386. *The Constitution of Complex Metallic Salts. Part VI. The Constitution of the Phosphine and Arsine Derivatives of Silver and Aurous Halides. The Configuration of the Co-ordinated Argentous and Aurous Complex.*

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It is shown that the trialkyl-phosphine and -arsine derivatives of silver iodide possess four-fold macro-molecules, $[R_3P(As)\rightarrow AgI]_4$, which have the same structure and configuration as the cuprous iodide derivatives previously described. It follows that the 4-covalent argentous complex is tetrahedral, and that the 3-covalent iodine atom can be regarded as being at one apex of a tetrahedron with its three valencies directed towards the remaining apices. The phosphine and arsine derivatives of the aurous halides are, however, unimolecular, $[R_3P(As)\rightarrow AuX]$, and the 2-covalent aurous complex is probably linear. The phosphine–gold compounds are remarkably stable and can be distilled without decomposition. The electronic significance of the results is discussed.

WE have already shown (J., 1936, 1503) that the trialkyl-phosphine and -arsine derivatives of cuprous iodide, previously considered to be $R_3P(As),CuI$, possess a four-fold macro-molecule, $[R_3P(As)\rightarrow CuI]_4$, and must therefore be termed tetrakis-[iodotrialkylphosphine(or arsine)copper]. A complete *X*-ray examination of the triethylarsine member, $[Et_3As\rightarrow CuI]_4$, showed that the four copper atoms occupy the apices of a regular tetrahedron: the iodine atoms are situated each above the central point of one face of this tetrahedron, so that they also form a tetrahedron external to that of the copper atoms. Beyond each copper atom is an arsenic atom lying on the elongation of the axis joining the centre of the inner tetrahedron to the copper atom. The iodine atoms are thus 3-covalent, each being joined to the three neighbouring copper atoms apparently by one covalent and two co-ordinate links. Two important stereochemical results follow: (1) the 4-covalent cuprous atom has a tetrahedral configuration, and since each is joined by a covalent link to one iodine and by co-ordinate links to one arsenic and two iodine atoms, it acquires 7 electrons and so attains the electronic state of krypton; (2) the stereochemistry of the 3-covalent iodine atom must be similar to that of the 3-covalent sulphur atom, *i.e.*, the iodine atom occupies one apex of a tetrahedron with its valencies directed towards the other three apices. This is the first available evidence for the stereochemistry of 3-covalent iodine. Furthermore, it was shown that each co-ordinated arsenic atom lies at the centre of a tetrahedron, the apices of which are occupied by one cuprous atom and three carbon atoms.

The corresponding silver iodide derivatives, which are readily formed when the phosphine or arsine is shaken with silver iodide dissolved in concentrated aqueous potassium iodide solution, have now been investigated and prove also to possess a four-fold macro-molecule, $[R_3P(As)\rightarrow AgI]_4$, identical in chemical structure with the corresponding cuprous derivatives. This is indicated by their molecular weights in various solvents (Table I), and conclusively proved by a comparison of the crystal structure of the cuprous and the argentous compounds. Thus, whereas $[Et_3As\rightarrow CuI]_4$ is cubic, the *compound* $[Et_3As\rightarrow AgI]_4$ is tetragonal, and its space-group is the sub-group (or tetragonal equivalent) of the cubic space-group of the cuprous compound: it follows that the structure of $[Et_3As\rightarrow AgI]_4$ is merely a distorted version of that of $[Et_3As\rightarrow CuI]_4$. The *compound* $[Pr^a{}_3As\rightarrow AgI]_4$ is, however, strictly isomorphous with $[Et_3As\rightarrow CuI]_4$, the effects of the replacement of the cuprous by the argentous atom and of the ethyl by the *n*-propyl group being compensatory. This remarkable, and probably unique, example of isomorphism shows without doubt that the cuprous and argentous compounds have identical chemical structures. It follows that the 4-covalent argentous atom has also a tetrahedral configuration, in confirmation of the results of Cox, Wardlaw, and Webster (J., **1936**, 775), and that the argentous atoms in the above compounds, by acquiring 7 electrons, attain the electronic structure of xenon. It is rather surprising that silver should build up the macro-molecule in order to obtain a covalency of 4 instead of forming the simple 2-covalent compound $[R_3P(As)\rightarrow AgI]$, because whereas in the complex cyanides the cuprous atom shows a co-ordination number of 2 or 4 (as in $K[Cu(CN)_2]$ and $K_3[Cu(CN)_4]$ respectively), the argentous atom shows only a co-ordination number of 2 (as in $K[Ag(CN)_2]$) and does not apparently form compounds such as $K_3[Ag(CN)_4]$. It should be emphasised that the crystallographic evidence shows conclusively that the phosphine- and arsine-silver compounds exist as four-fold macro-molecules in the solid state: since, however, the molecular weights in various organic solvents (Table I) usually indicate an association of 3—4 $[R_3P(As)\rightarrow AgI]$ units, it is possible that in these solvents the four-fold molecule does undergo partial dissociation. Similar results were obtained for the molecular weights of the cuprous compounds (*loc. cit.*).

