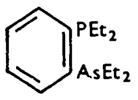
544. *The Constitution of Complex Metallic Salts. Part XVI.* The Cuprous, Argentous, and Aurous Derivatives of* o-*Diethylphosphinophenyldiethylarsine.*

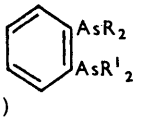
By W. Cochran, F. A. Hart, and Frederick G. Mann.

The various types of co-ordination derivatives which the di-tertiary phosphine-arsine *o*-diethylphosphinophenyldiethylarsine forms with cuprous, argentous, and aurous halides have been surveyed. Stable salts of type [(phosphine-arsine)$_2$M]I are formed only in the cuprous and aurous series. These salts should be resolvable into optically active forms, if the tetraco-ordinate metal has the tetrahedral configuration. Salts of the aurous cation with eight different optically active acid radicals gave, however, no indication of resolution. The above cuprous and aurous iodides, and the analogous aurous iodide obtained from *o*-phenylenebisdiethylarsine have therefore been examined by *X*-ray crystal analysis. They prove to be isomorphous, and the central metal atom has the tetrahedral configuration, the chelated ligand in all cases forming an angle of *ca.* 90° with the metallic atom. An explanation of the failure to resolve certain of these cuprous and aurous salts is suggested by the crystal-structure analysis.

The synthesis of *o*-diethylphosphinophenyldimethylarsine and of *o*-diethylphosphinophenyldiethylarsine (I) has been described by Jones and Mann,[1] who showed that the former acted as a strong chelating molecule with palladium bromide, giving compounds similar in type to those prepared earlier from the analogous *o*-phenylenebisdimethylarsine (II; R = R^1 = Me) by Chatt and Mann.[2]



(I)



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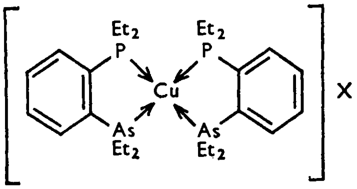

(III)

The fully chelated derivatives of the phosphine-arsine (I) with tetraco-ordinate metals are of greater interest than those of the diarsine (II; R = R^1 = Me), since theoretically they should be capable of showing *cis–trans* isomerism if the metal has the planar configuration, or optical activity if it has the tetrahedral configuration.

We have therefore investigated the derivatives of the phosphine-arsine (I) with cuprous, argentous, and aurous halides, to see if certain of these derivatives appeared promising for optical resolution, for the quadricovalent cuprous and argentous complexes are known to have the tetrahedral configuration,[3] and there appeared to be considerable reason [4] to believe that the aurous complex also has this configuration.

We find that the phosphine-arsine (2 mols.) in ethanol readily reacts with cuprous chloride (1 mol.) in aqueous sodium chloride to give bis-(*o*-diethylphosphinophenyldiethylarsine)cuprous chloride (III; X = Cl), m. p. 211—212°. The structure of this compound is confirmed by its molar conductivity in nitrobenzene, 21·3 mhos, which is in the normal range for a uni-univalent electrolyte.

When this experiment was repeated with the phosphine-arsine (1 mol.), or alternatively

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* Part XV, *J.*, 1955, 1269.

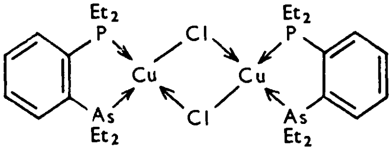
[1] Emrys R. H. Jones, and Mann, *J.*, 1955, 4472.

[2] Chatt and Mann, *J.*, 1939, 610.

[3] Cox, Wardlaw, and Webster, *J.*, 1936, 775; Mann, Purdie, and Wells, *J.*, 1936, 1503; Mann, Wells, and Purdie, *J.*, 1937, 1828.

[4] Nyholm, *Nature*, 1951, **168**, 705; Nyholm and Stephenson, *Rec. Trav. chim.*, 1956, **75**, 687.

when the salt (III; X = Cl) was heated at 150°/0·3 mm., a compound, m. p. 194—196°, was obtained, in which the phosphine-arsine and the cuprous chloride components were in the 1 : 1 stoicheiometric ratio. The evidence for the structure of this compound follows that adduced by Kabesh and Nyholm[5] for a similar derivative of the diarsine (II; $R = R^1 = Me$). Our compound could be a bridged derivative (IV) or a derivative of trico-ordinate copper (V) or the dichlorocuprite of the cation in (III). The compounds (IV) and (V) would be null-valent, and our compound has a molar conductivity in nitrobenzene, 21·1 mhos, which shows it to be a uni-univalent salt, and hence the dichlorocuprite (III; $X = CuCl_2$). The molecular weight of this compound in boiling ethyl methyl ketone agreed, however, closely with that of the un-ionised salt (III; $X = CuCl_2$).



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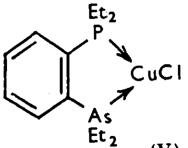


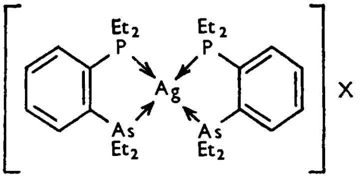
(V)

This salt underwent rapid atmospheric oxidation in hot organic solvents, and recrystallisation was performed under nitrogen. Prolonged boiling of an unprotected ethanolic solution, to promote this oxidation, gave a pale lemon-yellow crystalline compound, the analysis and molecular weight of which indicated a composition $2C_6H_4(PEt_2)(AsEt_2),3CuCl$: its solution in nitrobenzene had a molar conductivity of 25·7 mhos. It was not further investigated.

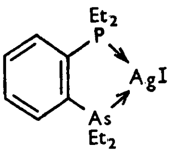
Cuprous bromide similarly gave the bromide (III; X = Br), which when heated at 100°/0·2 mm. gave the dibromocuprite (III; $X = CuBr_2$). The latter was almost insoluble in most boiling organic liquids. In boiling chloroform low values for the molecular weight were obtained, and although great accuracy cannot be claimed for these determinations owing to the very low concentration of the solutions, there is no doubt concerning the general order of the results. Their possible significance is discussed below in connection with an analogous argentous compound. The compound (III; $X = CuBr_2$) did not show ready atmospheric oxidation in solution.

Cuprous iodide also gave the iodide (III; X = I), which had greater stability than the chloride and bromide, being unaffected by heating at 100°/0·1 mm. and by even prolonged boiling of its ethanolic solution.

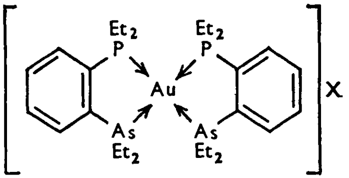
When a suspension of silver chloride in aqueous sodium chloride was vigorously shaken with the ethanolic phosphine-arsine (2 mols), only the dichloro-argentite (VI; $X = AgCl_2$) was obtained, and the instability of this compound necessitated very careful treatment to obtain it reasonably pure. In view of this factor, and the apparent non-existence of the chloride (VI; X = Cl) under our experimental conditions, further work in the argentous series was limited to the iodo-derivatives.



(VI)



(VII)



(VIII)

When a solution of silver iodide in aqueous potassium iodide was shaken with the ethanolic phosphine-arsine (2 mols.) for 3 hr., a white crystalline product, m. p. 190—230°, was obtained. A portion of this product, when treated in ethanol with an excess of

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[5] Kabesh and Nyholm, *J.*, 1951, 38.

the phosphine-arsine, gave the bis-(*o*-diethylphosphinophenyldiethylarsine)argentous iodide (VI; X = I), m. p. 158—160°, having a molar conductivity in nitrobenzene of 20·3 mhos.

