329. *The Constitution of Complex Metallic Salts. Part V. The Constitution of the Phosphine and Arsine Derivatives of Cuprous Iodide. The Configuration of the Co-ordinated Cuprous Complex.*

By Frederick G. Mann, Donald Purdie, and Alexander F. Wells.

One of the recognised methods for the characterisation of tertiary phosphines and arsines (particularly the aliphatic members) consists in the preparation of their highly crystalline non-ionic aurous chloride derivatives, of empirical formula $[R_3P(As)\rightarrow AuCl]$. We find that cuprous iodide and silver iodide give similar *derivatives*, of empirical formula $[R_3P(As)\rightarrow MI]$; they are prepared by shaking the phosphine or arsine with an equimolecular quantity of cuprous or silver iodide dissolved in excess of potassium iodide solution. The non-ionic character of the derivatives of the three metals is clearly shown by their insolubility in water and high solubility in most organic liquids.

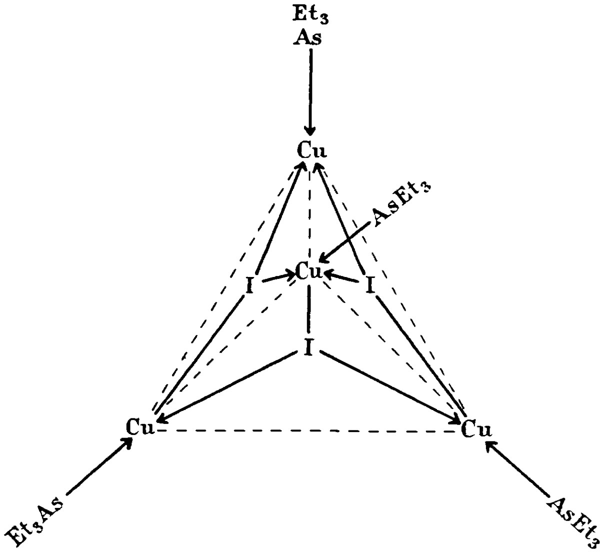
It appeared, therefore, that in these three classes of compound the metallic atom showed a co-ordination number of 2, and, by combining with the phosphorus (or arsenic) atom and the halogen radical by a co-ordinate and a covalent link respectively, was forming the neutral non-ionic (and presumably most stable) member of a series of complex compounds. In, *e.g.*, the cuprous compounds, this series (by analogy with the platinammines and the cobaltammines) should consist of three classes, of formulæ $[(PR_3)_2Cu]I$, $[PR_3,CuI]$, and $K[CuI_2]$, the middle (non-ionic) member being therefore termed monoiodotrialkylphosphinecopper.

Decisive evidence for the true co-ordination number of the cuprous atom was lacking, owing to the comparative instability of its known complex derivatives. The most characteristic derivatives were, however, the complex cyanides: these had been investigated by many workers, notably Grossmann and von der Forst (*Z. anorg. Chem.*, 1905, **43**, 94), who showed that, although cuprous cyanide combines with the alkali cyanides to form a series of complex cyanides (including compounds such as $K[Cu(CN)_2]$ in which the copper atom has apparently a co-ordination number of 2), yet the most stable derivatives were the tetracyanides, *e.g.*, $K_3[Cu(CN)_4]$, in which the copper has undoubtedly a co-ordination number of 4. This is to be expected, since the 7 electrons which copper requires to attain the electronic structure of krypton are acquired in the tetracyanide, where the copper is joined by covalent links to the cyanide radicals and by electrovalent links to the potassium ions. Since, however, the phosphine (and arsine) derivatives are formed from potassium cuproiodide, $K_3[CuI_4]$, the neutral non-ionic member should have the composition $[(PR_3)_3CuI]$: in a compound of this type the copper would be joined by three co-ordinate and one covalent link, and so would again obtain the required 7 electrons. It follows therefore that a 2-co-ordination cuprous compound, such as $[R_3P \rightarrow CuI]$, in which the copper atom acquires only 3 electrons, should be very unstable : actually, however, many members of the phosphine and arsine series possess considerable stability. In view of this apparent contradiction, several homologous members of the phosphine- and arsine-cuprous iodide compounds were prepared, and their properties and structure investigated in detail. All members, with the exception of the amylarsine derivative, are white (or cream-coloured) crystalline compounds; the melting points (Table I) fall rapidly as the homologous series is ascended, the tri-*n*-amylarsine compound being liquid at room temperature.

The triethylarsine cuprous iodide compound crystallises in dodecahedra of which a complete *X*-ray analysis has been made. This analysis shows conclusively that the true molecule consists of a combination of four of the simple units, and therefore has the formula $[Et_3As \rightarrow CuI]_4$, *i.e.*, it is actually *tetrakis*(*monoiodotriethylarsinecopper*). In this four-fold molecule, the four cuprous atoms are arranged at the apices of a regular tetrahedron : the four iodine atoms lie each at the centre, but above the plane of, one face of the tetrahedron (Figs. 1 and 2). Beyond each cuprous atom is an arsenic atom lying on the elongation of the axis joining the centre of the tetrahedron to the copper : the three ethyl groups are then joined to each arsenic atom so that the tetrahedral angle is subtended both at the arsenic and at the first (or α) carbon atom of the ethyl groups [Fig. 2(B)].

FIG. 1.

Tetrakis(*monoiodotriethylarsinecopper*).



The broken lines represent the edges of the tetrahedron formed by the four copper atoms, the apex occupied by the central copper atom being tilted forward to show all the four bonds joined to this atom. The iodine atoms are depicted on the faces of the tetrahedron in order to show their linkage to the neighbouring copper atoms : actually they lie well above the plane of the tetrahedral faces, as shown in Fig. 2 (A). The iodine atom on the rear face of the tetrahedron is not shown.

The unbroken lines without barbs represent covalent links, those with barbs co-ordinate links.