It is noteworthy that, whereas the m. p.'s of the homologous $[R_3P(As)\rightarrow CuI]_4$ compounds fall as each series is ascended, no such regularity occurs in the $[R_3P(As)\rightarrow AgI]_4$ compounds, where the m. p. in each series rises from the ethyl to the *n*-propyl member and then falls markedly to the *n*-butyl member, which in the arsine series is liquid at room temperature. The argentous, unlike the cuprous, compounds do not apparently react with αα'-dipyridyl: furthermore, they are stable towards air and light. When heated in a vacuum they behave similarly to the cuprous compounds, decomposing into silver iodide and the free phosphine or arsine.

The corresponding aurous compounds, *e.g.*, $[R_3P(As)\rightarrow AuCl]$, are best prepared by the method of Cahours and Gal (*Compt. rend.*, 1870, **70**, 1380; **71**, 208), a cooled aqueous-alcoholic solution of chloroauric acid being shaken with 2 equivs. of the phosphine or arsine: it is probable that in these circumstances an auric derivative of 1 equiv. of the phosphine or arsine is first formed, and then rapidly undergoes reduction by the second equiv. to give the required compound. Derivatives of the alkyl sulphides, *e.g.*, *monochlorodiethylsulphidegold*, [$Et_2S\rightarrow AuCl$], are similarly prepared. It has now been found that if the chloroauric acid solution is first treated with excess potassium iodide

TABLE I.

*Molecular complexity of the phosphine and arsine derivatives of silver and aurous halides in various solvents.**

(The values given are those of *n* in the formulæ [$R_3P(As)\rightarrow AgI]_n$ and [$R_3P(As)\rightarrow AuX]_n$ at the lowest concentration measured. For values at higher concentrations, see Experimental.)

Silver compounds.

	M. p.	$COMe_2$.	C_6H_6.	$C_2H_4Br_2$.
[Et_3P,AgI]	208—209°	3·70	3·40	3·88
[Pr^{α}_3P,AgI]	258—265		3·78	3·38
[Bu^{α}_3P,AgI]	43		4·21	3·54
[Et_3As,AgI]	182—185		3·56	4·04
[Pr^{α}_3As,AgI]	219—221		3·33	3·62

Aurous compounds.

	M. p.	$COMe_2$.	C_6H_6.	$C_2H_4Br_2$.	$CHBr_3$.
[$Et_3P,AuCl$]	78°		1·32	1·13	1·15
[Et_3P,AuI]	67		1·25	1·09	1·02
[$Pr^{\alpha}_3P,AuCl$]	40		1·20	1·12	1·14
[$Me_3As,AuCl$]	decomp.	1·11			
[Me_3As,AuI]	176—178	1·13			
[$Me_3As,AuSCN$]	127—128	1·11			
[$Et_3As,AuCl$]	94—95		1·34	1·05	1·03
[Et_3As,AuI]	77		1·18	1·06	1·10
[$Et_2S,AuCl$]	38—40	1·01		1·09	1·10

* Determinations in acetone are ebullioscopic, the others cryoscopic.

or thiocyanate, the corresponding *compounds* [$R_3P(As)\rightarrow AuI$] and [$R_3P(As)\rightarrow AuSCN$] are formed. All the aurous compounds studied, however, proved to have the simple unimolecular formula. So striking is the difference between these aurous compounds and the cuprous and argentous compounds that extensive determinations of the molecular weights of a variety of aurous compounds were made in various solvents (Table I): the evidence throughout showed that the aurous compounds had the unimolecular formula, a result which has been confirmed crystallographically. Levi-Malvano (*Atti R. Accad. Lincei*, 1908, **17**, 857) found that the compounds [$(MeO)_3P\rightarrow AuCl$] and [$Ph_3P\rightarrow AuCl$] also gave normal molecular weights in freezing benzene. It follows that the gold in all the above compounds, as in the well-known $K[Au(CN)_2]$, shows a true co-ordination number of 2.

Considerable interest attaches to the structure of these aurous compounds, as there is very little evidence available for the configuration of 2-co-ordinate metallic complexes generally. Unfortunately, it has not been possible to elucidate the complete crystal structure of any of these compounds, although the four isomorphous ethyl members, [$Et_3P(As)\rightarrow AuCl$] and [$Et_3P(As)\rightarrow AuI$], have been examined in detail. These four compounds crystallise in the monoclinic system with space group $P2_1$, there being 4 simple molecules in the unit cell. The absence of a centre of symmetry in the projection along the *a* axis, together with the large number of parameters, makes a complete determination of the structure difficult, but the positions of the gold atoms have been fixed from Patterson–Fourier projections, and the structure shown in Fig. 3, based on the packing of linear molecules of [$Et_3As\rightarrow AuCl$], is suggested as being in accord with the available data.

The phosphine–gold compounds, [$R_3P\rightarrow AuCl(I)$], possess remarkable stability and may be distilled without decomposition at low pressures. The *n*-butyl chloro-compound is a liquid at room temperature and can be volatilised even at atmospheric pressure: if the vapour is passed through a heated tube, decomposition occurs with formation of a fine film of metallic gold. The arsine–gold compounds, [$R_3As\rightarrow AuCl(I)$], are very much less stable, and merely on exposure to light slowly decompose with deposition of metallic gold.

