar{1}11\}$, and $\{\bar{1}01\}$ being commonly developed. Goniometric measurements established monoclinic symmetry, but few faces were perfect enough to give measurements leading to accurate axial ratios. Cell dimensions (Table I) were determined from oscillations photographs about the three crystallographic axes. A rough measurement gave the density as 2·3 g./c.c., whence the number of molecules of composition $[(Pr_3As)_2(CdI_2)_2]$ in the unit cell is 2, and the calculated density is 2·35 g./c.c.

Class 3. Two compounds of this type were investigated, *viz.*, $[(Pr^{a}_3P)_3(CdBr_2)_2]$ and $[(Bu^{a}_3P)_3(CdBr_2)_2]$. Both substances were found to be orthorhombic, and the results of the crystallographic investigation, together with the cell dimensions, are summarised in Table II.

TABLE II.

Compound.	Crystallographic constants by goniometric measurements.	Cell dimensions, A.
$[(Pr_3P)_3(CdBr_2)_2]$	$a:b:c = 0{\cdot}84:1:1{\cdot}13$	$a = 14{\cdot}0$, $b = 16{\cdot}3$, $c = 18{\cdot}7$; whence $a:b:c = 0{\cdot}86:1:1{\cdot}14$
$[(Bu_3P)_3(CdBr_2)_2]$	$a:b:c = 0{\cdot}790:1:1{\cdot}126$	$a = 14{\cdot}1$, $b = 18{\cdot}0$, $c = 20{\cdot}5$; whence $a:b:c = 0{\cdot}78:1:1{\cdot}14$

The similarity in the crystallographic constants and cell dimensions suggests a close similarity in the structures of the two compounds, and this is supported by the similarity in the optical properties, described below, and especially by the strikingly perfect cleavage parallel to {001} shown by both substances.

$[(Pr^{a}_3P)_3(CdBr_2)_2]$ occurs as colourless crystals of extremely simple habit, square plates showing {100}, {010}, and {001} and flattened parallel to {010} being common. Small {110} and {011} faces on some crystals enabled the axial ratios to be determined goniometrically, but the quality of these faces was poor and the values correspondingly not very accurate. Optical examination showed the crystals to be optically positive with very low double refraction. The optic axial plane is parallel to {100} and the acute bisectrix to [010]. The optic axial angle is very large and shows very marked dispersion. When tested in liquid air the crystals showed no signs of pyroelectricity and therefore probably do not belong to the class *mm* of the orthorhombic system.

Cell dimensions (Table II) were determined from oscillation photographs about the three crystallographic axes. The approximate density determined by flotation was 1·53 g./c.c., whence the number of molecules of composition $[(Pr_3P)_3(CdBr_2)_2]$ in the unit cell is 4, and the calculated density is 1·59 g./c.c. The oscillation photographs showed no absent reflections of the general type and the lattice is therefore primitive.

$[(Bu^{a}_3P)_3(CdBr_2)_2]$ usually crystallised as colourless prisms showing the forms {110} and {001}, but occasionally crystals much richer in forms were observed and these enabled fairly accurate goniometric measurements of the axial ratios to be made. As with the preceding compound, the crystals were optically positive with very low double refraction, had a large optic axial angle, and showed marked dispersion. The acute bisectrix is again parallel to [010], but the optic axial plane is parallel to {001} instead of to {100} as in $[(Pr_3P)_3(CdBr_2)_2]$. In crystals of such low double refraction, however, such a change in the orientation of the optic axial plane could arise from trivial changes in the refractive indices and does not suggest any marked structural difference between the two compounds. On the other hand, it is not possible to make any positive deductions about the structure from these optical properties.