A further portion, when recrystallised thrice from dimethylformamide, gave the corresponding di-iodoargentite (VI; X = AgI_2), m. p. 253—255°. It is probable therefore that the original crude product was a mixture of these two salts.

The iodide (VI; X = I) crystallises pure apparently only if the solution contains an excess of the phosphine-arsine. An ethanolic solution of the salt, moreover, even on being gently warmed, deposits the much less soluble di-iodoargentite (VI; X = AgI_2). These facts indicate strongly that in organic solvents an equilibrium may be formed: 2(VI; X = I) $\rightleftharpoons$ (VI; X = AgI_2) + $2C_6H_4(PEt_2)(AsEt_2)$. This explains the need in most solvents for an excess of the phosphine-arsine to stabilise the more soluble iodide (VI; X = I). A dilute solution of this iodide in nitrobenzene had a molar conductivity of 20·3 mhos, and gave no indication of deposition of the salt (VI; X = AgI_2).

The probable structure of the di-iodoargentite (VI; X = AgI_2) calls for comment. Its solution in nitrobenzene has a molar conductivity of 16·4 mhos, which is well below the range of the other values encountered in this investigation. In boiling chloroform it shows an apparent molecular weight of 380—390, whereas the structure (VI; X = AgI_2) requires a value of 1066. (The compound is very slightly soluble in most solvents, and the very low concentration even in boiling chloroform precluded accurate values for the molecular weight.) The explanation of these values may be that the salt in cold nitrobenzene solution exists partly as an ion-pair and is thus incompletely ionised, whereas in boiling chloroform it is completely ionised. This explanation is improbable in view of the highly ionising properties of nitrobenzene. Moreover, if it were true, the salt (VI; X = AgI_2) differs from the dichlorocuprite (III; X = $CuCl_2$), the conductivity of which in nitrobenzene indicates virtually complete ionisation, and from the dibromocuprite (III; X = $CuBr_2$), the molecular weight of which in boiling chloroform is consistent with only partial ionisation.*

An alternative explanation of our results is that the salt (VI; X = AgI_2) in solution is in equilibrium with the null-valent compound (VII), *i.e.*, (VI; X = AgI_2) $\rightleftharpoons$ 2(VII) and that the equilibrium point lies on the left-hand side in cold nitrobenzene solution, and well over on the right in boiling chloroform. The existence of the compound (VII) is not improbable, for Cass, Coates, and Hayter[6] have recently recorded stable compounds having silver iodide co-ordinated with 2 molecules of a tertiary phosphine; these compounds were monomeric in solution, the silver thus showing a co-ordination number of 3. There is at present insufficient evidence to determine the structure of compounds such as (III; X = $CuBr_2$) and (VI; X = AgI_2) when in solution. They were not further investigated as they lie outside the main line of this investigation.

Chloroauric acid, when treated in aqueous solution with an excess of the ethanolic phosphine-arsine, readily underwent reduction and co-ordination to give a colourless solution: addition of aqueous potassium iodide deposited bis-(*o*-diethylphosphinophenyldiethylarsine)aurous iodide (VIII; X = I), which readily crystallised from ethyl methyl ketone in magnificent large colourless crystals having considerable stability. Alternatively, the chloroauric acid could be co-ordinated with the phosphine-arsine and then reduced with sodium hypophosphite solution, and the more soluble chloride (VIII; X = Cl) isolated. We have prepared many salts of the cation (VIII), but have never obtained any indication of their conversion into salts comparable in structure with the dichlorocuprite (III; X = $CuCl_2$) or the di-iodoargentite (VI; X = AgI_2).

Our aurous compound (VIII; X = I) has apparently the same structure as the analogous salt which Nyholm[4] prepared from *o*-phenylenebisdimethylarsine (II;

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* For a fuller discussion correlating conductivity, apparent molecular weight in solution, and structure of analogous diarsine dihalogenocuprite salts, see ref. 5.

[6] Cass, Coates, and Hayter, *J.*, 1955, 4007.

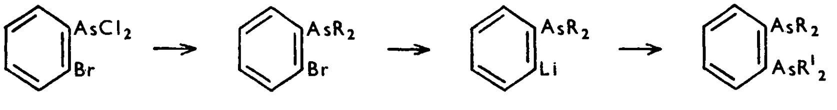
$R = R^1 = Me$), and which he finds by *X*-ray powder photographs to be almost certainly isomorphous with the cuprous salt prepared from this diarsine.

Of the above stable phosphine-arsine derivatives, only the cuprous and the aurous salts, (III) and (VIII) respectively, should theoretically be susceptible to optical resolution.

A brief survey of the cuprous salts (III) gave no indication of resolution, but we have investigated in considerable detail the possibility of resolving the aurous salts (VIII), particularly as they have considerable stability except in the presence of other heavy metallic ions.

The aurous iodide (VIII; $X = I$), when treated in aqueous ethyl methyl ketone cautiously with an aqueous solution of silver (+)-camphorsulphonate, ultimately gave the (+)-camphorsulphonate (VIII; $X = C_{10}H_{15}O_4S$); after repeated crystallisation this salt was converted into the picrate [VIII; $X = C_6H_2(NO_2)_3O$], which proved inactive. This method of double decomposition with silver salts was satisfactory, however, only if the latter were reasonably soluble in cold solvents, and consequently rapidly precipitated the silver halide: prolonged exposure of the cation (VIII) to silver salts, or (more particularly) even gentle warming of such mixtures caused decomposition of the cation by partial co-ordination of the silver with the phosphine-arsine. To avoid this difficulty, the iodide (VIII; $X = I$) was treated in solution with an equivalent of silver sulphate. The sulphate thus obtained proved difficult to purify, but with dilute sulphuric acid gave the crystalline hydrogen sulphate (VIII; $X = HSO_4$) from which, by treatment with barium hydroxide, an aqueous solution of the hydroxide (VIII; $X = OH$) of known concentration was obtained. Quantitative treatment of this solution with the appropriate acid gave the following crystalline salts.

(*a*) The (+)-bromocamphorsulphonate, which after ten recrystallisations from diethyl carbonate gave the inactive iodide; (*b*) the (+)-hydrogen tartrate, which gave no evidence of resolution after ten recrystallisations from ethyl methyl ketone: repeated crystallisation from water gave conversion into the (+)-tartrate, again without resolution; (*c*) the (—)-menthoxyacetate; (*d*) the (+)-camphornitronate; (*e*) the (—)-*N*-menthylphthalamate; and (*f*) the (—)-*N*-1-phenylethylphthalamate. Fractional crystallisation of the salts (*c*)—(*f*) from various solvents failed to effect resolution. The salt (*f*) appeared most promising, for fractional precipitation from acetone solution by diethyl carbonate gave a crop having $[M]_D$ +116°, increased to +128° by repeated recrystallisation from acetone: it gave however an inactive picrate [VIII; $X = C_6H_2(NO_2)_3O$]. The anomalous rotations given by various (—)-*N*-1-phenylethylphthalamate salts and the probable cause of their irregular values are discussed elsewhere.[7]



(IX) (X) (XI) (II)

In view of these failures, attempts were made to demonstrate the required dissymmetry by employing a di-arsine (II), in which the pairs of groups, R and R^1, were different.