It is clear, therefore, that the simple $[R_3As \rightarrow CuI]$ units must be unstable in the free state, but that considerable stability is acquired in the formation of the tetrakis-molecule by virtue of each iodine atom, in addition to being covalently linked to its original copper atom, also becoming joined by co-ordinate links to the other two copper atoms of the same tetrahedral face (Fig. 1). (When such a union is once effected, there is clearly no essential difference in the electronic linkage between the iodine atom and each of the three surrounding copper atoms, such a difference being limited to the *origin* of the electrons concerned: hence *X*-ray analysis shows the iodine atom to have an absolutely symmetrical disposition relative to all three copper atoms lying at the corners of the same tetrahedral face.) It follows therefore that each copper atom in the four-fold or tetrakis-molecule is actually showing a co-ordination number of four, being joined by a covalent link to one iodine atom and by co-ordinate links to two iodine atoms and one arsenic atom. It is thus acquiring 7 electrons, and the interesting fact emerges that these cuprous atoms are therefore identical both in co-ordination number and in electronic structure with that in potassium cuprocyanide, $K_3[Cu(CN)_4]$. It is remarkable, however, that the large four-fold molecule has evidently a far greater stability than the (at present unknown) compound $[(AsEt_3)_3CuI]$ in which the copper atom would again have the same electronic structure.

It follows further from the structure shown in Figs. 1 and 2 that, since each iodine atom is raised considerably above the centre of each tetrahedral face, the copper atoms are themselves at the centre of tetrahedra, each of the latter having thus one arsenic and three iodine atoms at its apices. This tetrahedral configuration of the cuprous complex is thus completely in accord with the results of Cox, Wardlaw, and Webster (this vol., p. 775), who by *X*-ray analysis have determined the tetrahedral configuration for $K_3[Cu(CN)_4]$ and for tetrakisthioacetamidecuprous chloride, $[Cu\{SCMe{\cdot}NH_2\}_4]Cl$.

Tetrakis(monoiodotriethylphosphinecopper) is strictly isomorphous with the above ethylarsine compound and has therefore the same structure. The phosphine and arsine compounds in the *n*-butyl series are not, however, isomorphous: it is extremely unlikely that this is due to any difference in chemical structure between the two compounds, but is due rather to the fact that the packing of the molecules and the resulting symmetry are very readily changed by small alterations in the atomic sizes.

Tetrakis(monobromotriethylarsinecopper) also is strictly isomorphous with its iodine analogue, and the structure shown in Figs. 1 and 2 is therefore not peculiar to the iodo-compounds.

Further evidence confirming the structure shown in Figs. 1 and 2 has been obtained both from molecular-weight determinations and from a study of certain αα′-dipyridyl derivatives.

(1) *Molecular Weights.*—The molecular weights of homologous members of the phosphine(and arsine)cuprous iodide compounds have been determined in various solvents, and for purposes of ready comparison, the degree of association of the simple unit molecules, calculated on the basis of these molecular weights, is shown in Table I.

TABLE I.

Molecular weights of the phosphine- and arsine-cuprous iodide derivatives in various solvents.

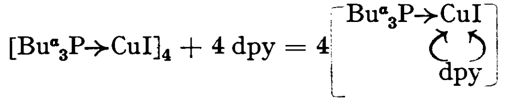
		n in $[R_3P{\rightarrow}CuI]_n$.				n in $[R_3As{\rightarrow}CuI]_n$.		
	M.p.	$COMe_2$.*	C_6H_6.	$C_2H_4Br_2$.†	M.p.	$COMe_2$.*	C_6H_6.	$C_2H_4Br_2$.†
R = Et	236—240°	—	3·47*	—	(Decomp.)	—	3·86*	—
n-Pr	207°	3·39	3·57†	3·68	205—212°	3·94	3·55†	4·18
n-Bu	75°	3·59	3·36†	3·46	61·5°	4·21	3·73†	3·70
n-Am	27°	3·28	3·62†	3·91	Liquid	—	—	—

* Ebullioscopic. † Cryoscopic.

These results show clearly that the molecular weight is not appreciably affected by the nature of the solvent, and that, even in a dissociating solvent such as acetone, the arsine compounds (in particular) exist almost entirely as the four-fold molecule $[R_3As{\rightarrow}CuI]_4$. The fact that the phosphine compounds in all the above solvents, and the arsine compounds (with one exception) in benzene and ethylene dibromide, give values for *n* which are uniformly between 3 and 4 shows, however, that some dissociation must occur in these solutions. Its nature is unknown: it may be of the type $[R_3P{\rightarrow}CuI]_4 \rightleftarrows 4[R_3P{\rightarrow}CuI]$, or dissociation to some intermediate complex. It is noteworthy that Mr. A. E. Finn finds the dipole moment of the tri-*n*-butylarsine compound in benzene solution at 25° to be 1·60 D: the symmetric four-fold molecule should, of course, have zero moment, whereas the simple unit $[Bu^{a}_3As{\rightarrow}CuI]$ should have only a very small moment if the links to the copper atom are linear, but a larger value if these links are set at an angle.

(2) *αα′-Dipyridyl Derivatives.*—If non-ionic compounds in the phosphine and arsine series are formed when the cuprous atoms are joined to neighbouring groups by one covalent and three co-ordinate links, similar but simpler compounds should exist provided the same four linkages are available for the metallic atom. Such compounds, *e.g.*, $[(NH_3)_3CuI]$ (Biltz and Stollenwerk, *Z. anorg. Chem.*, **1921**, **119**, 97), have been prepared, but readily lose ammonia on exposure to air. We have now prepared compounds of this general type by utilising the stabilising effect of the chelated αα′-dipyridyl group.