Cell dimensions (Table II) were determined from oscillation and Weissenberg photographs about the three axes. A rough determination of the density gave 1·36 g./c.c., whence the number of molecules of composition $[(Bu_3P)_3(CdBr_2)_2]$ in the unit cell is 4, and the calculated density is 1·46 g./c.c. The photographs showed only the following absent reflections: (h00), (0k0), and (00l) when h, k, and l are odd. The space-group is therefore necessarily $P\,2_1\,2_1\,2_1$, and the crystals belong to the bisphenoidal class 222 of the orthorhombic system. In this space-group the number of equivalent general positions in the unit cell is 4 and there are no special positions. The four molecules in the unit cell must therefore occupy general positions, so that the molecule does not necessarily possess any intrinsic symmetry and it is not possible to make any deductions concerning its configuration from the space-group alone. One conclusion which can, however, be drawn from the crystallographic evidence is that the compound $[(Bu_3P)_3(CdBr_2)_2]$ cannot be regarded as an intimate lattice compound composed of molecules of the unbridged compound $[(Bu_3P)_2CdBr_2]$ and of $[(Bu_3P)_2(CdBr_2)_2]$, as its method of preparation might suggest. If this were the case the four molecules of $[(Bu_3P)_3(CdBr_2)_2]$ in the unit cell would correspond to $4[(Bu_3P)_2CdBr_2] + 2[(Bu_3P)_2(CdBr_2)_2]$. As is explained above, however, all equivalent positions in the space-group $P\ 2_1\ 2_1\ 2_1$ are necessarily fourfold, and the presence of only two molecules of $[(Bu_3P)_2(CdBr_2)_2]$ in the unit cell is therefore an impossibility. A comparison of the cell dimensions of the propyl and the butyl compound shows that the a axis is almost unaltered, but that the b and c axes increase by roughly the same amount when the propyl group is replaced by the butyl group. These observations suggest that the lengths of the alkyl groups are roughly parallel to the plane {100} and equally inclined to the [010] and [001] axes. A detailed structure analysis of these two compounds has not, however, yet been carried out.

Mercury Compounds.—Class B. Three compounds of this type have been investigated, *viz.*, $[(Et_3As)_2(HgI_2)_2]$, $[(Pr^a{}_3P)_2(HgBr_2)_2]$, and $[(Pr^a{}_3As)_2(HgI_2)_2]$. The results of the morphological and *X*-ray investigations showed the crystals all to be monoclinic with the crystallographic constants and cell dimensions summarised in Table III. These data show that, in contrast to the similar group of cadmium compounds (Class 2), the three mercury compounds are morphologically distinct. On the other hand, $[(Pr_3As)_2(HgI_2)_2]$ and $[(Pr_3As)_2(CdI_2)_2]$ have very nearly identical cell dimensions and are clearly isomorphous, a relationship further emphasised by the striking similarity in habit. On the basis of the close chemical resemblance of cadmium and mercury and their closely similar atomic radii such isomorphism is to be anticipated. It is, however, noteworthy that within the limited number of mercury compounds of Class B studied, a greater variety in structures exists than in the similar group of cadmium compounds (Class 2), where all three substances are isomorphous.

TABLE III.

Compound.	Crystallographic constants by goniometric measurements.	Cell dimensions, A.
$[(Et_3As)_2(HgI_2)_2]$	$a : b : c = 1{\cdot}50 : 1 : [0{\cdot}77]$; $\beta = 94° 58'$	$a = 15{\cdot}3$, $b = 10{\cdot}3$, $c = 8{\cdot}0$; whence $a : b : c = 1{\cdot}49 : 1 : 0{\cdot}775$
$[(Pr_3P)_2(HgBr_2)_2]$	$a : b : c = 1{\cdot}93 : 1 : ?$; $\beta = 116° 10'$	$a = 16{\cdot}75$, $b = 8{\cdot}75$, $c = 11{\cdot}7$; whence $a : b : c = 1{\cdot}91 : 1 : 1{\cdot}34$
$[(Pr_3As)_2(HgI_2)_2]$	$a : b : c = 1{\cdot}47 : 1 : 0{\cdot}67$; $\beta = 132° 1'$	$a = 19{\cdot}1$, $b = 13{\cdot}3$, $c = 8{\cdot}6[5]$; whence $a : b : c = 1{\cdot}43[5] : 1 : 0{\cdot}65$

$[(Et_3As)_2(HgI_2)_2]$ (VII) forms excellent pale yellow crystals. The following forms occur on almost every crystal: {100}, {001}, {110}, {201}, and {111}. The habit varies considerably, but crystals elongated along [001] or flattened parallel to (110) are common. The density was found to be approximately 3·1 g./c.c., whence there are two molecules per unit cell, corresponding to a calculated density of 3·25 g./c.c. There were no absent reflections of the general type in oscillation photographs, and Weissenberg and oscillation photographs showed ($0k0$) reflections for k even only, and ($h0l$) reflections for h even only. The space-group is thus $P2_1/a$. In this space-group there are four equivalent general positions and the only special positions are centres of symmetry. It follows that the molecules must be at centres of symmetry and from the space-group alone it can be at once concluded that the molecule itself must be centrosymmetrical.