o-Phenylene-*as*-dimethyldiphenyldiarsine (II; $R = Ph$, $R^1 = Me$) was prepared by converting *o*-bromophenyldichloroarsine (IX)[1] by phenylmagnesium bromide into *o*-bromophenyldiphenylarsine (X; $R = Ph$): this compound gave the lithio-derivative (XI; $R = Ph$) which, on treatment with iododimethylarsine, gave the required diarsine (II; $R = Ph$, $R^1 = Me$). This diarsine readily gave the bisdiarsinecopper iodide (as III; $X = I$) and the di-iodocuprite (as III; $X = CuI_2$), but did not yield a satisfactory aurous salt.

o-Phenylene-*as*-diethyldimethyldiarsine (II; $R = Et$, $R^1 = Me$) was similarly prepared in order to strengthen the co-ordinating power of the diarsine. This readily gave the

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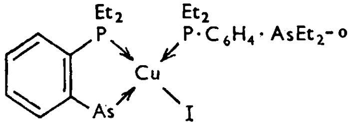
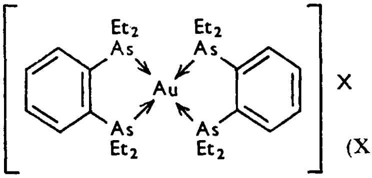
[7] Hart and Mann, following paper.

highly crystalline bisdiarsineaurous iodide, which in turn gave the corresponding (+)-camphorsulphonate and (+)-bromocamphorsulphonate: these salts crystallised with ominous readiness, and their m. p.s and rotations were unaffected by recrystallisation, which gave no evidence of resolution. The (—)-menthoxyacetate could not be obtained crystalline.

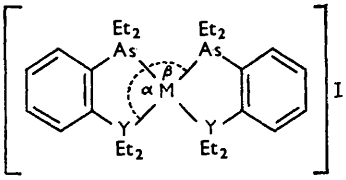
These repeated failures to obtain resolution may well have been due to mixed-crystal formation or other experimental difficulties normally attending this process. Alternatively, it is possible that the chelated ring in these spirocyclic cations may open in solution, and that, for example, the cuprous iodide (III; X = I) is in equilibrium with a minute proportion of a compound of type (XII), a process that might cause rapid racemisation if it affected the configurational stability of the copper atom in (XII). This opening of a chelated ring occurs however only when the co-ordination of one group is much weaker than that of the second group [8] and the co-ordinative power of the tertiary phosphine and arsine groups in the compound (I) are almost certainly of the same order. Moreover, no indication of such change was observed in any of our compounds, the aurous derivatives being, in the absence of other heavy metals, particularly stable.

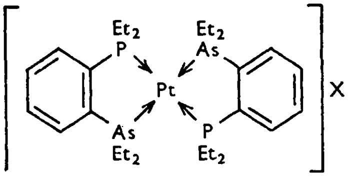

(XII)


(XIII)

It became advisable however to seek decisive physical evidence that the tetraco-ordinated aurous complex was in fact tetrahedral. We have therefore prepared *o*-phenylenebisdiethylarsine (II; $R = R^1 = Et$) by the route outlined above. This diarsine gave the highly crystalline bis-(*o*-phenylenebisdiethylarsine)aurous iodide (XIII; X = I), which could therefore be investigated by *X*-ray crystal analysis, together with the analogous phosphine-arsine aurous iodide (VIII; X = I) and the phosphine-arsine cuprous iodide (III; X = I).

These three salts may conveniently be represented by the general formula (XIV), so that in (XIII), M = Au, Y = As; in (VIII), M = Au, Y = P; in (III), M = Cu, Y = P. The fact that these salts are all isomorphous is shown by oscillation and Weissenberg-type photographs. The central metallic atoms have a tetrahedral configuration without full tetrahedral symmetry, for in the cation (XIII), the angles $\alpha = 90^\circ \pm 2^\circ$, $\beta = 120^\circ \pm 2^\circ$, and in (III), $\alpha = 92^\circ \pm 1{\cdot}5^\circ$, $\beta = 119^\circ \pm 1{\cdot}5^\circ$. It is noteworthy that the shortest distances between iodine atoms and the gold atom range from 6·2 to 7·1 Å: these distances are too great to allow bonding between the iodine and the gold, and the latter is therefore showing without doubt a co-ordination number of four.


(XIV)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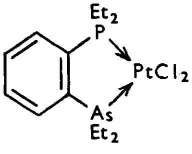
(XVI)

In the crystal structure of the compounds (VIII) and (III) an important factor arises, namely, that although the positions of the phosphorus or arsenic atoms are clearly defined, the atoms of the two elements cannot be differentiated owing to an apparently random distribution, *i.e.*, sites which for convenience we can label A and B may at one place in the crystal be occupied by phosphorus and arsenic atoms, but crystallographically equivalent sites A^1 and B^1 (related to A and B by the symmetry of the space group) may be occupied

[8] Mann and Stewart, *J.*, 1955, 1269.

by phosphorus and arsenic, or by arsenic and phosphorus, respectively. This random distribution is quite distinct from the regular arrangement to be expected in a racemate. Its occurrence might well make resolution by fractional crystallisation of a salt having an optically active anion impossible; for example, if a (+)-anion were used, there would be no physical differentiation between the (+)-cation-(+)-anion and the (−)-cation-(+)-anion, because mixed crystals would almost certainly be formed. This factor * probably accounts for our failure to resolve the phosphine-arsine cation (VIII): it is unlikely however to apply to the analogous cation prepared from the diarsine (II; R = Et, R^1 = Me).

For convenience, the conductivities obtained in the above investigation are collected in the following Table, where the symbol P-As has been used to represent the phosphine-arsine (I).

	$10^4 \times$ Concn. (M)	Conductivity (μ mho)	Λ (mho)	$\Lambda_{0\cdot005}$
$[(\text{P-As})_2\text{Cu}]\text{Cl}$	64·5	436	21·3	22·2
$[(\text{P-As})_2\text{Cu}][\text{CuCl}_2]$	84·6	571	21·1	23·3
$[(\text{P-As})_2(\text{CuCl})_2]$	31·6	259	25·7	23·9
$[(\text{P-As})_2\text{Ag}]\text{I}$	49·4	320	20·3	20·25
$[(\text{P-As})_2\text{Ag}][\text{AgI}_2]$	21·9	115	16·4	14·4
$[(\text{P-As})_2\text{Au}]\text{I}$	53·5	350	20·5	20·7

In the last column, the values of Λ have been converted into $\Lambda_{0\cdot005}$, *i.e.*, the molecular conductivity at a uniform concentration of 0·005 mole/l., by using a curve based on the tabulated values obtained by Chatt [9] for a uni-univalent platinum compound. The curve can be used here with reasonable accuracy, and makes due allowance for the concentration of the solutions. The low conductivity of the $[(\text{P-As})_2\text{Ag}][\text{AgI}_2]$ salt now becomes even more apparent in comparison with that of the other compounds.

The interaction of the phosphine-arsine (I) with sodium chloroplatinite has been briefly investigated. The chloroplatinite, when treated in aqueous solution with the ethanolic phosphine-arsine (2 mols.) gave an immediate precipitate: the mixture, when then boiled, gave the pale salmon-pink bis-(*o*-diethylphosphinophenyldiethylarsine)platinous chloroplatinite (XV; X = $PtCl_4$), which readily crystallised from hydrochloric acid. This compound, when heated at 200°, was slowly converted into the colourless dichloro-(*o*-diethylphosphinophenyldiethylarsine)platinum (XVI). The mother-liquor from the initial preparation on evaporation gave a residue which, when recrystallised from dimethylformamide containing free phosphine-arsine, gave the colourless dichloride (XV; X = Cl_2): recrystallisation from the pure solvent caused decomposition with the formation of the null-valent compound (XVI). The cation in the salts (XV) has been depicted as the *trans*-form, solely on the basis of probability: there is at present no evidence for its configuration.