It is noteworthy that, although gold differs so markedly from copper and silver in the above compounds, yet the " unimolecular " condition of these gold derivatives brings the metal electronically in line with mercury and thallium, *i.e.*, with neighbouring metals in the same series. Thus the gold atom, having originally 2, 8, 18, 32, 18, 1 electrons, gains 3 electrons in compounds such as [$Et_3P\rightarrow AuCl$]. Mercury (2, 8, 18, 32, 18, 2) is remarkable for the stability of its 2-covalent compounds, such as HgR_2 and $Hg(SR)_2$, in all of which the metal acquires 2 electrons: it is significant that the molecules of the mercapto-compounds do not co-ordinate with one another through the sulphur atoms to increase further the mercury electrons, although those of the palladium mercaptans, $Pd(SR)_2$, readily do so (Mann and Purdie, J., 1935, 1549; Wells, *Z. Krist.*, 1937, **96**, 435). In the case of thallium (2, 8, 18, 32, 18, 3), the thallous alkyls TlR are unknown, and thallic alkyls, TlR_3, are difficult to prepare and exceedingly reactive (Groll, *J. Amer. Chem. Soc.*, 1930, **52**, 2998), the normal stable alkyl derivatives being true salts of the type $[TlR_2]X$, in which the metal gains 1 electron. It is clear, therefore, that for all three metals a group of 4 shared electrons in the 6th quantum group permits considerable stability.

Compounds of all these metals are, however, known in which the metal attains the electronic state of radon, but those of aurous gold and thallium are rare. Thus gold in the compounds $[(NH_3)_3AuCl]$ (Meyer, *Compt. rend.*, 1906, **143**, 280), $[(NH_3)_2Et_3PAuCl]$, and $[(NH_3)_2(MeO)_3PAuCl]$ (Levi-Malvano, *loc. cit.*), all of which are stable at room temperature, shows a co-ordination number of 4 and a gain of 7 electrons: mercury in the complex cyanides, *e.g.*, $K_2[Hg(CN)_4]$ acquires 6 electrons: thallium tribromide combines with the quaternary pyridinium bromides to give compounds such as $[C_5H_5N{\cdot}Bu^{\alpha}][TlBr_4]$, in which thallium gains 5 electrons (Krause and von Grosse, *Ber.*, 1926, **59**, 1712).

An aurous chloride derivative of an unsymmetrical phosphine, $[R_1R_2R_3P{\rightarrow}AuCl]$, will be stereochemically parallel to an unsymmetrical phosphinimine, $R_1R_2R_3P{\rightarrow}N{\cdot}SO_2{\cdot}C_7H_7$ (Mann and Chaplin, this vol., p. 527), and experiments are now in progress to resolve both classes into optically active forms.

EXPERIMENTAL.

Chemical Data.

The names of the solvents used for recrystallising the compounds are given in parentheses immediately after the names of the compounds concerned. All molecular weights were determined cryoscopically except those in acetone, which were ebullioscopic.

Tetrakis(monoiodotrialkylphosphinesilver), $[R_3P{\rightarrow}AgI]_4$.—All members were prepared by the same method, which is therefore given in detail only for the *ethyl* compound. Freshly distilled triethylphosphine (6 g.) was shaken with a solution of silver iodide (13·2 g., 1·1 mols.) in saturated aqueous potassium iodide solution (50 c.c.) for 2 hours, a white solid, not apparently wetted by water, rapidly separating. This was collected, washed with potassium iodide solution and water in turn, and dried. The crystals (acetone) have m. p. 208—209° with preliminary softening, and are soluble in most organic liquids (Found: C, 20·5; H, 4·4; *M*, in 5·213% acetone solution, 1300; in 9·432%, 1390; in 4·688% benzene solution, 1200; in 9·307%, 1240; in 13·44%, 1190; in 1·508% ethylene dibromide solution, 1367. $C_{24}H_{60}I_4P_4Ag_4$ requires C, 20·4; H, 4·3%; *M*, 1412).

The n-*propyl* compound (acetone), when placed in a sealed tube in an oil-bath at 220° and rapidly heated, melted at 258—265° to a clear liquid; it is less soluble generally than the ethyl compound [Found: C, 27·4; H, 5·3; *M*, in 4·329% benzene solution, 1490; in 2·059% ethylene dibromide solution, 1340 (slight turbidity appeared in the latter solution). $C_{36}H_{84}I_4P_4Ag_4$ requires C, 27·3; H, 5·4%; *M*, 1580].

The n-*butyl* compound separated in a viscous form which on exposure to air soon solidified; from a hot concentrated alcoholic solution it separated on cooling as a fine emulsion which, on being stirred, rapidly crystallised. The crystals, m. p. 43°, were much more soluble than the propyl compound in most liquids [Found: C, 32·9; H, 6·26; AgI (direct ignition), 53·7; *M*, in 6·077% benzene solution, 1840; in 1·444% ethylene dibromide solution, 1550; in 2·856%, 1630; in 4·112%, 1700. $C_{48}H_{108}I_4P_4Ag_4$ requires C, 33·0; H, 6·22; AgI, 53·7%; *M*, 1748].