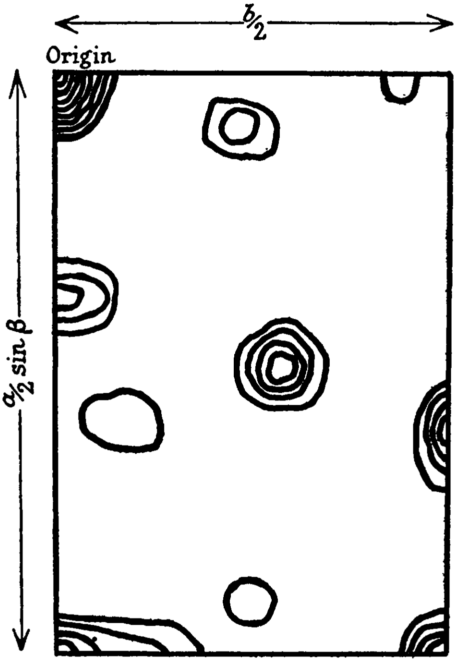
Weissenberg photographs were taken about [010] and [001]. Some considerable care was taken to cut and roll the specimens used for this purpose into small cylinders whose axes were parallel to the crystallographic axes along which the photographs were taken. From the intensities of reflections of the Weissenberg photograph about [001] the Patterson synthesis shown in Fig. 2 was derived. On the assumption that matter is present only at the approximate co-ordinates ± (35°, 0°, —) and ± (55°, 90°, —) relative to a centre of symmetry, all atomic distances within one molecule and between neighbouring molecules can be seen to be represented by sharp peaks, and no other conspicuous peaks exist to suggest matter at different co-ordinates.

It is clear that the mercury atoms cannot have the co-ordinates ± (55°, 90°, —) because, even if they were lying exactly in the plane $c = 0$, such an arrangement would correspond to a Hg–Hg distance of about 5 A., a distance quite inconceivable on the basis of any reasonable chemical molecule. Thus the mercury co-ordinates must be approximately ± (35°, 0°, —) with the iodine and arsenic atoms either at the same co-ordinates or at ± (55°, 90°, —). The only explanation of these facts would be a tetrahedral co-ordination of iodine and arsenic atoms round each mercury atom, with the bridging iodine atoms vertically above or below the mercury atoms, and the terminal iodine and arsenic atoms at (55°, 90°, —) and (55°, — 90°, —). In the resulting crystal structure the mercury atoms are roughly octahedrally surrounded by iodine atoms, and the terminal alkyl groups envelop neighbouring molecules. Exact interatomic distances have not yet been determined.

$[(Pr^{a}_3P)_2(HgBr_2)_2]$ forms fine crystals of very simple habit elongated along [001] and showing only the forms {110} and {001}. Its density is less than that of bromoform (2·85 g./c.c.), whence the number of molecules per unit cell is less than 2·5, and therefore must be 2.

Oscillation photographs failed to show absent reflections of the general type, and Weissenberg photographs taken about the [100] and [010] axes showed systematic halving of the (0*k*0) reflections (always absent when *k* is odd) and of the (*h*0*l*) reflections (always absent when *h* is odd). Therefore the space-group is $P2_1/a$, and by the same argument as for the previous compound, it follows that the molecule must be centro-symmetrical.

FIG. 2.



$[(Et_3As)_2(HgI_2)_2]$. *Patterson synthesis perpendicular to* [001]. *The pattern repeats by reflection across all the edges of the diagram.*

$[(Pr^{a}_3As)_2(HgI_2)_2]$ forms soft crystals with poor faces, which made accurate goniometric measurements difficult. The crystals are commonly elongated along [001] with prominent prism faces {110}, and are occasionally terminated by {$\bar{1}$11} faces.