A striking reaction occurs on mixing cold acetone solutions of tetrakis(monoiodotributylphosphinecopper) and of four molecular equivalents of αα′-dipyridyl; the colourless component solutions immediately give a deep red mixture, from which dark orange crystals of *monoiodo-αα′-dipyridyltri-*n*-butylphosphinecopper* (I) separate :

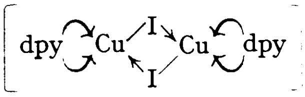


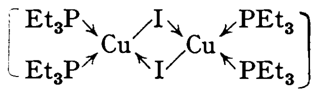
$$[\mathrm{Bu^a_3P{\rightarrow}CuI}]_4 + 4\,\mathrm{dpy} = 4\left[\begin{matrix}\mathrm{Bu^a_3P{\rightarrow}CuI} \\ \mathrm{dpy}\end{matrix}\right]$$ (I.)

Molecular-weight determinations show that the compound (I) has the simple molecule containing only one atom of copper, and the reaction has thus caused complete disruption of the four-fold molecule of the original compound; yet it is clear that the co-ordination number and the electronic state of the copper atoms are identical in the two compounds. Tetrakis(monoiodotributylarsinecopper) when treated with dipyridyl gives a similar but less stable *derivative.*

The compound (I) is freely soluble in most organic solvents; when, however, its solution (particularly in alcohol and benzene) is boiled, butylphosphine is readily lost and a deep red insoluble compound is precipitated. This compound is identical with that which Tartarini (*Gazzetta*, **1933**, **63**, 597) prepared by reducing a cupric salt with hydrazine and then adding dipyridyl and potassium iodide in turn, and to which he assigned the molecular formula dpy CuI. There is little doubt, however, that during the formation of this compound from the phosphine derivative, the co-ordination number of the copper atom remains unchanged, and the red compound must therefore have two copper atoms now again linked through bridged iodine atoms as in (II) : it is therefore *bisdipyridyl-μ-di-iododicopper.*

(II.)





(III.)

This compound is thus very similar in general type to the bridged palladium compounds described in Part IV (Mann and Purdie, this vol., p. 873); moreover, like these palladium compounds, it is both of darker colour and of considerably lower solubility than the unbridged compound from which it is derived, although the presence of the two chelated dipyridyl residues undoubtedly serves further to reduce its solubility. The same compound can be prepared even more readily from *monoiododipyridyltributylarsinecopper*, which in solution at room temperature spontaneously loses butylarsine with precipitation of the compound (II).

In this connection, it should be noted that Arbusow (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, ii, 293) prepared a compound, m. p. 37—39°, of empirical formula $2PEt_3,CuI$, which on warming readily lost one molecule of ethylphosphine to give the compound now known to be $[Et_3P{\rightarrow}CuI]_4$. There is little doubt in view of the above results that Arbusow's compound has the molecular formula $[(PEt_3)_2CuI]_2$ and the constitution (III), being identical in general type with the dipyridyl compound (II). The instability of compounds such as (III) renders a detailed investigation of their constitution very difficult.

In the early stages of the present work, the parachors of certain of the phosphine- and arsine-cuprous iodide compounds were determined on the assumption that the molecules had the simple structure $[R_3P(As){\rightarrow}CuI]$ and that therefore the results might further elucidate the cause of the abnormal parachors of complex metallic compounds previously described (Mann and Purdie, J., 1935, 1549; this vol., p. 873). Since the compounds have actually the four-fold or tetrakis-molecule, the results now obtained cannot be interpreted.

Their general nature, however, is precisely similar to that found for the palladium and the mercury derivatives, since the copper compounds clearly possess a marked negative parachor anomaly, and the apparent parachor of the constituent copper atoms decreases as the homologous series is ascended. The parachors for the simple unit $[R_3P(As)\rightarrow CuI]$ are given in Table II in order to illustrate this point: the molecular parachors should be four times those shown in col. 2.

TABLE II.

Parachors of complex copper compounds.

Compound.	[*P*], obs.	Σ[*P*].*	Parachor of Cu.
	Phosphine compounds, $[R_3P\rightarrow CuI]$.		
R = *n*-Bu.................	643	651	− 8
n-Am	749	772	− 23
	Arsine compound, $[R_3As\rightarrow CuI]$.		
R = *n*-Bu.................	654	666	− 12

* Σ[*P*] represents the sum of the parachors of all the elements except copper.

The structure of the aurous chloride and the silver iodide derivatives of the tertiary phosphines and arsines is now being investigated. Preliminary results indicate that they have a four-fold molecule closely akin to that of the corresponding cuprous compounds.

EXPERIMENTAL.

Chemical Data.

The dipole measurements were made by Mr. A. E. Finn in the Dyson Perrins Laboratory of Oxford University, and are gratefully acknowledged. All molecular weights were determined cryoscopically except those marked,* which were ebullioscopic. The parachor measurements were made with the apparatus already described (J., 1935, 1555). The symbols have their usual significance; in no case did the m. p. of the compounds fall by more than 0·5° during the density and surface-tension determinations.

The names of the solvents used for recrystallising the compounds are given in parentheses immediately after the name of the compound concerned.

Tetrakis(monoiodotrialkylphosphinecopper), $[R_3P\rightarrow CuI]_4$.—All members were prepared by the same method, which is therefore given in detail only for the ethyl compound. This was apparently prepared by Arbusow (*loc. cit.*), who gave few details and no m. p. Freshly distilled triethylphosphine (6 g.) was shaken with a solution of cuprous iodide (13 g.; 1·3 mols.) in saturated aqueous potassium iodide solution (100 c.c.) for 2 hours, a white solid rapidly separating. The latter was collected, washed thoroughly with water, drained, and dried. The crystals (benzene) soften at 230° and melt 236—240° (no apparent decomp.); they are almost insoluble in hot alcohol and acetone (Found: C, 23·3; H, 4·9; Cu, 20·7; *M*, in 5·953% benzene solution, 1070 *; in 10·74%, 1070.* Calc. for $C_{24}H_{60}I_4Cu_4P_4$: C, 23·3; H, 4·9; Cu, 20·6%; *M*, 1234).

The n-*propyl* compound (acetone) softens at 197°, m. p. 206—207° (Found: C, 30·9; H, 5·8; Cu, 18·1; *M*, in 6·106% acetone solution, 1200 *; in 9·573%, 1210 *; in 2·631% benzene solution, 1250; in 1·541% ethylene dibromide solution, 1290. $C_{36}H_{84}I_4Cu_4P_4$ requires C, 30·8; H, 6·0; Cu, 18·2%; *M*, 1402).