Tetrakis(monoiodotrialkylarsinesilver), $[R_3As{\rightarrow}AgI]_4$.—These were prepared precisely as the phosphine compounds. The *ethyl* compound (acetone), when heated in a sealed tube with rapid preliminary heating, has m. p. 182—185° (Found: C, 18·1; H, 3·7; *M*, in 5·247% benzene solution, 1410; in 10·17%, 1390; in 1·877% ethylene dibromide solution, 1600. $C_{24}H_{60}I_4Ag_4As_4$ requires C, 18·1; H, 3·8%; *M*, 1587).

The n-*propyl* compound (acetone), rapidly heated in a sealed tube, has m. p. 219—221° (decomp.) (Found: C, 24·8; H, 4·8; AgI, 53·5; *M*, in 6·204% benzene solution, 1460; in 10·91%, 1460; in 1·655% ethylene dibromide, 1590. $C_{36}H_{84}I_4Ag_4As_4$ requires C, 24·6; H, 4·8; AgI, 53·5%; *M*, 1756). The *n*-butyl compound is an oil at room temperature and was not further investigated.

All the above silver compounds form colourless crystals, and all are apparently decomposed by cold bromoform. The arsine members are the least stable, and decompose when boiled with most organic liquids; decomposition is slowest in boiling acetone, which for crystallisation purposes should be heated rapidly on a water-bath and not directly, the solution being filtered immediately before cooling.

Monohalogenotrialkylphosphinegold, $[R_3P\rightarrow AuX]$.—The method of preparation is similar for all the gold compounds, and is given in detail for the chlorotriethylphosphine compound only. To prepare the corresponding iodo- or thiocyanato-compounds, the chloroauric acid solution is first treated with a concentrated aqueous solution of 6 equivs. of potassium iodide or thiocyanate respectively, and the mixture cooled before dilution with alcohol; after addition of the alcoholic phosphine or arsine solution, the mixture should be vigorously shaken until no coloured product remains. For all preparations, an aqueous solution of chloroauric acid, $HAuCl_4$, containing 20% of gold was used. All the following gold compounds were colourless when pure.

Monochlorotriethylphosphinegold was prepared by cautiously adding a solution of freshly distilled triethylphosphine (5 g., 2 mols.) in alcohol (20 c.c.) to a well-cooled, agitated mixture of the chloroauric acid (20 c.c., 0·95 mol.) and alcohol (20 c.c.). An orange product first separated and was rapidly replaced by the required white solid. The mixture was shaken for 1 hour, diluted with water (50 c.c.), and the white product collected, washed with water, and dried. Cooling and (in particular) the presence of alcohol appear to be essential for such preparations. The chloro-triethyl compound (alcohol) has m. p. 78°, b. p. 210°/0·03 mm., subliming slightly before boiling (Found: C, 20·5; H, 4·4; *M*, in 3·932% benzene solution, 463; in 7·504%, 532; in 1·682% ethylene dibromide solution, 395; in 3·586%, 433; in 1·632% bromoform solution, 402. Calc. for $C_6H_{15}ClAuP$: C, 20·5; H, 4·3%; *M*, 351). Cahours and Gal (*loc. cit.*) prepared this compound and its arsine analogue: all the other gold compounds are new.

Monoiodotriethylphosphinegold (alcohol) had m. p. 67°, b. p. 195—200°/0·03 mm. (Found: C, 16·55; H, 3·6; *M*, in 5·327% benzene solution, 555; in 10·69%, 662; in 1·923% ethylene dibromide solution, 484; in 3·723%, 524; in 1·573% bromoform solution, 450. $C_6H_{15}IAuP$ requires C, 16·3; H, 3·4%; *M*, 442). The thiocyanato-analogue was obtained as an uncrystallisable liquid and was not further investigated.

Monochlorotri-n-*propylphosphinegold* separated as a liquid which crystallised after many days' standing; it is freely soluble in all organic liquids tried(16) except *cyclo*hexane and petrol. It was recrystallised from a small quantity of alcohol, a fine emulsion first forming and rapidly crystallising on cooling; m. p. 40°, b. p. 205—207°/0·04 mm. (Found: C, 27·8; H, 5·6; *M*, in 4·563% benzene solution, 472; in 9·139%, 557; in 1·866% ethylene dibromide solution, 440; in 3·826%, 458; in 5·732%, 474; in 1·509% bromoform solution, 448. $C_9H_{21}ClAuP$ requires C, 27·5; H, 5·4%; *M*, 393).

The n-*butyl* homologue separated as an oil which did not crystallise. It was extracted with chloroform, and the extract washed with water, dried (sodium sulphate), filtered, and the solvent evaporated. The residual oil when distilled gave a first fraction, b. p. 110°/0·05 mm., which on cooling gave white deliquescent crystals, presumably of the phosphine oxide, and a higher fraction, b. p. 218—225°/0·025 mm., as a viscous colourless liquid. The latter on refractionation gave the required compound as a colourless liquid, b. p. 215—225°/0·03 mm. (Found: C, 33·3; H, 6·4. $C_{12}H_{27}ClAuP$ requires C, 33·1; H, 6·3%).