An oscillation photograph about [001] and a Weissenberg photograph about the same axis gave the cell dimensions which were identified with the help of the morphological axial ratios. Both the (*h*00) and (0*k*0) reflections are absent for *h* and *k* odd respectively, limiting the possible space-groups to $P2_1/a$ or $P2_1/n$. The density of the crystals is 2·66 g./c.c., whence the number of molecules per unit cell is 2, and the calculated density is 2·70 g./c.c. The molecules are therefore again in special positions, whichever is the correct space group, and so must be centro-symmetrical. On the basis of its isomorphism with the cadmium compounds of Class 2, the structure must be analogous to that discussed for $[(Et_3P)_2(CdBr_2)_2]$, and for this reason no further investigations were carried out on this substance.

Class C. Of this group of compounds $[(Et_3As)_2(HgI_2)_3]$, $[(Pr^{a}_3As)_2(HgCl_2)_3]$, and $[(Bu^{a}_3As)_2(HgBr_2)_3]$ were selected for more detailed crystallographic investigation and structure analysis. Morphological data from goniometric measurements and cell dimensions are summarised in Table IV. The constants for the last two compounds, which are both monoclinic, correspond closely, suggesting isomorphism and therefore a similar structural arrangement, a suggestion confirmed both by the identity in crystal habit and by the results of the more detailed *X*-ray investigations described below. The first compound, on the other hand, is orthorhombic with cell dimensions widely different from those of the other two compounds.

TABLE IV.

Compound.	Crystallographic constants by goniometric measurements.	Cell dimensions, A.
$[(Pr_3As)_2(HgCl_2)_3]$	$a : b : c = 1{\cdot}11 : 1 : \ ?; \ \beta = 94°$ [0′]	$a = 14{\cdot}6, b = 13{\cdot}4, c = 8{\cdot}5;$ whence $a : b : c = 1{\cdot}09 : 1 : 0{\cdot}63$[4]
$[(Bu_3As)_2(HgBr_2)_3]$	$a : b : c = 1{\cdot}14 : 1 : \ ?; \ \beta = 94°\ 50'$	$a = 15{\cdot}4, b = 14{\cdot}4, c = 8{\cdot}8;$ whence $a : b : c = 1{\cdot}07 : 1 : 0{\cdot}61$[0]
$[(Et_3As)_2(HgI_2)_3]$	$a : b : c = 1{\cdot}48 : 1 : 0{\cdot}63$	$a = 21{\cdot}5, b = 14{\cdot}9, c = 9{\cdot}4;$ whence $a : b : c = 1{\cdot}44 : 1 : 0{\cdot}63$

$[(Pr^a{}_3As)_2(HgCl_2)_3]$ crystallises in soft, rather imperfect, colourless crystals without any marked cleavage. Most crystals appear to be twinned, but on being touched with a needle they tend to break into single crystals of remarkably constant habit, namely, plates parallel to {010}, elongated along [001], showing the forms {010}, very prominent, {110}, small, and {001}, very small. Although a large number of crystals were measured on a goniometer, no other faces were found. The poor character of the faces made accurate measurements impossible.

Optical investigation showed the crystals to be optically negative with low double refraction and large optic axial angle.

Oscillation photographs about [100], [010], and [001], and Weissenberg photographs of crystals carefully cut and rolled into cylindrical shape about [100] and [010] gave the cell dimensions and showed only the following absent reflections : $(h0l)$ when h is odd and $(0k0)$ when k is odd. The space-group is therefore $P2_1/a$. The density was found to be 2·5 g./c.c., whence the number of molecules of composition $[(Pr_3As)_2(HgCl_2)_3]$ per unit cell is 2, and the calculated density is 2·44 g./c.c. If molecules of this composition exist in the structure they must therefore occupy the special positions at the symmetry centres and so themselves be centro-symmetrical. The space-group evidence is thus sufficient to exclude the possibility of a molecule of structure (VIII) based on a tetrahedral distribution of bonds round the mercury atoms, since such an arrangement would necessarily lack a centre of symmetry. Only if the co-ordination round the central mercury atom were planar could a centro-symmetrical molecule exist. It was, however, possible to deduce the distribution of atoms in the unit cell without any preconceived assumptions concerning the molecular configuration.