The n-*butyl* compound (alcohol–acetone) had m. p. 75° (Found: C, 36·4; H, 6·9; Cu, 16·2; *M*, in 10·22% acetone solution, 1410 *; in 2·747% benzene solution, 1330; in 7·400%, 1310; in 2·540% ethylene dibromide solution, 1360. $C_{48}H_{108}I_4Cu_4P_4$ requires C, 36·7; H, 6·9; Cu, 16·2%; *M*, 1570); *t* 78°, 99°; *d* 1·390, 1·336; *γ* 26·83, 25·34; [*P*] ‡ 643·0, 644·1; mean, 643·5; $[P]_{Cu} = -8$. When heated at a pressure of *ca.* 0·01 mm., it decomposed smoothly at 200—210°, evolving tributylphosphine and leaving a residue of crystalline cuprous iodide.

The n-*amyl* compound separated at first as an oil, which was extracted with benzene, dried over sodium sulphate, and the benzene evaporated; the residual oil, which crystallised on cooling, was recrystallised from alcohol and collected in a chilled filter; m. p. 27° (Found: C, 41·2; H, 7·25; Cu, 14·9; *M*, in 12·55% acetone solution, 1420 *; in 1·968% benzene solution, 1550; in 5·471%, 1600; in 1·137% ethylene dibromide solution, 1700. $C_{60}H_{132}I_4Cu_4P_4$ requires C, 41·4; H, 7·6; Cu, 14·6%; *M*, 1738); *t* 56°, 77°, 99°; *d* 1·332, 1·308, 1·285; *γ* 27·60, 25·87, 24·18; [*P*] 747·8, 749·6, 750·3; mean 749·3; $[P]_{Cu} = -23$.

‡ See above.

The lower members of the phosphine series are stable almost indefinitely at room temperature, whereas the higher members tend ultimately to decompose, giving green viscous syrups; the onset of this decomposition varies with individual samples and may be long delayed, but when once started it proceeds to completion. The solubility in organic liquids increases as the homologous series is ascended, the increase being greatest between the lower members of the series.

Tetrakis(monoiodotrialkylarsinecopper), $[R_3As{\rightarrow}CuI]_4$.—The method of preparation was similar to that of the analogous phosphine compounds. The *methyl* compound (R = Me) decomposed slowly in hot solvents with deposition of cuprous iodide; it was therefore rapidly recrystallised from alcohol or (less suitably) *cyclo*hexane, the hot solution being immediately filtered and chilled. The white crystals decomposed above 300° without melting (Found : C, 11·7; H, 3·0. $C_{12}H_{36}I_4As_4Cu_4$ requires C, 11·6; H, 2·9%); on prolonged exposure to air at room temperature, they slowly dissociate, leaving pseudomorphs of cuprous iodide; consequently, the compound, unless freshly recrystallised, has a faint odour of trimethylarsine.

The *ethyl* compound (benzene) on heating decomposes slowly at 190—240°, but is far more stable than the methyl compound, decomposition being barely perceptible after several weeks' standing at room temperature; it is almost insoluble in hot alcohol and acetone (Found : C, 20·5; H, 4·3; Cu, 18·1; *M*, in 9·541% benzene solution, 1360.* $C_{24}H_{60}I_4As_4Cu_4$ requires C, 20·4; H, 4·3; Cu, 18·1%; *M*, 1410).

The n-*propyl* compound (acetone) forms beautiful white crystals which soften at *ca.* 190°, m. p. 205—212° (decomp.) (Found : C, 27·5; H, 5·5; Cu, 16·3; *M*, in 7·516% acetone solution, 1580 *; in 9·354%, 1530 *; in 2·597% benzene solution, 1400; in 4·646%, 1400; in 2·385% ethylene dibromide solution, 1630; in 4·352%, 1670. $C_{36}H_{84}I_4As_4Cu_4$ requires C, 27·4; H, 5·4; Cu, 16·1%; *M*, 1578).

The n-*butyl* compound (acetone or alcohol : the initial crystallisation from either solvent gave an oil which subsequently solidified; further crystallisations deposited the pure crystals) forms colourless needles, m. p. 61° (Found : C, 33·1; H, 6·1; Cu, 14·5; *M*, in 4·597% acetone solution, 1950 *; in 9·466%, 1730 *; in 1·900% benzene solution, 1680; in 4·956%, 1570; in 1·044% ethylene dibromide solution, 1570; in 2·466%, 1660. $C_{48}H_{108}I_4As_4Cu_4$ requires C, 33·0; H, 6·2; Cu, 14·6%, *M*, 1746); *t* 77°; *d* 1·521; γ 26·93; [*P*] 653·9; $[P]_{Cu} = -12$. When heated at a pressure of *ca.* 0·01 mm., it decomposed vigorously at 140—150°, liberating tributylarsine and leaving a residue of apparently amorphous cuprous iodide.

Dipole measurement on the n-*butyl compound in benzene at* 25°.

f_2.	$d^{25°}$.	$\epsilon^{25°}$.	$n^2_{25°}$.	P_2.	$_EP_2$.
0·0	0·8737	2·2727	—	—	—
0·001827	0·8893	2·2845	2·2628	426·38	(377·34)
0·002625	0·8958	2·2897	2·2644	428·91	372·91
0·003280	0·9012	2·2941	2·2668	429·39	374·66
0·005237	0·9167	2·3047	2·2716	424·75	371·84

$_\infty P_2 = 427{\cdot}36$ c.c.; $_EP_2 = 373{\cdot}14$ c.c.; $_\infty P_2 - {}_EP_2 = 54{\cdot}2$ c.c.; $\mu = 1{\cdot}60$D.

The *n*-amyl compound separated as an oil; this was extracted with benzene, the extract dried and filtered, and the benzene removed in a vacuum. The compound remained as a colourless oil, the m. p. of which was well below 0°, and it was therefore not further investigated.