Monoiodotri-n-*butylphosphinegold* also separated as an oil, which on distillation gave the same crystalline first fraction, followed by a pale green (almost colourless) fraction, b. p. 220—225°/0·2 mm., of the pure liquid compound (Found: C, 27·7; H, 5·3. $C_{12}H_{27}IAuP$ requires C, 27·4; H, 5·2%). On one occasion this oil crystallised on standing, and its m. p. is probably about room temperature.

Monohalogenotrialkylarsinegold, $[R_3As\rightarrow AuX]$.—Owing to the comparative instability of these arsine compounds, gold could be estimated by direct ignition. *Monochlorotrimethylarsinegold* (acetone), m. p. 165—175° (decomp.), on exposure to air slowly became purple and ultimately deposited gold (Found: C, 10·55; H, 2·6; Au, 55·8; *M*, in 3·330% acetone solution, 393. $C_3H_9ClAsAu$ requires C, 10·2; H, 2·6; Au, 55·9%; *M*, 352·7). The corresponding *iodo*-compound (acetone) had m. p. 176—178° (decomp., with preliminary darkening) (Found: C, 7·95; H, 2·0; Au, 44·1; *M*, in 3·036% acetone solution, 501. C_3H_9IAsAu requires C, 8·1; H, 2·0; Au 44·4%; *M*, 444); and the *thiocyanato*-analogue (alcohol or acetone), when rapidly heated had m. p. 127—128° (decomp.) (Found: C, 12·9; H, 2·5; N, 3·7; Au, 52·65; *M*, in 3·715% acetone solution, 415; in 6·610%, 440. $C_4H_9NSAsAu$ requires C, 12·8; H, 2·4; N, 3·7; Au, 52·6%; *M*, 375).

Monochlorotriethylarsinegold (carbon tetrachloride or acetone) had m. p. 94—95° (followed by decomp.) (Found : Au, 49·8; *M*, in 2·963% benzene solution, 529; in 5·653%, 656; in 7·295%, 707; in 1·380% ethylene dibromide solution, 414; in 2·766%, 449; in 0·9228% bromoform solution, 406; in 2·046%, 440. Calc. for $C_6H_{15}ClAsAu$: Au, 50·0%; *M*, 395). The *iodo*-compound (alcohol), m. p. 77° (slight decomp.), gives in carbon tetrachloride a green solution which becomes colourless on dilution with alcohol; crystals separating from the undiluted solution are also green, but become colourless on exposure to air (Found : C, 14·6; H, 3·3; Au, 40·1; *M*, in 3·267% benzene solution, 573; in 6·784%, 730; in 1·664% ethylene dibromide solution, 517; in 3·243%, 559; in 1·231% bromoform solution, 534; in 2·398%, 561. $C_6H_{15}IAuP$ requires C, 14·8; H, 3·1; Au, 40·5% ; *M*, 486).

The gold derivatives of the higher alkylarsines appear to be liquid at room temperature. None of the above gold compounds apparently reacts with αα′-dipyridyl.

Monochlorodiethylsulphidegold separated first as a colourless oil which on chilling crystallised. It is unstable on exposure to light, and soluble in most organic liquids; the crude product was rapidly dried, dissolved in a minimum of acetone or (better) methyl ethyl ketone, and the solution filtered, chilled in ice-water, and largely diluted with pure petrol (b. p. 40—50°). A fine emulsion formed, and was rapidly replaced by fine colourless crystals. These were collected, dried, and investigated without delay; m. p. 38—40° (slight decomp.) [Found : C, 15·1; H, 3·3; Au (direct ignition), 61·20; *M*, in 4·646% acetone solution, 325; in 1·596% ethylene dibromide solution, 352; in 1·210% bromoform solution, 356. $C_4H_{10}ClSAu$ requires C, 14·9; H, 3·1; Au, 61·1%; *M*, 322·8].

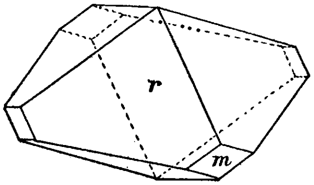
Crystallographic Data.

Tetrakis(*monoiodotriethylphosphinesilver*).—Rhombic crystals, usually prisms elongated along the *a* axis, with the forms {100}, {010} and {001}. The approximate cell dimensions are : $a = 10·9$, $b = 20·8$, $c = 20·0$ A., and for a density of 2·05 the cell contains 16 $[Et_3P{\rightarrow}AgI]$ components. The halvings observed are : $0kl$, k even; $h0l$, h even; $hk0$, $h + k$ even. The space group is *P ban*. The reflexions on a Weissenberg photograph about the *a* axis could be indexed for a cell having $b = 10·4$, $c = 20·0$ A., since $0kl$ reflexions occur only with k even, and furthermore only the fourth and the eighth order from (010) are observed. This pseudo-cell has almost exactly the same dimensions as the tetragonal cell of $[Et_3As{\rightarrow}AgI]_4$, showing that the structures of the two compounds are closely related.