EXPERIMENTAL

Chemical Data.

All compounds were colourless except when otherwise stated. All rotations were determined with Na-*D* light (λ, 5893 Å).

Preparation of the Ligands.—The phosphine-arsine (I) was prepared as Jones and Mann [1] direct.

o-*Phenylene*-as-*dimethyldiphenyldiarsine* (II; R = Ph, R^1 = Me).—*o*-Bromophenyldichloroarsine [1] when treated with phenylmagnesium bromide (2 mols.) afforded, after the normal working-up, o-*bromophenyldiphenylarsine* (X; R = Ph), m. p. 101·5—103·5°, after two recrystallisations from ethanol (Found: C, 56·5; H, 3·6. $C_{18}H_{14}BrAs$ requires C, 56·1; H, 3·7%). A solution of this arsine (21·8 g.) in ether (200 c.c.) was treated under nitrogen with *n*-butyl-lithium (1 mol.) in light petroleum (b. p. 40—60°) solution (45·4 c.c.; 1·25N). After being stirred for 15 min., the mixture was treated with iododimethylarsine (13·15 g., 1 mol.) dissolved in the petroleum (100 c.c.), and then boiled for 1 hr. After hydrolysis with water and working

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* It is of interest to note that a crystal of (VIII; X = I) or of (III; X = I), composed entirely of (+)-molecules, could achieve internal compensation by this same device of ignoring the difference between phosphorus and arsenic, although the optical activity would of course be manifest in solution.

[9] Chatt, *J.*, 1951, 652.

up, the *diarsine* (II; R = Ph, R^1 = Me) was obtained initially as a crude distillate, b. p. 194—209°/1 mm. (11·0 g., 48%), which solidified on cooling, and when thrice recrystallised from ethanol had m. p. 103—104° (Found: C, 58·9; H, 5·0. $C_{20}H_{20}As_2$ requires C, 58·6; H, 4·9%).

o-*Phenylene*-as-*diethyldimethyldiarsine* (II; R = Et, R^1 = Me).—A solution of *o*-bromophenyldiethylarsine [1] (X; R = Et) (32·4 g.) in the petroleum (150 c.c.) and ether (20 c.c.) was treated as above with *n*-butyl-lithium (1 mol.) in petroleum (64·3 c.c.; 1·74N). After treatment with iododimethylarsine (26·0 g., 1 mol.) in petroleum (80 c.c.), working up gave the liquid *diarsine* (II; R = Et, R^1 = Me), b. p. 97·5—98·5°/0·15 mm. (Found: C, 46·0; H, 6·4. $C_{12}H_{20}As_2$ requires C, 45·9; H, 6·4%); 28·0 g., 80%.

o-*Phenylenebisdiethylarsine* (II; R = R^1 = Et).—This diarsine was similarly prepared by treating *o*-bromophenyldiethylarsine (10 g.) in ether (50 c.c.) with a solution of *n*-butyl-lithium (1 mol.) in the petroleum (24·3 c.c., 1·42N), and then with diethyliodoarsine (9·0 g., 1 mol.) in ether (50 c.c.). The liquid *diarsine* (II; R = R^1 = Et) had b. p. 116·5—117°/0·3 mm. (Found: C, 49·45; H, 7·0. $C_{14}H_{24}As_2$ requires C, 49·1; H, 7·1%).

Derivatives of the Phosphine-arsine (I).—*Cuprous Derivatives.*—*Bis-*(o-*diethylphosphinophenyldiethylarsine*)*cuprous chloride* (III; X = Cl). A solution of the phosphine-arsine (I) (2·61 g.) in ethanol (2 c.c.) was added to cuprous chloride (0·434 g., 1 mol. CuCl) in water (20 c.c.) containing sodium chloride (5 g.), which was shaken for 1 hr. The oily deposit which separated was collected, dried in a vacuum desiccator, and then well stirred with ethyl acetate (50 c.c.), whereupon it crystallised. The *chloride* (III; X = Cl) (2·5 g.) had m. p. 211—212°, unchanged by crystallisation from ethyl methyl ketone (Found: C, 48·4; H, 7·4. $C_{28}H_{48}ClP_2As_2Cu$ requires C, 48·3; H, 7·0%).

The dichlorocuprite (III; X = $CuCl_2$). Repetition of the above experiment, using the phosphine-arsine (5·50 g., 1 mol.) in ethanol (6 c.c.) and cuprous chloride (1·83 g., 1 mol.) in water (80 c.c.) and sodium chloride (20 g.), gave on 1 hour's shaking a solid which when collected, washed with water and dried, had m. p. 179—184°: 6·7 g. To avoid oxidation it was recrystallised rapidly from boiling ethyl methyl ketone, the solution being filtered into a vessel filled with the ketone vapour, which was replaced by nitrogen as the filtrate cooled. A second such recrystallisation gave the *dichlorocuprite* (III; X = $CuCl_2$) as very pale greenish-cream crystals, m. p. 194—196° (Found: C, 42·45; H, 6·3%; *M*, in boiling ethyl methyl ketone, 820. $C_{28}H_{48}Cl_2P_2As_2Cu_2$ requires C, 42·3; H, 6·1%; *M*, 795).

The powdered chloride (III; X = Cl) (0·4108 g.), when heated at 150°/0·3 mm. for 16 hr., furnished the dichlorocuprite (III; X = $CuCl_2$), m. p. 194·5—196° (0·2166 g.).

A solution of the crude dichlorocuprite (3·0 g.), of m. p. 175—187°, in ethanol (150 c.c.) was boiled under reflux for 7 hr. and on cooling deposited pale lemon-yellow crystals, m. p. 170—176° (slight decomp.). These crystals, when thrice recrystallised from the ketone as described above, to avoid further change, gave lemon-yellow crystals, m. p. 163—169° (preliminary sintering, slight decomp.) in an open tube, m. p. 183·5—184·5° in an evacuated tube, apparently of a di(phosphine-arsine)–tri(cuprous chloride) *complex* (Found: C, 37·8; H, 6·1; Cl, 12·6; Cu, 20·8%; *M*, in boiling 1·53% and 2·73% ethyl methyl ketone solution, 970. $2C_{14}H_{24}PAs,3CuCl$ requires C, 37·6; H, 5·4; Cl, 11·9; Cu, 21·3%; *M*, 893).

The bromide (III; X = Br). The phosphine-arsine (1·92 g., 2 mols.) in ethanol (5 c.c.) was added to cuprous bromide (0·479 g., 1 mol.) in water (20 c.c.) containing potassium bromide (10 g.), the mixture shaken for 5 min., and then evaporated to half volume to remove the ethanol. The solid which separated on cooling furnished on crystallisation from ethyl methyl ketone the *bromide hemi*(*ethyl methyl ketone*), fine needles, m. p. 181—182·5° (Found: C, 46·5; H, 7·2. $C_{28}H_{48}BrP_2As_2Cu,\frac{1}{2}C_4H_8O$ requires C, 46·4; H, 6·75%). No atmospheric oxidation was detected during the handling of this compound.