From the intensities of the reflection visually estimated on the Weissenberg photographs Patterson F^2 syntheses were constructed. The most conspicuous peaks in these syntheses must clearly be interpreted as Hg–Hg vectors, and lead immediately to the co-ordinates (0, 0, 0) and approximately ± (42°, 0°, 138°) for the mercury atoms. This arrangement of these atoms on planes through the symmetry centres parallel to (010) receives strong support from the very marked pseudo-halving of the $(hk0)$ reflections, which on the average are conspicuously stronger for $(h + k)$ even than for $(h + k)$ odd. A comparatively weak (040) reflection, however, indicates that the greater part of the remaining scattering matter must lie close to the planes $y = b/8$. From the known positions of the mercury atoms the signs of the F values of a considerable fraction of the observed reflections could be deduced and, only the terms of unquestionable sign being used, rough Fourier projections were constructed perpendicular to [010] and [001]. Apart from the mercury peaks these projections showed only one other conspicuous peak, which must represent the arsenic atom, at the approximate co-ordinates ± (90°, 50°, 180°).

Although smaller peaks in these Fourier diagrams were later found to have some significance, it was felt at this stage that the scattering power of the chlorine atoms was too small compared with that of mercury and arsenic to make it possible to locate these atoms with certainty. For the following stages of the structure analysis the following isomorphous compound was therefore considered more suitable.

$[(Bu^a{}_3As)_2(HgBr_2)_3]$ occurs in colourless plate-like crystals almost indistinguishable morphologically from crystals of $[(Pr_3As)_2(HgCl_2)_3]$. They are optically negative with moderately low double refraction and large optic axial angle. The acute bisectrix is [010] and the optic picture shows very marked crossed dispersion.

Oscillation and Weissenberg photographs about the axes [100], [010], and [001] gave the cell dimensions (Table IV) and established the space-group as $P2_1/a$ with 2 molecules per unit cell. Patterson F^2 projections showed conspicuous peaks which enabled the mercury atoms to be approximately located in positions very little different from those found in $[(Pr_3As)_2(HgCl_2)_3]$.

From the known positions of the mercury atoms it was possible to deduce the signs of a considerable number of the F values, and from these values Fourier syntheses were constructed which gave approximate co-ordinates for the bromine and arsenic atoms. By a series of successive approximations the signs of almost all the F values were determined, and a structure was achieved which gave good agreement between observed and calculated intensities for all three directions. From the final Fourier syntheses the following atomic co-ordinates were deduced : Hg^{1}, (0, 0, 0); Hg^{2}, ± (40°, 3°, 143°); Br^{1}, ± (37°, 45°, 15°); Br^{2}, ± (43°, − 50°, 91°); Br^{3}, ± (− 17°, 26°, 114°); As, ± (73°, 46°, 184°), together with the equivalent positions demanded by the space-group symmetry.

A comparison of observed and calculated F values, expressed in arbitrary units and arranged in order of increasing θ up to $\xi = 1$, based on these co-ordinates is shown in Table V. Higher-order reflections up to ξ-values of about 1·5 were included in the Fourier syntheses. In the calculated structure factors no account has been taken of the contribution from the butyl groups since it is not possible to locate matter of such low scattering power with any certainty. This contribution will in general be small but in isolated cases may account for relatively large differences between observed and calculated values. The extremely high absorption coefficients of all crystals of this type make absorption corrections difficult to estimate and very accurate F values correspondingly difficult to obtain.

TABLE V.