The stability of the above arsine compounds, in the dry state or in solution, increases markedly as the homologous series is ascended, and, unlike the phosphine analogues, they decompose to a green product only very rarely. The solubility in organic solvents increases steadily as the series is ascended.

Tetrakis(monobromotriethylarsinecopper).—This was prepared in an analogous manner by using a solution of cuprous bromide in potassium bromide solution, and formed white dodecahedra (benzene) which on rapid heating have m. p. 234—235° (decomp.) with preliminary softening (Found : Cu, 20·7. $C_{24}H_{60}Br_4As_4Cu_4$ requires Cu, 20·8%). It is almost insoluble in alcohol and acetone, and is strictly isomorphous with the corresponding iodide, evidently having the same structure.

Action of αα'-Dipyridyl.—(1) *On tetrakis(monoiodotri*-n-*butylphosphinecopper)*. Solutions of the latter compound (3 g.) and of dipyridyl (1·191 g.; 4 mols.), each in cold acetone (20 c.c.), were mixed, a deep red colour immediately developing. The mixture was allowed to evaporate spontaneously, and the orange-red crystals that remained were recrystallised from acetone, in which they were very soluble. *Monoiodo-αα'-dipyridyltri*-n-*butylphosphinecopper* (I) was thus obtained as deep orange crystals, m. p. 123° (Found : C, 48·1; H, 6·5; N, 4·9; I, 23·1; *M*, in 1·061% benzene solution, 527; in 0·941% ethylene dibromide solution, in which very slight decomposition occurred, giving a faintly turbid solution, 588. $C_{22}H_{35}N_2ICuP$ requires C, 48·1; H, 6·4; N, 5·1; I, 23·1%; *M*, 548·8).

This compound, when boiled in alcoholic or benzene solution, rapidly decomposed, with loss of butylphosphine and deposition of the insoluble, deep red, microcrystalline *bisdipyridyl-μ-di-iododicopper* (II), m. p. 274—275° (decomp.) (Found: C, 34·8; H, 2·4; N, 7·9; I, 37·1. $C_{20}H_{16}N_4I_2Cu_2$ requires C, 34·6; H, 2·3; N, 8·1; I, 36·6%). The same decomposition occurs (but far more slowly) in hot acetone solution: recrystallisation from acetone must therefore be performed rapidly, and the hot solution filtered and cooled without delay. Pure samples of the original compound, when kept at room temperature for several weeks, underwent the same reaction.

In marked contrast with this ready loss of phosphine, the compound (I) when heated at *ca.* 0·01 mm., gave first a sublimate of dipyridyl at 90—110°, and then a distillate of butylphosphine at 190—200°, crystalline cuprous iodide finally remaining.

(2) *On tetrakis(monoiodotri-*n*-butylarsinecopper).* Solutions of the latter compound (2 g.) and dipyridyl (0·716 g., 4 mols.) in cold acetone (20 and 10 c.c. respectively) behaved on admixture as in (1), and fine deep orange crystals separated. On standing for 1 hour, these were slowly replaced by minute deep red crystals of bisdipyridyl-μ-di-iododicopper, which were collected, washed with acetone to remove all trace of the soluble orange crystals, dried, and then identified both by analysis (Found: C, 34·8; H, 2·6%) and by mixed m. p. determinations with the sample obtained in the previous experiment. The acetone filtrate and washings were united and allowed to evaporate spontaneously; the residual orange crystals were recrystallised rapidly from a small quantity of acetone by using the same precautions as above. Orange crystals of *monoiodo-αα'-dipyridyltri-*n*-butylarsinecopper* [as (I)] were thus obtained (Found: C, 44·7; H, 6·15; N, 4·9. $C_{22}H_{35}N_2IAsCu$ requires C, 44·5; H, 6·0; N, 4·7%); on heating, the orange colour changed to deep red at 102—104°, presumably owing to loss of arsine and formation of (II). This compound is even less stable in solution than the corresponding phosphine derivative, and in cold organic solvents spontaneously deposits the di-iodo-compound, this decomposition occurring rapidly when the solutions are boiled; consequently, no reliable molecular-weight determinations could be made.

Direct Preparation of Bisdipyridyl-μ-di-iododicopper (by Tartarini's Method).—A solution of crystalline copper acetate (0·5 g.) in water (20 c.c.) was reduced by careful addition of a 50% aqueous hydrazine hydrate solution until the precipitated cuprous oxide redissolved and a clear pale grey solution was obtained. A solution of dipyridyl (0·6 g.; 1·5 mols.) in alcohol (20 c.c.) was then added, a deep red solution being at once obtained. Saturated aqueous potassium iodide solution (20 c.c.) was now added, a red precipitate immediately forming. Water (50 c.c.) was finally added to coagulate this precipitate, which was collected on a filter, washed in turn with water and acetone, and then dried. The bisdipyridyl-μ-di-iododicopper was identical with, although less pure than, that obtained in expts. (1) and (2) above. The colour of the compound prepared by Tartarini's method varies between brownish-red and deep red, depending apparently on the state of division.

When solutions of dipyridyl (0·50 g.) in freshly prepared hydriodic acid (*d* 1·70) and of cuprous iodide (0·61 g.; 1 mol.) in saturated aqueous potassium iodide (15 c.c.) were rapidly mixed, an immediate precipitation of orange-coloured needles occurred, but within a few minutes these changed to minute heavy, bright red crystals. After 3 hours, the red crystals were separated, washed in turn with water and alcohol, and dried. This *compound* has m. p. 142—145° (decomp.) and the empirical formula dpy,$HCuI_2$ (Found: C, 25·3; H, 2·2; N, 5·7. $C_{10}H_9N_2I_2Cu$ requires C, 25·3; H, 1·9; N, 5·9%). Its identity is uncertain: it may be dipyridyl cupro-iodide, or alternatively a derivative in which one nitrogen atom of the dipyridyl molecule has remained neutralised by the hydriodic acid while the second has co-ordinated to the cuprous iodide. Its bright red colour serves to distinguish it at once from the dark red di-iodo-compound (II).