Tetrakis(*monoiodotri*-n-*propylphosphinesilver*).—Well-developed tetragonal crystals showing the forms *m*{110} and *r*{101} (Fig. 1). This is the tetragonal equivalent of the dodecahedral development of the cubic tetrakis(monoiodotri-*n*-propylarsinesilver). The dimensions of the unit cell are : $a = 15·5$, $c = 12·3$ A., and for 8 $[(C_3H_7)_3P{\rightarrow}AgI]$ components in the unit cell the calculated density is 1·77. The lattice is body-centred. A Weissenberg photograph about an *a* axis shows only the fourth-order reflexion from the basal plane, but in view of the weakness of 202 and the absence of 402 and 602 (204, 404, and 604 are present), the quartering of $00l$ is not to be taken as a space-group absence. There are no halvings other than those due to the body-centring, so that the same considerations apply here as to the triethylarsine analogue, and the space-group is $I\,\bar{4}2m$ or $I\,\bar{4}m2$.

FIG. 1.

Tetrakis(*monoiodotri*-n-*propylphosphinesilver*).



Tetrakis(*monoiodotriethylarsinesilver*).—Tetragonal crystals, the usual habit being bipyramids terminated by *c*(001). Oscillation photographs gave the following approximate cell dimensions (from layer line separations) : $a = 10·7$, $c = 19·7$ A. The density of the crystals (determined by flotation) is 2·24, requiring 8 $[(C_2H_5)_3As{\rightarrow}AgI]$ components in the unit cell. The symmetry of the oscillation photographs about the [001], [100], and [110] axes shows that the Laue symmetry is D_{4h}, and the halvings observed are those due to a body-centred lattice only. There are therefore five possible space-groups : $I\,42$ (D_4^9), $I\,4/mmm$ (D_{4h}^{17}), $I\,4mm$ (C_{4v}^9), $I\,\bar{4}m2$ (D_{2d}^9) and $I\,\bar{4}2m$ (D_{2d}^{11}). As in the cuprous analogue, the unit cell contains two macro-molecules, and of the above space-groups the first three are improbable since they would require the macro-molecules to lie on 4-fold axes with point symmetry 42, $4/mmm$ or $4mm$ respectively. The probable space-group is therefore either $I\,\bar{4}m2$ or $I\,\bar{4}2m$, in each of which the point symmetry of the 2-fold positions is $\bar{4}2m$. Although the cell dimensions of this compound are quite different from those of the cubic copper analogue

(a = 13·08 A.), there are in each case two macro-molecules in the body-centred cell, and the symmetry of these complexes is $\bar{4}3m$ for $[(C_2H_5)_3As\rightarrow CuI]_4$ and $\bar{4}2m$ for $[(C_2H_5)_3As\rightarrow AgI]_4$.

*Tetrakis(monoiodotri-*n*-propylarsinesilver).*—Cubic crystals of dodecahedral habit, isomorphous with the ethyl-copper analogue; a = 14·4 A. The density is 1·94, hence there are 8 $[(C_3H_7)_3As\rightarrow AgI]$ components in the unit cell. This case of isomorphism is important in establishing the constitution of the silver compounds (see above).

Monochloro- and Monoiodo-triethylphosphine- and -triethylarsine-gold.—These four isomorphous compounds separate from acetone or alcohol as monoclinic crystals, usually tabular on (010) or (001) and elongated along the a axis. The birefringence is low, and the dispersion high. Twinning across the (001) plane was observed in monoiodotriethylarsinegold, this being shown by etch-pits and by X-ray photographs. A photograph about the normal to the plane (001) of such a twin is symmetrical about the equatorial line, giving the appearance of a b-axis photograph. When tested in liquid air the crystals showed an appreciable pyroelectric effect. Oscillation photographs and Weissenberg photographs about the a and b axes gave the following cell dimensions :

	a.	*b.*	*c.*	*β.*		*a.*	*b.*	*c.*	*β.*
$[Et_3P\rightarrow AuCl]$	7·05	18·9	7·61	73°	$[Et_3As\rightarrow AuCl]$	7·05	19·2	7·70	74°
$[Et_3P\rightarrow AuI]$	7·30	19·4	7·87	75	$[Et_3As\rightarrow AuI]$	7·17	19·7	8·00	75

The only halving is $0k0$ absent for k odd, and the space-group is accordingly $P\ 2_1$, the holohedral group $P\ 2_1/m$ being excluded on account of the pyroelectricity. The densities show that in each case there are 4 molecules in the unit cell. The molecules must occupy two sets of general positions, (xyz) $(\bar{x}, \frac{1}{2} + y, \bar{z})$, the screw diad axes separating similar atoms of each pair of molecules by $b/2$ = 9·6 A. Consequently four-fold macro-molecules like those of the cuprous and argentous analogues are not present in these crystals. This would also, of course, apply to the higher space-group $P\ 2_1/m$.

The precise crystal structure of these compounds has not been determined, but the following account of monochlorotriethylarsinegold shows the essential features of the structure and establishes the important point that the crystals are built up of single, presumably linear, molecules.

Monochlorotriethylarsinegold. The unit cell contains four molecules of $[(C_2H_5)_3As\rightarrow AuCl]$, and in the space-group $P\ 2_1$ the general position is 2-fold : (xyz), $(\bar{x}, \frac{1}{2} + y, \bar{z})$. A complete structure determination would therefore involve the evaluation of 18 parameters apart from those of the carbon atoms. The gold atoms were located first by means of Patterson–Fourier projections. Intensities estimated on Weissenberg photographs about the a and b axes were used to obtain F^2 projections in the directions of these axes, and showed the arrangement of gold atoms depicted in Fig. 2. The relation of the atoms to the screw diad axes in the [010] projection may be that shown in (a) or (b).