hkl.	$F_{calc.}$.	$F_{obs.}$.	*hkl.*	$F_{calc.}$.	$F_{obs.}$.	*hkl.*	$F_{calc.}$.	$F_{obs.}$.	*hkl.*	$F_{calc.}$.	$F_{obs.}$.
001	−11	11	080	24	29	$20\bar{4}$	− 9	9	250	0	0
011	3	0	081	− 2	4	602	− 9	13	440	3	3
020	34	18	005	8	21	204	7	9	530	− 4	6
021	− 7	4	054	0	0	$60\bar{3}$	−12	14	600	− 6	8
002	16	16	015	4	5	$40\bar{4}$	2	0	350	3	9
012	− 1	4	025	14	21	800	15	20	610	− 6	0
031	− 6	4	073	1	0	$80\bar{1}$	0	0	060	20	22
022	11	8	082	25	18	603	6	10	620	− 4	0
040	2	5	001	−11	11	404	15	25	160	6	7
041	− 4	4	200	16	10	801	18	21	540	11	11
032	1	3	$20\bar{1}$	32	16	200	16	18	450	3	3
003	20	30	201	2	0	020	34	17	260	3	6
013	− 7	10	002	16	12	210	0	2	630	4	6
042	3	6	$20\bar{2}$	− 3	0	120	− 8	11	360	4	4
051	−12	10	400	−18	18	220	20	17	710	4	6
023	20	16	202	7	8	320	6	9	550	− 4	7
033	− 4	8	$40\bar{1}$	9	5	130	12	16	720	3	6
052	8	7	401	14	12	230	0	0	640	2	4
060	20	24	$40\bar{2}$	9	6	400	−18	23	170	19	22
061	− 5	5	003	20	21	410	5	5	460	−11	10
043	14	10	$20\bar{3}$	33	33	040	2	4	270	6	0
004	11	13	402	8	6	140	4	0	730	10	8
014	− 8	11	203	10	8	330	14	13	370	−14	11
024	− 9	7	600	− 6	8	420	− 4	5	650	15	17
062	7	7	$60\bar{1}$	−14	8	240	14	13	800	15	23
053	9	3	$40\bar{3}$	9	14	510	−11	16	560	5	10
071	2	7	601	26	29	430	9	7	810	9	10
034	−13	7	$60\bar{2}$	18	19	340	1	0	740	9	13
072	5	5	403	− 9	9	150	10	11	820	12	13
044	−20	15	004	11	9	520	2	0	080	24	31
063	4	4									

A plan of part of the structure perpendicular to [010] showing the co-ordination round the mercury atoms of the two kinds is given in Fig. 1. The interatomic distances (in A.) and bond angles for the atoms shown in this plan are :

Hg^{1}—Br^{1} = 2·25
Hg^{1}—Br^{2} = 3·2
Hg^{1}—Br^{3A} = 3·1
Hg^{1}—Hg^{2A} = 3·8
Hg^{2A}—Hg^{2B} = 4·0

Hg^{2A}—Br^{2A} = 2·25
Hg^{2A}—As^{A} = 2·25
Hg^{2A}—Br^{3A} = 2·6
Hg^{2A}—Br^{3B} = 2·9

As^{A}—Hg^{2A}—Br^{2A} = 135°
Br^{2A}—Hg^{2A}—Br^{3A} = 102°
Br^{3A}—Hg^{2A}—Br^{3B} = 87°
As—Hg^{2A}—Br^{3B} = 94°

Br^{1B}—Hg^{1}—Br^{3A} = 98°
Br^{2A}—Hg^{1}—Br^{3A} = 72°
Br^{1A}—Hg^{1}—Br^{2A} = 85°

From these figures it will be seen that the two Hg^2 atoms may be regarded as forming part of a bridged molecule $[(Bu_3As)_2(HgBr_2)_2]$ of Class B, in which the molecule is strictly centro-symmetrical with a considerably distorted tetrahedral distribution of the mercury valency bonds. The atom Hg^1 lies at a symmetry centre and is surrounded by a much distorted octahedron of six bromine atoms. Of these, four, which are very much more remote, belong to the bridged molecule, whereas the other two at the close distance of 2·25 A. are directly bound only to the Hg^1 atoms. The structure may therefore be qualitatively described as composed of bridged molecules, $[(Bu_3As)_2(HgBr_2)_2]$, and of linear mercuric bromide molecules. There is no evidence for the existence of a single independent bridged molecule of composition $[(Bu_3As)_2(HgBr_2)_3]$ and of structure as (VIII).