When cuprous iodide dissolved in potassium iodide solution was shaken with *two* equivalents of triethylarsine, a white precipitate, apparently of empirical formula $[(AsEt_3)_2CuI]$, separated. It melted at *ca.* 55°, evolving ethylarsine and then resolidifying as crude $[Et_3As\rightarrow CuI]_4$; since warming in organic solvents caused the same decomposition, the compound was not further investigated.

When a similar solution of cuprous iodide was shaken with *one* equivalent of ethyl sulphide, a white precipitate was again obtained. This decomposed without melting when heated in the open, but had m. p. 128—130° (decomp.) in a sealed tube. It decomposed freely in hot solvents and could not be obtained pure.

Crystallographic Data.

The essential evidence for the structure of the compounds is given in brief below; the full crystallographic details will be published elsewhere.

Tetrakis(monoiodotriethylarsinecopper).—Unit cell and space-group. The compound crystallises in the cubic system with dodecahedral habit, {110} being the only form observed. Oscillation photographs taken with Cu-K_α radiation give $a = 13{\cdot}08 \pm 0{\cdot}02$ A. The density (by flotation) is 2·05, requiring 8$As(C_2H_5)_3$,CuI components in the unit cell. Oscillation and Weissenberg photographs about the [100], [110], and [111] axes show the absences characteristic of a body-centred lattice. The Laue symmetry is O_h. The only space-group consistent with this symmetry in which the arsenic, copper, and iodine atoms may each occupy 8-fold positions is $I\bar{4}3m(T_d^3)$.

Determination of structure. The atoms must occupy the following equivalent positions: (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ + ; I — (8-fold) uuu, $u\bar{u}\bar{u}$, $\bar{u}u\bar{u}$, $\bar{u}\bar{u}u$; As — (8-fold) vvv, etc.; Cu — (8-fold) www, etc.; CH_2 — (24-fold) $x_1x_1z_1$, etc.; CH_3 — (24-fold) $x_2x_2z_2$, etc., the axes being those of the " International Tables." The iodine, arsenic and copper atoms lie on 3-fold axes in the diagonal planes of symmetry. No structure in which linear molecules $As(C_2H_5)_3$,CuI containing 2-covalent copper exist as discrete units could explain the observed intensities. Since the structure factors (F) of the $hh0$ planes are all positive (the contributions from the carbon atoms being neglected), a one-dimensional Fourier projection on [110] could be used to determine approximately the iodine parameter u. Then the signs of the structure factors of the stronger $h00$ and $hk0$ planes were deduced, and a rough 2-dimensional projection on (001) showed the position of a second heavy atom (Cu or As). Two of the parameters being known, the signs of more factors, F_{hk0}, could be found, and the projection was repeated. By these means the approximate positions of the heavy atoms were found, the parameters being refined by utilising relationships between the structure factors of high-order $hk0$ reflections. The approximate F values used were obtained from visually estimated intensities on Weissenberg films. The positions of the carbon atoms were fixed only by considerations of packing. The parameters adopted were: $u = 0{\cdot}12$, $v = 0{\cdot}32$, $w = 0{\cdot}43$; $x_1 = 0{\cdot}365$, $x_2 = 0{\cdot}30$; $z_1 = 0{\cdot}18$, $z_2 = 0{\cdot}10$. In calculating F_{hkl}, the contribution from the carbon atoms has been omitted, since it is always small and usually negligible, but it is included in the calculated F's for the planes $h00$, $hh0$, and $hk0$, where it is sometimes appreciable.

Table III shows the observed and calculated values of F for reflexions $h00$, $hh0$, and $hk0$, where

$$F'_{\text{obs.}} = I \text{ estimated}/[(1 + \cos^2 2\theta)/\sin 2\theta]^{\frac{1}{2}}$$

The intensities were estimated on a Weissenberg photograph about [100]. Discrepancies between $F'_{\text{obs.}}$ and $F_{\text{calc.}}$ for very weak reflexions have little significance, since the intensity of weak spots is difficult to estimate and a small alteration in the estimated intensity causes a large alteration in $F'_{\text{obs.}}$, especially when the polarisation factor is small. Neither extinction nor temperature factor was allowed for, so at very small and at large values of $\sin\theta/\lambda$, the calculated F exceeds the observed value. Table IV contains data from Weissenberg photographs about the [$1\bar{1}0$] and [111] axes: indices (hhg) and ($h, \bar{h} + \bar{l}, l$) respectively.

TABLE III.

Plane.	$\frac{1}{4}F$.	$F'_{\text{obs.}}$.	Plane.	$\frac{1}{4}F$.	$F'_{\text{obs.}}$.	Plane.	$\frac{1}{4}F$.	$F'_{\text{obs.}}$.	Plane.	$\frac{1}{4}F$.	$F'_{\text{obs.}}$.
110	+107	63	550	+110	83	680	− 13	33	990	+72	50
200	− 20	10	170	− 3	0	$\underline{10}00$	+ 31	30	$8\underline{10}0$	+12	14
220	+ 45	37	460	+ 8	20	$2\underline{10}0$	− 15	0	$7\underline{11}0$	−23	0
130	− 50	38	370	− 40	30	590	− 50	63	$3\underline{13}0$	+52	22
400	− 95	100	800	− 5	0	$4\underline{10}0$	− 21	22	$6\underline{12}0$	+11	0
330	+ 85	65	280	+ 7	14	880	+107	90	$2\underline{14}0$	+34	16
240	+ 4	0	660	+ 60	64	790	+ 55	50	$\underline{10}\,\underline{10}\,0$	+10	0
150	− 55	50	570	− 20	0	$3\underline{11}0$	− 10	0	$9\underline{11}0$	−48	32
440	+ 88	88	480	− 50	55	$6\underline{10}0$	+ 10	0	$8\underline{12}0$	−70	43
350	− 4	0	190	+ 10	15	$2\underline{12}0$	− 2	0	$7\underline{13}0$	−41	25
600	− 4	10	390	− 16	0	$5\underline{11}0$	+ 50	25	$6\underline{14}0$	−39	20
260	− 44	48	770	+ 55	35	$4\underline{12}0$	+ 50	25			

Description of structure. The essential feature of the structure is the existence of well-defined four-fold or macro-molecules $(AsEt_3)_4Cu_4I_4$ [Fig. 2(A)], of which there are two per cell with centres

TABLE IV.