The bromide hemi-ketone complex, when heated at 35°/0·5 mm. for 14 hr., lost the ketone and then started to lose the phosphine-arsine (Found for the residue: C, 43·4; H, 6·7. $C_{28}H_{48}BrP_2As_2Cu$ requires C, 45·5; H, 6·5%). When it was heated at 100°/0·2 mm., for 36 hr., it afforded the pure *dibromocuprite* (III; X = $CuBr_2$), m. p. 222—240° (darkening) (Found: C, 38·2; H, 5·45%; *M*, in boiling 0·223% chloroform solution, 360, in 0·318% solution, 500. $C_{28}H_{48}Br_2P_2As_2Cu_2$ requires C, 38·1; H, 5·5%; *M*, 884). This salt has a low solubility in most boiling solvents, and great accuracy is not claimed for these molecular-weight determinations.

The iodide (III; X = I). This was prepared as the above bromide, the potassium bromide being replaced by potassium iodide. The *iodide* separated after the mixture had been shaken for 5 min., and when twice recrystallised from ethyl methyl ketone gave crystals, m. p. 205·5—207·5° (Found: C, 42·85; H, 6·1. $C_{28}H_{48}IP_2As_2Cu$ requires C, 42·7; H, 6·1%). It was unaffected by heating at 100°/0·5 mm. for 10 hr., and when its ethanolic solution was boiled under reflux.

The (+)-*bromocamphorsulphonate* (III; $X = O_3S{\cdot}C_{10}H_{14}OBr$). A solution of silver (+)-bromocamphorsulphonate monohydrate (2·77 g.) in water (25 c.c.) was added slowly to one of the bromide (III; X = Br) (5·0 g., 1 mol.) in water (30 c.c.) and acetone (50 c.c.). The mixture was vigorously shaken, filtered, and evaporated in a vacuum. The residual crystalline *bromo-sulphonate* (5·8 g.), after two recrystallisations from ethyl acetate, had m. p. 155·5—157°, unchanged by further recrystallisations (Found: C, 46·7; H, 6·6. $C_{38}H_{62}O_4BrSP_2As_2Cu$ requires C, 47·0; H, 6·4%). Its solution in cold aqueous acetone, when treated with potassium iodide, deposited the optically inactive iodide (III; X = I).

The crystalline (−)-menthoxyacetate was similarly prepared, but decomposed on attempted recrystallisation from ethyl methyl ketone and other solvents.

Argentous Derivatives.—*Bis-*(o-*diethylphosphinophenyldiethylarsine*)*argentous dichloroargentite* (VI; $X = AgCl_2$). Solutions of silver nitrate (1·43 g., 1 mol.) in water (2 c.c.) and of the phosphine-arsine (2·42 g., 1 mol.) in ethanol (4 c.c.) were added in this order to one of sodium chloride (10 g.) in water (40 c.c.), the mixture being then shaken for 11 hr. The crude dichloroargentite when collected, washed with water, and dried, had m. p. 224—226°: 3·5 g. Recrystallisation from boiling solvents was always attended by precipitation of silver chloride. A sample of reasonable purity was obtained by recrystallising first from dimethylformamide which was heated only to 60°, and then from equal volumes of the amide and acetone, the solution being again heated to 60°, and then cooled, filtered quickly to remove silver chloride, and set aside. The *dichloro-argentite* formed compact prisms, m. p. 230·5—231·5° (decomp.) (Found: C, 38·9; H, 5·8. $C_{28}H_{48}Cl_2P_2Ag_2As_2$ requires C, 38·05; H, 5·5%). The use of 2 mols. of the phosphine-arsine in this experiment gave the same compound.

The iodide (VI; X = I). A mixture of the phosphine-arsine (5 g., 2 mols.) in ethanol (15 c.c.) and of silver iodide (2·04 g., 1 mol.) and potassium iodide (20 g.) in water (35 c.c.) was shaken for 3 hr., giving a white crystalline deposit, m. p. 190—230°: 6·5 g.

A mixture of this product and ethanol (50 c.c.), when treated with the phosphine-arsine (2 g.), gave a clear solution, which was evaporated to dryness in a vacuum desiccator. The residue, after extraction with a small quantity of cold acetone, had m. p. *ca.* 170—190°. It was dissolved in cold ethanol (10 c.c.), ethyl acetate (30 c.c.) was added, and the solution filtered from precipitated di-iodo-argentite, warmed, and filtered again, thus ensuring a slight excess of the phosphine-arsine. The filtrate on spontaneous evaporation deposited massive tablets of the *iodide* (VI; X = I), m. p. 158—162° (preliminary sintering) (Found: C, 40·4; H, 5·55. $C_{28}H_{48}IP_2AgAs_2$ requires C, 40·4; H, 5·8%).

When the above white deposit was thrice recrystallised from dimethylformamide, it afforded the *di-iodo-argentite* (VI; $X = AgI_2$), m. p. 253—255° (Found: C, 31·6; H, 4·6; Ag, 20·1%; *M*, in boiling 0·370% chloroform solution, 390, in 0·416% solution, 385. $C_{28}H_{48}I_2P_2Ag_2As_2$ requires C, 31·5; H, 4·5; Ag, 20·25%; *M*, 1066).

The iodide (VI; X = I), when heated at 100°/0·4 mm. for 17 hr., gave the di-iodo-argentite, m. p. and mixed m. p. 250—255°: it was pure after one recrystallisation. An ethanolic solution of the iodide when boiled readily deposited the di-iodo-argentite.

Aurous Derivatives.—*Bis-*(o-*diethylphosphinophenyldiethylarsine*)*aurous iodide* (VIII; X = I). (*a*) A solution of the phosphine-arsine (0·90 g., 3 mols.) in ethanol (2 c.c.), when added to chloroauric acid tetrahydrate (0·41 g., 1 mol.) dissolved in water (10 c.c.), gave an immediate yellow precipitate which dissolved on shaking to give a colourless solution containing some undissolved oily chloride (VIII; X = Cl). Sufficient ethanol was added to dissolve the chloride, and then an excess of saturated aqueous potassium iodide (*ca.* 3 c.c.), and the solution carefully diluted with water (to *ca.* 150 c.c.) to precipitate the crystalline *iodide* (0·87 g., 95%), m. p. 208—211°, increased to 212—213° by crystallisation from ethyl methyl ketone (Found: C, 36·5; H, 5·3. $C_{28}H_{48}IP_2As_2Au$ requires C, 36·5; H, 5·2%).

(*b*) The phosphine-arsine (8·3 g., 2·3 mols.) in ethanol (5 c.c.) was added to the chloroauric acid (5·0 g., 1 mol.) in water (30 c.c.), and the mixture, after vigorous shaking and cooling, was diluted with 30% aqueous sodium hypophosphite (5 c.c.), shaken for 2 hr., and set aside overnight. The precipitated chloride (VIII; X = Cl) was collected and dissolved in ethanol (20 c.c.), and aqueous potassium iodide cautiously added with stirring. The precipitated iodide (VIII; X = I) (8·15 g.; 73%) had m. p. 209—211·5°, increased to 212—213° by crystallisation.