$[(Et_3As)_2(HgI_2)_3]$ forms yellow crystals which are optically positive and of fairly high double refraction $[\Delta_{\lambda Na} = 0{\cdot}025]$. Goniometric measurements established orthorhombic symmetry and suggested membership of the class *mm*, crystals bounded by {111} and $\{21\bar{1}\}$ being a common habit. Assignation to this class was confirmed by tests in liquid air which revealed marked pyroelectricity. *X*-Ray observations have so far been confined to measurements of the cell dimensions (Table IV). The density is not much greater than 3·3 g./c.c., whence the number of molecules per unit cell is 4, and the calculated density 3·70 g./c.c. The structural arrangement is clearly entirely distinct from the monoclinic structures of $[(Pr_3As)_2(HgCl_2)_3]$ and $[(Bu_3As)_2(HgBr_2)_3]$, and, in particular, the crystal class, lacking a centre of symmetry, admits the possibility of a non-centro-symmetrical molecule such as would occur in a single bridged molecule of three mercury atoms each tetrahedrally co-ordinated (VIII).

Class D. Only preliminary investigations of compounds in this group have so far been carried out, the compounds studied being $[(Et_3P)_2(HgBr_2)_4]$, $[(Et_3As)_2(HgCl_2)_4]$, and the acetone addition product of the latter, all three compounds being monoclinic. The results of morphological investigations and the cell dimensions are summarised in Table VI.

TABLE VI.

Compound.	Morphological data by goniometric measurements.	Cell dimensions, A.
$[(Et_3P)_2(HgBr_2)_4]$	$a : b : c = 0{\cdot}95 : 1 : 1{\cdot}17$; $\beta = 99{\cdot}5°$	$a = 10{\cdot}65$, $b = 11{\cdot}25$, $c = 13{\cdot}26$; whence $a : b : c = 0{\cdot}95 : 1 : 1{\cdot}18$
$[(Et_3As)_2(HgCl_2)_4]$	$a : b : c = 1{\cdot}19 : 1 : 0{\cdot}95$; $\beta = 99° 20'$	$a = 12{\cdot}9$, $b = 10{\cdot}8$, $c = 10{\cdot}5$; whence $a : b : c = 1{\cdot}19 : 1 : 0{\cdot}97$
$[(Et_3As)_2(HgCl_2)_4],COMe_2$	$a : b : c = 2{\cdot}0 : 1 :\ ?$; $\beta = 118°$	$a = 21{\cdot}8$, $b = 11{\cdot}4$, $c = 8{\cdot}6$; whence $a : b : c = 1{\cdot}92 : 1 : 0{\cdot}755$

$[(Et_3P)_2(HgBr_2)_4]$ forms colourless crystals of simple habit elongated along [001] showing the forms {100}, {110}, {010}, {001} and {011}. Oscillation photographs about the three axes gave the cell dimensions. The density was found to be *ca.* 3·7 g./c.c., whence the number of molecules per unit cell is 2, and the calculated density 3·54 g./c.c. The lattice is therefore necessarily primitive.

A Weissenberg photograph about [001] showed systematically absent reflections only of the type (0*k*0) for *k* odd. The space-group is therefore $P2_1/c$ or $P2_1/m$. From the intensities of the reflections on this Weissenberg photograph, a Patterson F^2 synthesis was constructed. If the structure were composed of discrete molecules of structure (IX), consisting of four tetrahedrally co-ordinated mercury atoms in a straight line, this synthesis would be expected to show a row of seven conspicuous peaks, three on each side of the origin, corresponding to Hg–Hg distances within the molecule. The fact that no such peaks were found is in itself strong evidence against such a molecular arrangement.

$[(Et_3As)_2(HgCl_2)_4]$ forms colourless, tabular crystals showing the forms {110} prominent, {011} small, and {001} very small. The faces are of very poor quality, making accurate goniometric measurements impossible. The crystals are almost invariably twinned, but break up into single crystals on touching with a needle. They are soft and brittle without showing any regular cleavage. Furthermore, they are optically positive with fairly high double refraction, $\gamma - \beta$ for Na light being 0·15. The density was found to be somewhat greater than that of bromoform (2·85 g./c.c.), whence the number of molecules per unit cell is 2, and the calculated density 3·22 g./c.c.

The acetone addition product of this compound (p. 1222) forms crystals which are elongated in habit showing even poorer faces of the forms {100}, {120}, and {001}. A comparison of the cell dimensions with those of the acetone-free crystals suggests no immediate relationship between the two structures.

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