$[1\bar{1}0]$ axis.

Plane.	$\frac{1}{4}F$.	$I_{obs.}$.	Plane.	$\frac{1}{4}F$.	$I_{obs.}$.	Plane.	$\frac{1}{4}F$.	$I_{obs.}$.	Plane.	$\frac{1}{4}F$.	$I_{obs.}$.
112	20	w	226	100	vs	662	53	m+	$22\underline{10}$	96	s
222	48	s	444	76	s	338	9	vw	558	9	a
114	71	s	552	9	a	556	39	w	$33\underline{10}$	65	s−
332	32	m+	336	68	s+	664	16	vw	$44\underline{10}$	63	s−
224	18	w	118	18	vw	448	59	s−	668	46	m
334	51	s	554	54	m+	$11\underline{10}$	62	s−	$55\underline{10}$	49	w
442	66	s−	446	38	m	666	67	s−	$66\underline{10}$	65	m
116	53	s−	228	33	w						

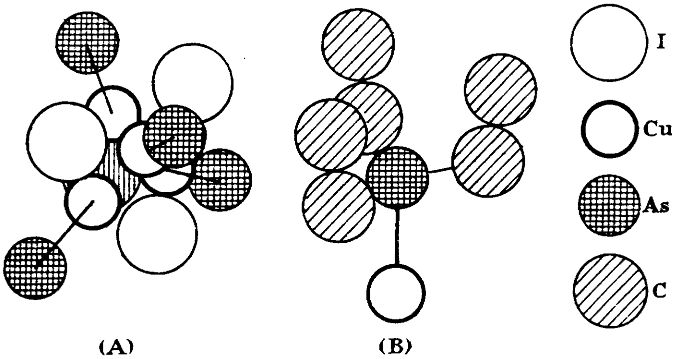
[111] axis.

Plane.	$\frac{1}{4}F$.	$I_{obs.}$.	Plane.	$\frac{1}{4}F$.	$I_{obs.}$.	Plane.	$\frac{1}{4}F$.	$I_{obs.}$.	Plane.	$\frac{1}{4}F$.	$I_{obs.}$.
$2\bar{3}1$	46	s−	$4\bar{5}1$	63	s	$4\bar{7}3$	33	vw	$5\bar{8}3$	64	m
$3\bar{4}1$	48	s−	$4\bar{6}2$	14	a	$5\bar{7}2$	49	m	$6\bar{8}2$	36	w
$3\bar{5}2$	70	s	$5\bar{6}1$	50	m	$6\bar{7}1$	29	w	$7\bar{8}1$	48	w

at (000) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$). This group consists of a tetrahedron of copper atoms, of side 2·60 A., with an iodine atom resting on each face of the tetrahedron. An arsenic atom is attached to each copper atom, the triethylarsine groups being directed away from the corners of the tetrahedron. Since the arsenic atoms lie on 3-fold axes, the triethylarsine groups themselves possess this symmetry, and the nearest neighbours of an arsenic atom are one copper and three carbon atoms in an approximately regular tetrahedral configuration. The angle between the Cu—As and As—CH_2 bonds when calculated from the parameters given above is about 100°, but it is quite possible that any distortion of the tetrahedral angles may be shared between this angle and that between the As—CH_2 and CH_2—CH_3 bonds. Fig. 2(B) shows a perspective view of a triethylarsine group attached to copper.

FIG. 2.

Tetrakis(monoiodotriethylarsinecopper).



(A) *shows the relative positions of the atomic centres. The atomic radii are reduced in size to reveal the rear atoms : the rear iodine atom is vertically shaded for identification.*

(B) *shows one triethylarsine group linked to copper.*

The more important interatomic distances are shown below.

Iodine.		Copper.		Arsenic.	
Nearest neighbours.	Distance, A.	Nearest neighbours.	Distance, A.	Nearest neighbours.	Distance, A.
3Cu	2·66	As	2·50	$3CH_2$	1·95
$3CH_3$	3·34	3Cu	2·60	Cu	2·50
3I	4·45	3I	2·66	3I	4·10

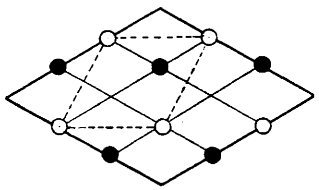
Each iodine is surrounded octahedrally by 3 copper and 3 carbon atoms, and the large distance between iodine and carbon (3·34 A.) indicates that the binding between these atoms is only of the van der Waals type. The fact that the forces within each macro-molecule are of covalent type, whereas those between neighbouring macro-molecules are thus of the van der Waals type, indicates clearly the molecular character of the crystals. The existence of these macro-molecules in the solid state, however, does not necessarily imply that single molecules of $AsEt_3$,CuI may not exist, *e.g.*, in solution. Each copper, with its arsine group attached, is equidistant from three iodine atoms in the crystal, and single molecules might possibly be formed as in the case of cuprous iodide. In the latter compound, each copper is equidistant from four iodine atoms in the crystal, but Cu_2I_2 and possibly CuI molecules apparently exist in the vapour, and in solution in certain organic solvents. In the ethylarsine compound, however, there seems to be little doubt that the four-fold molecule is essentially the form in which the compound exists in solution.

Tetrakis(*monoiodotriethylphosphinecopper*).—This is isomorphous with the above arsenic analogue, showing the same dodecahedral development and cubic symmetry. The unit translation is $a = 13{\cdot}05 \pm 0{\cdot}05$ A. (from layer line separations). The observed density (by flotation) is 1·84, giving 8 molecules in the unit cell.