Isolation of the aurous cation as the chloride is wasteful, for this salt is more soluble than the iodide, and crystallises poorly in the presence of impurities. The precipitated chloride (above), when recrystallised from ethyl methyl ketone, gave the pure *chloride hemi-ketone complex,* m. p. 224—230° (decomp.) (Found : C, 41·5; H, 6·2. $C_{28}H_{48}ClP_2As_2Au,\frac{1}{2}C_4H_8O$ requires C, 41·55; H, 6·1%), which when heated at 60°/0·05 mm. for 8 hr. gave the solvent-free *chloride,* of unchanged m. p. (Found : C, 40·2; H, 5·7. $C_{28}H_{48}ClP_2As_2Au$ requires C, 40·6; H, 5·8%).

This salt in ethanol readily gave the *picrate* [VIII; X = $O{\cdot}C_6H_2(NO_2)_3$] yellow crystals, m. p. 118—120°, from aqueous methanol (Found : C, 40·2; H, 4·8; N, 4·25. $C_{34}H_{50}N_3O_7P_2As_2Au$ requires C, 40·0; H, 4·9; N, 4·1%).

The hydrogen sulphate (VIII; X = HSO_4). A solution of silver sulphate (1·39 g.) in water (170 c.c.) was added slowly to a well-stirred solution of the iodide (VIII; X = I) (8·23 g., 2 mols.) in acetone (110 c.c.). The complete mixture was shaken for 1 min., filtered, and evaporated to dryness under reduced pressure. The residual sulphate, which could not be induced to crystallise, was converted into the hydrogen sulphate by crystallisation first from water (150 c.c.) containing concentrated sulphuric acid (0·5 c.c.), giving fine needles (5·55 g., 68%), and then in turn again from very dilute sulphuric acid and from water. The needles, when dried over phosphoric oxide in a vacuum-desiccator, gave the *hydrogen sulphate monohydrate,* m. p. 214—216° on slow heating, but immediately melting with effervescence on immersion at 200° (Found: C, 37·0; H, 5·6. $C_{28}H_{49}O_4SP_2As_2Au,H_2O$ requires C, 37·05; H, 5·7%). A solution of this salt in dilute sulphuric acid deposits a film of gold on the walls of the containing vessel when set aside for some weeks.

When aqueous solutions of the hydrogen sulphate and of barium hydroxide (1 mol.) were mixed, filtered, and evaporated to dryness under reduced pressure at room temperature, a crystalline residue, almost certainly the hydroxide (VIII; X = OH) was obtained. Recrystallisation was achieved only from diethyl carbonate, which afforded crystals, m. p. 222—224° (preliminary darkening), the composition of which indicated the formation of either a carbonate trihydrate or a hydrogen carbonate dihydrate (Found: C, 38·9; H, 6·0. $C_{57}H_{96}O_3P_4As_4Au_2,3H_2O$ requires C, 39·0; H, 6·2%. $C_{29}H_{49}O_3P_2As_2Au,2H_2O$ requires C, 39·1; H, 6·0%).

In the resolution experiments described below [except (i) and (v)], a freshly prepared solution of the hydroxide of known concentration was therefore neutralised directly by the appropriate acid to obtain certain salts.

Attempted Resolution of the Bis-(o-*diethylphosphinophenyldiethylarsine*)*aurous Cation* (VIII).—(i) A solution of silver (+)-camphorsulphonate (0·386 g.) in water (5 c.c.) was slowly added to a well-stirred solution of the iodide (VIII; X = I) (1 g., 1 mol.) in water (20 c.c.) and ethyl methyl ketone (25 c.c.). The filtered solution was evaporated to dryness under reduced pressure, and the residual *sulphonate* (VIII; X = $O_3S{\cdot}C_{10}H_{15}O$) when twice recrystallised from the ketone had m. p. 225—226°, unchanged by further crystallisation (Found : C, 44·9; H, 6·1. $C_{38}H_{63}O_4SP_2As_2Au$ requires C, 44·5; H, 6·2%). It was converted into the picrate, which was inactive in ethanolic solution.

(ii) Barium hydroxide solution was carefully added to a solution of the hydrogen sulphate (VIII; X = HSO_4) (15 g.) in ethanol (15 c.c.) and water (30 c.c.) until the addition of a further few drops to the filtered solution gave no further cloudiness. An aqueous solution of (+)-bromocamphorsulphonic acid (1 mol.) was now added, and the solution evaporated to dryness under reduced pressure. The *bromo-sulphonate* (VIII; X = $O_3S{\cdot}C_{10}H_{14}OBr$) had m. p. 165—165·5° after 2 and after 10 recrystallisations from diethyl carbonate (Found: C, 41·6; H, 5·35. $C_{38}H_{62}O_4BrSP_2As_2Au$ requires C, 41·4; H, 5·7%). A solution of the final product (0·4272 g.) in ethanol (10 c.c.) which was then made up to 30 c.c. with water had $[M]$ +306°. A solution of the silver sulphonate (0·2508 g.) in this volume of the mixed solvents had $[M]$ +292°. The sulphonate was converted into the inactive iodide.

(iii) The solution of the hydroxide (VIII; X = OH), prepared as in (ii), was treated with a solution of tartaric acid (2·53 g., 1 mol.) in water (10 c.c.), and evaporated to *ca.* 70 c.c. under reduced pressure at 60°. The *hydrogen tartrate* (VIII; X = $C_4H_5O_6$) (13·3 g., 84%) crystallised on cooling, and when collected, washed with water, and dried over phosphoric oxide, had m. p. 188—190·5° (immersed at 180°) : after four recrystallisations from water, it had m. p. 187—189° (Found : C, 41·1; H, 5·95. $C_{32}H_{53}O_6P_2As_2Au$ requires C, 40·8; H, 5·7%). A sample was recrystallised ten times from ethyl methyl ketone, and then had m. p. 188·5—190° : the rotation in ethanol changed from $[M]$ +33° to +29° during this process. The final product gave an inactive picrate.

This salt, when recrystallised 9 times from water gave the (+)-*tartrate monohydrate*, m. p. 185—187° on slow heating to ensure preliminary dehydration, 140° (efferv.) when immersed at 130° (Found: C, 40·55; H, 5·8. $C_{60}H_{100}O_6P_4As_4Au_2,H_2O$ requires C, 40·7; H, 5·9%). A solution of this salt (0·2125 g.) in ethanol (30 c.c.) had $[M]$ +89°. One recrystallisation from aqueous tartaric acid regenerated the hydrogen tartrate. The distinction between the two tartrates was confirmed by (*a*) a mixture of the two salts when slowly heated showed a depression in m. p., (*b*) aqueous solutions were acidic and neutral respectively.

(iv) A solution of the hydroxide, treated with (−)-menthoxyacetic acid (1 mol.) and then evaporated in a vacuum desiccator gave ultimately a sticky solid, which when stirred thoroughly with cold ethyl acetate afforded the very deliquescent crystalline (−)-*menthoxyacetate* (VIII; $X = C_{12}H_{21}O_3$), m. p. 171·5—173·5°, unchanged by 3 recrystallisations from ethyl acetate–*cyclo*hexanone (10 : 1 by vol.) (Found: C, 47·9; H, 7·0. $C_{40}H_{69}O_3P_2As_2Au$ requires C, 47·7; H, 6·9%). The nature and quantity of this salt precluded further crystallisation. It was converted into the inactive iodide.