Owing to the large scattering power of the gold atoms, the main features of the a and b axis Weissenberg photographs are immediately accounted for. The $h0l$ reflexions are, in general, very weak when h is odd, though three small-angle reflexions (101, 102, $10\bar{1}$) have appreciable intensities. The above arrangement exactly halves the a axis, so the weaker $h0l$ reflexions with h odd are probably due to the lighter atoms. Further, the strongest reflexions in this zone are 200 and 201, and in Table II the value of F' (from visually estimated intensities) is compared with the contribution from the gold atoms, calculated for the parameters (0·05, y_1, 0·10) and (0·45, y_2, 0·10). The planes are arranged in order of increasing sin θ/λ.

TABLE II.

Plane.	f_{Au}.	F', obs.	Plane.	f_{Au}.	F', obs.	Plane.	f_{Au}.	F', obs.
001	3·2	31	300	0	14	$40\bar{1}$	1·2	18
100	0	0	$20\bar{2}$	1·2	15	205	3·2	52
002	1·2	18	004	3·2	65	005	4·0	60
201	4·0	85	204	1·2	23	$20\bar{4}$	4·0	53
200	3·2	85	$20\bar{3}$	3·2	58	$40\bar{2}$	3·2	34
202	3·2	58	401	3·2	58	206	4·0	29
$20\bar{1}$	1·2	17	402	4·0	59	006	3·2	21
003	1·2	23	400	1·2	11	$40\bar{3}$	4·0	37
203	1·2	40	403	3·2	35			

Similarly the alternations in intensity of the $0kl$ reflexions follow from the parameters of the gold atoms. For a given set of $0kl$ reflexions with a fixed value of l, the intensities show a greater or less degree of alternation according to whether k is odd or even, the nature and amount of this alternation being different in the various sets of reflexions. These data are summarised in the following table, which also shows the calculated contributions from the gold atoms.

Intensities of 0kl *Reflexions.*

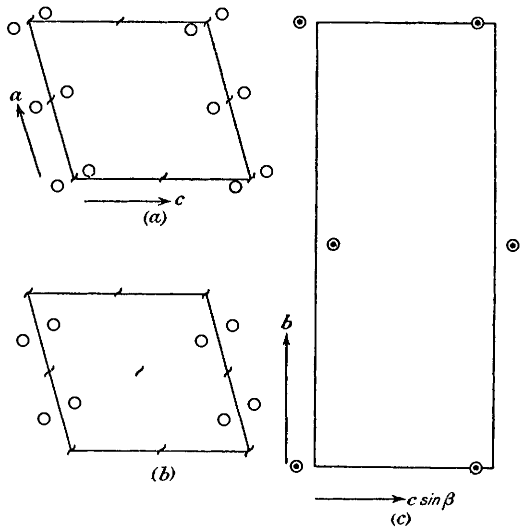
	f_{Au}.		
	k odd.	k even.	Observed intensity.
$0k1$	1·2	1·6	k odd $<$ k even
$0k2$	1·9	0·6	k odd $\gg$ k even
$0k3$	1·9	0·6	k odd $\gg$ k even
$0k4$	1·2	1·6	Very little alternation
$0k5$	0·0	2·0	k odd $\lll$ k even

It is important to establish the position of the gold atoms, since this proves conclusively that there is no complex formation in the crystal involving linkage between gold atoms, the closest approach between these atoms being $a/2 = 3·5$ A.

Examination of the packing of linear molecules of $[Et_3As\rightarrow AuCl]$ shows that the probable structure is of the type shown in Fig. 3. To maintain reasonable interatomic distances the molecules must be inclined at a considerable angle to the b axis, and in addition the molecules at $y = 0$ must be inclined to one another. Fig. 3 shows the structure viewed along the a axis. Full lines joining atoms indicate that these atoms lie above those joined by dotted lines, and ethyl groups are shown attached only to those arsenic atoms which lie within the unit cell. The corresponding [010] projection may be derived from Fig. 2 (b) which shows only the gold atoms. It should be emphasised that no attempt has been made to find the precise positions of the lighter atoms necessary to account for the weaker $h0l$ reflexions with h odd. In order to investigate the packing of the molecules some type of molecular model had to be adopted, and the following intramolecular distances were assumed: As–C, 1·95; Au–Cl, 2·25; Au–As, 2·40; the last two being taken as 10% less than the sum of the standard tetrahedral radii to allow for the 2-co-ordination of the gold atom. A knowledge of the lengths of the links in such a molecule would be of interest, but it was decided that these particular compounds are not suitable for an exact structure determination.

FIG. 2.