Tetrakis(*monoiodotri*-n-*propylphosphinecopper*).—Compact colourless crystals and occasionally needles elongated along the *b* axis. Oscillation photographs show that the structure may be referred to the following monoclinic unit cell (dimensions from layer line spacings) : $a = 18{\cdot}9$, $b = 15{\cdot}4$, $c = 19{\cdot}9$ A., $\beta = 78°$. The density (by flotation) is 1·70, requiring 16 molecules in the unit cell. On account of the existence of various pseudo-halvings, the space group cannot at present be established with certainty.

Tetrakis(*monoiodotri*-n-*butylarsinecopper*).—Very slender colourless rhombic needles showing the forms {100}, {010}, and {110}. Oscillation photographs about the three axes confirm the rhombic symmetry and give the following unit translations : $a = 26{\cdot}3$, $b = 22{\cdot}3$, $c = 12{\cdot}3$ A. The calculated density for 16 molecules in the unit cell is 1·60, which is about that to be expected (compare the tributylphosphine compound, $d = 1{\cdot}47$). The halvings are as follows : *hk*0 absent when *h* is odd, 0*kl* when $k + l$ is odd, *h*0*l* all types present. The crystals show no signs of pyroelectricity when tested in liquid air (contrast the phosphine analogue), indicating that the space-group is $Pnma(D_{2h}^{16})$. Of the four-fold positions, (a) and (b) are unlikely since they have point symmetry $\bar{1},(C_i)$, whereas in (c), $x\frac{1}{4}z$, the macro-molecules would have point symmetry $m,(C_s)$. The chief interest attaching to this compound is that it is not isomorphous with its phosphine analogue.

FIG. 3.



Arrangement of molecular centres in tetrakis(*monoiodotri*-n-*butylphosphinecopper*) *and the relation of the pseudo cell to the unit cell of the structure.*

Tetrakis(*monoiodotri*-n-*butylphosphinecopper*). — Colourless hexagonal prisms $(11\bar{2}0)$ with moderate negative birefringence. The dimensions of the hexagonal unit cell, obtained from layer line separations on oscillation photographs (Cu-K_α radiation), are $c = 23{\cdot}7$, $a = 22{\cdot}4$ A. The symmetry of oscillation photographs about the *c* axis shows that the principal axis is trigonal and that there is no horizontal plane of symmetry. Photographs about the *a* axis are symmetrical with respect to the equatorial line; those about a $[1\bar{1}00]$ axis are not. There are no systematic absences for general planes, so that the lattice is hexagonal and not rhombohedral. The only halvings are 000*l* for *l* odd and $h0\bar{h}l$ for *l* odd. These, together with the low Laue symmetry indicated by the oscillation photographs, limit the possible space-groups to $C\bar{3}c(D_{3d}^4)$ and $C3c(C_{3v}^3)$, the latter being more probable since the crystals are strongly pyroelectric. The density (by flotation) is 1·47, requiring 24 molecules in

TABLE V.

Observed Intensities.

Plane.	I.	Plane.	I.	Plane.	I.	Plane.	I.
0002	s	$11\bar{2}0$	vs	$12\bar{3}0$	—	$23\bar{5}0$	—
0004	vw	$22\bar{4}0$	m	$13\bar{4}0$	—	$24\bar{6}0$	—
0006	w	$33\bar{6}0$	m	$14\bar{5}0$	m	—	—
$11\bar{2}2$	m	$11\bar{2}1$	vw	$11\bar{2}\bar{1}$	vw	$11\bar{2}\bar{2}$	m
$10\bar{1}6$	w	$10\bar{1}2$	m	$10\bar{1}\bar{2}$	vs	$10\bar{1}\bar{6}$	s+
$10\bar{1}4$	m	$10\bar{1}0$	—	$10\bar{1}\bar{4}$	m—	—	—
$20\bar{2}6$	ms	$20\bar{2}2$	vs	$20\bar{2}\bar{2}$	vw	$20\bar{2}\bar{6}$	w
$20\bar{2}4$	vw	$20\bar{2}0$	—	$20\bar{2}\bar{4}$	vw	—	—
$30\bar{3}2$	vw	$30\bar{3}0$	s	$30\bar{3}\bar{2}$	—	—	—

the unit cell : this multiple of 4 indicates that the compound may well have a structure analogous to that of the ethylarsine derivative.

The Atomic Positions.—In this space-group ($C\ 3c$) the general position is 6-fold with point symmetry 1, (C_1), and, if it is assumed that the 24 molecules form six 4-fold macro-molecules, these must be placed in the cell with their centres in the positions : xyz; $y - x, \bar{x}, z$; $\bar{y}, x - y, z$; $x, x - y, z + \frac{1}{2}$; $\bar{y}, \bar{x}, z + \frac{1}{2}$; $y - x, y, z + \frac{1}{2}$.

In addition to the space-group halvings, it is observed that for small-angle reflexions $h0\bar{h}0$ is thirded and $hh\bar{2}\bar{h}l$ is halved for l odd. Further, $11\bar{2}0$ is the strongest reflexion recorded (Table III). These observations strongly suggest a hexagonal close packing of the 4-fold molecules, referable to a pseudo-cell with $a' = a/\sqrt{3} = 12{\cdot}93$ A. and axial ratio $c : a = 1{\cdot}83$, and related to the larger unit cell as shown in Fig. 3. Such an arrangement is derived from the general position in $C\ 3c$ by putting $x = \frac{1}{3}$ and $y = 0$. The observations on planes ($h, k, \bar{h} + \bar{l}, 0$) confirm this suggestion. Such planes should be observed only if $h - k = 3n$, and reference to Table V shows that this is the case. Further intensity comparisons are not justified since the macro-molecules cannot be treated as diffracting points for large angles of reflexion. It seems very probable, however, that the structure of the compound is essentially similar to that of the triethylarsine derivative.

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