(v) A solution of sodium (+)-camphornitronate (5·3 g.; 5 mols.) in water (15 c.c.), when added with stirring to one of the chloride (VIII; X = Cl) (4·0 g.) in water (20 c.c.) and ethanol (5 c.c.), deposited a sticky product which, when collected, washed with water, dried, and washed with ethyl acetate, gave a powder, m. p. 158—168° : 3·6 g. This was recrystallised thrice from ethyl methyl ketone, in which it was markedly soluble, and twice from ethyl acetate–ethyl methyl ketone. The (+)-*camphornitronate* (VIII; $X = C_{10}H_{14}O_3N$) then had m. p. 173—182° (Found: C, 46·0; H, 6·5; N, 1·6. $C_{38}H_{62}O_3NP_2As_2Au$ requires C, 46·1; H, 6·3; N, 1·4%) : it gave an inactive iodide.

(vi) The (−)-menthylphthalamate was prepared as in (ii) and obtained as an oil which crystallised only on exposure to moist air for 5 days. This salt in contact with most solvents either dissolved readily, or became an oil. Spontaneous evaporation of a 10% solution in diethyl carbonate, containing just sufficient acetone to give complete initial dissolution, gave large tablets of the (−)-*menthylphthalamate* (VIII; $X = C_{18}H_{24}O_3N$), m. p. 86·5—88·5° (immersed at 80°) after 2 and 6 such crystallisations (Found: C, 50·6; H, 7·0; N, 1·3. $C_{46}H_{72}O_3NP_2As_2Au$ requires C, 50·4; H, 6·6; N, 1·3%). The final crop gave an inactive complex picrate.

(vi) The (−)-N-1-*phenylethylphthalamate* was prepared by neutralising the hydroxide with the phthalamic acid. The oily product would not crystallise if kept dry, but slowly crystallised when exposed to the air for several days in contact with diethyl carbonate. The salt could not be recrystallised at this stage, and it was therefore precipitated from its acetone solution by the addition of diethyl carbonate, and then had $[M]$ +116° in 3·106% ethanolic solution. The salt, when now recrystallised from acetone, had m. p. 108—110° (efferv.), unchanged by further recrystallisations. After 2 and 4 such recrystallisations, the salt had $[M]$ +125° (2·603% solution) and +128° (1·039% solution) respectively (Found: C, 49·6; H, 5·85; N, 1·3. $C_{43}H_{61}O_3NP_2As_2Au$ requires C, 49·8; H, 5·9; N, 1·3%). The final crop, treated in ethanolic solution with sodium picrate, gave the inactive picrate.

Derivatives of o-*Phenylene*-as-*dimethyldiphenyldiarsine* (II; R = Me, R^1 = Ph).—A solution of the diarsine (0·5 g., 4 mols.) in acetone (5 c.c.) was added to one of cuprous iodide (0·1164 g., 1 mol.) in water (2 c.c.) containing potassium iodide (4 g.), and the mixture shaken for 6 hr. The solid product was collected, washed with boiling water, and recrystallised from ethanol. The hot filtered solution rapidly deposited small hard highly insoluble crystals (*ca.* 0·05 g.) of *bis*-(o-*phenylene*-as-*dimethyldiphenyldiarsine*)*cuprous di-iodocuprite* (as III; $X = CuI_2$), m. p. 214—215·5° after washing with ethanol and acetone (Found: C, 40·0; H, 3·2. $C_{40}H_{40}I_2As_4Cu_2$ requires C, 40·0; H, 3·4%). When this deposition was complete, the hot solution was filtered, and on cooling gave the *iodide* (as III; X = I) (0·35 g.), m. p. 179·5—180·5° after recrystallisation from ethanol (Found: C, 48·1; H, 3·9. $C_{40}H_{40}IAs_4Cu$ requires C, 48·5; H, 4·1%). This iodide slowly turns green when exposed to air : its ethanolic solution when boiled slowly deposits the di-iodocuprite.

The insolubility of the first product prevented an investigation of its structure, and it is classed as a di-iodocuprite solely in harmony with the other halogenocuprites which have arisen in this investigation.

The iodide was converted into the (+)-bromocamphorsulphonate, an oil which could not be induced to crystallise.

Derivatives of o-*Phenylene*-as-*diethyldimethyldiarsine* (II; R = Me, R^1 = Et).—*Aurous derivatives.* The *bis-diarsine-aurous iodide* (as XIII; X = I) was prepared exactly as the "phosphine-arsine" salt, by the sodium hypophosphite method, and obtained as crystals, m. p. 157—157·5°, when recrystallised from ethyl methyl ketone (Found: C, 30·3; H, 4·4. $C_{24}H_{40}IAs_4Au$ requires C, 30·2; H, 4·2%).

Solutions of this iodide (1 g.) in acetone and of silver (+)-camphorsulphonate (0·356 g., 1 mol.) in water (5 c.c.) were mixed, shaken, filtered, and evaporated to dryness in a desiccator. The residual *sulphonate* (as XIII; X = $O_3S{\cdot}C_{10}H_{15}O$), after three recrystallisations from diethyl carbonate, had m. p. 184·5—186° (Found: C, 38·85; H, 5·35. $C_{34}H_{55}O_4SAs_4Au$ requires C, 38·6; H, 5·2%). A solution of the final crop (0·2933 g.) in ethanol (5 c.c.) made up to 30 c.c. with water had $[M]$ +54°: this rotation is that of the sulphonate ion alone.[10]

The (+)-bromocamphorsulphonate (as XIII; X = $O_3SC_{10}H_{14}OBr$) was similarly prepared, and after one crystallisation from ethyl acetate had m. p. 175—177·5°, unchanged by further crystallisation (Found: C, 35·9; H, 5·05. $C_{34}H_{54}O_4BrSAs_4Au$ requires C, 35·95; H, 4·8%). It gave an optically inactive picrate.

The (−)-menthoxyacetate was obtained by neutralisation of the complex hydroxide, but could not be induced to crystallise.

Bis(o-*phenylenebisdiethylarsine*)*aurous salts* (XIII). Sodium chloroaurate in aqueous solution was treated with the ethanolic diarsine (2·2 mols.) and then with sodium hypophosphite, as described for the bis-phosphine-arsine salt. The solution was diluted with ethanol until clear and then divided into two portions. One portion, when treated with aqueous sodium bromide, deposited crystals, which when recrystallised from ethyl methyl ketone gave the *bromide hemi*(*ethyl methyl ketone*) *complex*, m. p. 181—182° (Found: C, 36·5; H, 4·7. $C_{28}H_{48}BrAs_4Au,\frac{1}{2}C_4H_8O$ requires C, 36·1; H, 5·25%). This compound, when heated at 60°/0·2 mm. for 8 hr., gave the solvent-free *bromide* (XIII; X = Br), of unchanged m. p. (Found: C, 34·8; H, 5·0. $C_{28}H_{48}BrAs_4Au$ requires C, 35·0; H, 5·0%).

The second portion, treated with aqueous potassium iodide, gave the *iodide* (XIII; X = I), m. p. 166—167° after crystallisation from ethyl methyl ketone (Found: C, 33·2; H, 4·7. $C_{28}H_{48}IAs_4Au$ requires C, 33·35; H 4·8%).

It will be noted that ethyl methyl ketone proved to be the most useful solvent for many of the salts isolated in this investigation. Furthermore, whereas the chlorides and bromides of the cuprous cation (III) and the aurous cations (VIII) and (XIII) often crystallised with half a molecule of the ketone, the crystalline iodides were always solvent-free.