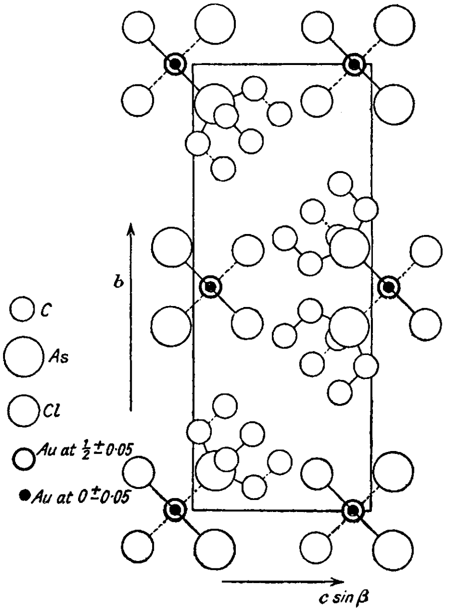
Arrangement of gold atoms in $[(C_2H_5)_3As\rightarrow AuCl]$.



(*a*) *and* (*b*) *show the two possibilities for the projection along the* b *axis, and* (*c*) *the projection along the* a *axis.*

FIG. 3.

Suggested structure of $[(C_2H_5)_3As\rightarrow AuCl]$, *viewed along the* a *axis.*

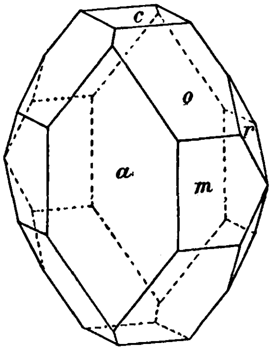


Monoiodotrimethylarsinegold. Orthorhombic crystals from acetone with the development shown in Fig. 4, the forms being *a*{100}, *m*{110}, *o*{111}, *r*{021}, and *c*{001}; also as pseudo-tetragonal prisms elongated along the *c* axis and terminated by the same faces. The development is pseudo-cubic except for the presence of (021) and the absence of (010), the angles 100 ∧ 111, 111 ∧ 001 and 111 ∧ 010 all being 54—55°. The crystal faces were not sufficiently perfect for exact measurement, but the development suggests the holohedral class *mmm*. The measured angles were: *am*, 45°; *om*, 36°; *cr*, 63°; all ±1°. The optics show that the symmetry is not higher than orthorhombic. The crystals, tested in liquid air, showed no signs of pyroelectricity, in contrast to the ethyl analogue.

Oscillation photographs gave the following unit translations: $a = 12{\cdot}0$, $b = 11{\cdot}7$, $c = 11{\cdot}7$ A., all ±0·1 A. Photographs about the *a* and *b* axes show that the symmetry of the crystals is strongly pseudo-tetragonal; *e.g.*, 200 and 020 are very similar in intensity, whereas 002 is extremely weak. The pseudo-tetragonal axis is, however, the *c* and not the *a* axis as suggested by the cell dimensions. The halvings observed are: *hk*0, $h + k$ even, 0*kl*, *k* even, *h*0*l*, *l* even, indicating *Pbcn* (D_{2h}^{14}) as the space-group. The crystals have a density greater than 3·3, hence there are 8 molecules in the unit cell (*d*, calc.: 3·85). The molecules therefore occupy general positions (8-fold, *xyz*) without point symmetry. There is no 2-fold position in this space-group, showing that four-fold macro-molecules do not exist in the crystals.

FIG. 4.

Monoiodotrimethylarsinegold.



Monothiocyanatotrimethylarsinegold.—Small tetragonal crystals. The cell dimensions are $a = 17{\cdot}3$, $c = 11{\cdot}9$ A., and for a density of 2·79 the unit cell contains 16 molecules. Oscillation photographs and a Weissenberg photograph about the *c* axis show the halvings characteristic of a body-centred lattice together with the following: 00*l*, $l = 4n$, *hh*0, *h* even, *h*0*l*, *h* and *l* even. The space group is therefore *I* 4*cd*, the molecules occupying the general 16-fold position without point symmetry.

The crystallographic data are summarised below.

Compound.	System.	*a.*	*b.*	*c.*	*β.*	*d.*	*n.*	Space-group.
$[Et_3P{\to}AgI]_4$	Rhombic	10·9	20·8	20·0	—	2·05	16	*P ban*
$[Pr_3P{\to}AgI]_4$	Tetragonal	15·5	15·5	12·3	—	1·77	8	$I\,\bar{4}2m$ $I\,\bar{4}m2$
$[Et_3As{\to}AgI]_4$	Tetragonal	10·7	10·7	19·7	—	2·24	8	$I\,\bar{4}2m$ $I\,\bar{4}m2$
$[Pr_3As{\to}AgI]_4$	Cubic	14·4	—	—	—	1·94	8	$I\,\bar{4}3m$
$[Et_3P{\to}AuCl]$	Monoclinic	7·05	18·9	7·61	73°	2·38	4	$P\,2_1$
$[Et_3P{\to}AuI]$	,,	7·30	19·4	7·87	75	2·71	4	$P\,2_1$
$[Et_3As{\to}AuCl]$	,,	7·05	19·2	7·70	74	2·60	4	$P\,2_1$
$[Et_3As{\to}AuI]$	,,	7·17	19·7	8·00	75	2·94	4	$P\,2_1$
$[Me_3As{\to}AuI]$	Rhombic	12·0	11·7	11·7	—	3·85	8	*P bcn*
$[Me_3As{\to}AuSCN]$	Tetragonal	17·3	17·3	11·9	—	2·79	16	*I* 4*cd*

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