Platinous Derivatives of the Phosphine-arsine (I).—A solution of the phosphine-arsine (1·26 g., 2 mols.) in ethanol (1·5 c.c.) when added to one of sodium chloroplatinite (0·81 g., 1 mol.) in water gave an immediate precipitate, but the mixture after shaking for 30 min. was still red and smelt of the arsine. Ethanol (25 c.c.) was added, and the solution boiled under reflux for 10 min., and the deposited pale salmon-pink *bis*-(o-*diethylphosphinophenyldiethylarsine*)*platinous chloroplatinite* (XV; X = $PtCl_4$), when collected, twice recrystallised from concentrated hydrochloric acid diluted with an equal volume of water, and dried, on heating became white at *ca.* 250—260° but did not melt below 310° (Found: C, 30·2; H, 4·3. $C_{28}H_{48}Cl_4P_2As_2Pt_2$ requires C, 29·8; H, 4·3%).

This salt, when heated at 220°/760 mm. for 18 hr., gave the *dichloro*(*phosphine-arsine*)-*platinum* (XVI), separating from dimethylformamide as colourless crystals, unmelted at 310° (Found: C, 29·5; H, 4·6. $C_{14}H_{24}Cl_2AsPPt$ requires C, 29·8; H, 4·3%).

The mother-liquor from which the crude chloroplatinite had separated was evaporated almost to dryness under reduced pressure, and gave a residue, m. p. 244—246°: 0·7 g. This product, when recrystallised from dimethylformamide, was steadily converted into the compound (XVI): recrystallisation from the amide containing much free phosphine-arsine gave the pure *dichloride* (XV; X = Cl_2), m. p. 258·5—261·5° (Found: C, 38·7; H, 5·8. $C_{28}H_{48}Cl_2P_2As_2Pt$ requires C, 38·9; H, 5·6%).

Crystallographic Data.

The bis(diarsine)aurous iodide (XIII; X = I), the bis-(phosphinearsine)aurous iodide (VIII; X = I), and the bis(phosphine-arsine)cuprous iodide (III; X = I) have been investigated by *X*-ray diffraction methods: a general representation of these compounds is given in (XIV) (p. 2820).

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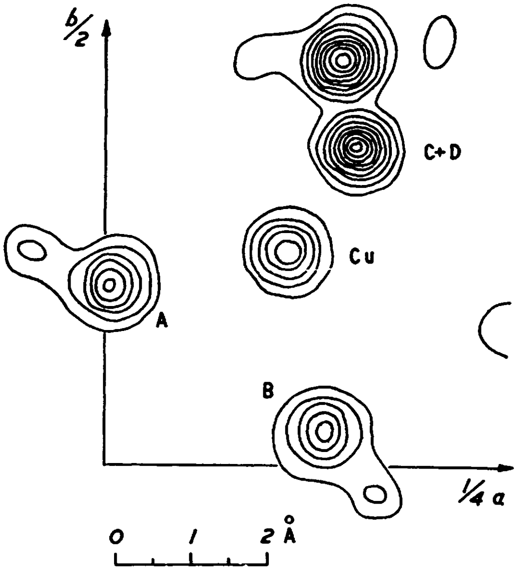
[10] Graham, *J.*, 1912, **101**, 746.

Photographs were taken with use of Cu and also Mo characteristic radiations. Oscillation and Weissenberg-type photographs showed the three compounds to be isomorphous, with orthorhombic unit cells having *a*, *b*, and *c* dimensions (Å) as follows : (XIII) 21·7, 11·6, 14·1; (VIII) 21·7, 11·3, 13·7; (III) 21·5, 11·4, 13·5. These values have an estimated standard deviation of 0·7%.

There were no systematic absences among the general reflections. Zero-layer Weissenberg photographs showed the following systematic absences :

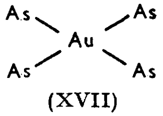
$$\text{Zone (010)};\ F(h0l) = 0 \text{ for } h \text{ odd},\ F(00l) = 0 \text{ for } l \text{ odd}$$
$$\text{Zone (001)};\ F(h00) = 0 \text{ for } h \text{ odd},\ F(0k0) = 0 \text{ for } k \text{ odd}$$

These absences establish the space group as $Pna2_1$ (No. 33) or *Pnam* (No. 62). The systematic absences in the (100) zone, which was not investigated, would not serve to distinguish these two possibilities. Space group *Pnam* would require a molecular plane of symmetry or centre of symmetry, with metal and iodine ions occupying special positions. The *X*-ray intensities rule out this possibility, and the structure analysis has proceeded satisfactorily on the assumption that the space group is $Pna2_1$, with four formula units per unit cell [calculated density for (XIII) = 1·89 g. c.c.].



The compound (III ; X = I). *Electron density projected on* (001). *Approximately half the unique area is shown. Contours are drawn at an equal* (*arbitrary*) *interval.*

The Patterson function projected on planes (001) and (010) has been calculated for (XIII), and the corresponding projection on (001) for (III). From these the approximate co-ordinates of the heavier atoms could be found, and the signs of most of the (*hk*0) structure factors calculated. Essentially the same set of signs was found by the EDSAC method.[11] Projections of the electron density on (001) have been calculated for (XIII) and for (III); part of the latter, showing the arrangement of the heavier atoms, is shown in the Figure. The refinement of the two structures has not yet been carried beyond the stage where bond lengths and angles involving the heavier atoms are established with standard deviations of about 0·03 Å and 1·5° respectively. It is in fact doubtful whether it will ever be possible to establish the positions of the carbon atoms with worthwhile accuracy. The following points concerning the stereochemistry of the molecule are however well established : in the compound (XIII) the group (XVII) has tetrahedral symmetry (point group symmetry $\bar{4}2m$) within the present limits of experimental error. The Au–As bonds are of length 2·48 ± 0·04 Å, there are two bond angles of 90° ± 2° and four of 120° ± 2°. There is no question of an approach to five-fold co-ordination around the gold atom, the four nearest iodine atoms to any gold atom being at distances ranging from 6·2 to 7·1 Å.



(XVII)

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[11] Cochran and Douglas, *Proc. Roy. Soc.*, 1955, *A*, **227**, 486.

For compound (III) the results are consistent with the assumption that the arrangement of bonds around the cuprous atom also has symmetry $\bar{4}2m$. The equality of the peaks A and B (Figure), and the fact that the peak C + D is approximately twice the height of either, shows that arsenic and phosphorus atoms are not distinguished in the crystal structure. This does not conflict with the chemical evidence that a benzene ring always bridges one phosphorus and one arsenic atom; it merely indicates that if an arsenic atom occupies site A in one unit cell and is bridged by a benzene ring to a phosphorus atom in site B, in a neighbouring unit cell it is just as likely that a phosphorus atom occupies site A with an arsenic atom in site B. The bond length and angles corresponding to those given above are 2·38 ± 0·03 Å, 92° ± 1½° and 119° ± 1½°. Small peaks representing single carbon atoms do not show in the electron-density map at the present stage of refinement, but the peaks of moderate height immediately adjacent to A and to B (Figure) must each represent two $\cdot CH_2\cdot CH_3$ groups with all four carbon atoms nearly superimposed in projection. The positions of these peaks indicate that a benzene ring bridges atoms A and B, and another bridges C and D. This is as would be expected from the fact that it is the angles ACuB and CCuD which equal 92°.

Approximate atomic co-ordinates in (XIII)

Atom	As^1	As^2	As^3	As^4	Au	I
x/a	0·133	0	0·153	0·153	0·108	0·150
y/b	0·038	0·194	0·374	0·374	0·243	0·475
z/c	0	0	0·126	−0·126	0	0·500

Further work should establish more accurate bond lengths and angles.

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