12. *Complexes of a Ditertiary Arsine with Univalent and Tervalent Gold.*

By C. M. Harris and R. S. Nyholm.

A stable series of four-covalent complexes of univalent gold with the ditertiary arsine chelate group *o*-phenylenebis(dimethylarsine) ("as") has been prepared. These compounds are of the general type $[Au(as)_2]^+X^-$ (where $X^- = ClO_4$, Br, I, picrate, CuI_2, and AuI_2) and behave as uni-univalent electrolytes in nitrobenzene solution.

With this chelate group tervalent gold forms three types of complex, in which the gold atom appears to be severally four-, five-, and six-covalent. The compounds prepared were: $[Au(as)_2][ClO_4]_3$, $[Au(as)_2I][ClO_4]_2$, $[Au(as)_2X_2]ClO_4$ (X = Br and I), $[Au(as)_2I_2]I$, and $Au(as)_2(NO_3)_3$. Electrical conductivity and spectrophotometric measurements were used in investigating the structure of the complexes. The type of bonding possibly present in these compounds is discussed.

The preparation of four-, five- and six-covalent palladium(II) complexes with the ligand *o*-phenylenebis(dimethylarsine), termed below (as), had been previously reported.[1-5] The present paper is concerned with the complexes of univalent and tervalent gold with this diarsine. This work was pursued in order (*a*) to prepare and study four-covalent complexes of univalent gold and to obtain evidence for the disposition of the four bonds about the gold(I) atom, and (*b*) to determine whether tervalent gold forms complexes of higher co-ordination number than four with this diarsine, similar to those of palladium(II). It was reported in a preliminary note [6] that *o*-phenylenebis(dimethylarsine) forms stable four-covalent univalent gold complexes of the type $[Au(as)_2]X$ (where X = Br or ClO_4), and some data concerning tervalent gold complexes were presented. The structures of the latter have now been more fully investigated.

It is well known that univalent copper, silver, and gold can form two-covalent linear complexes, consistent with the use of *sp* hybrid orbitals.[7] Copper(I) and silver(I) are also known to form four-covalent compounds in which the bonds are arranged tetrahedrally, as shown by structure determination on compounds such as $K_3Cu(CN)_4$,$[M(S{\cdot}CMe{\cdot}NH_2]_4]Cl$ (M = Cu, Ag)[8] and $M_4I_4(AsEt_3)_4$ (M = Cu, Ag).[9] The number of univalent gold compounds which apparently exhibit a co-ordination number of four is limited. Meyer [10] has reported a compound of the formula $(NH_3)_3AuCl$ and the triethylphosphine complex ammine $(NH_3)_2PEt_3$,AuCl has been described by Levi-Malvano.[11] The compound $KAu(CN)_2$–dipyridyl has been reported as possessing square-co-ordinated gold(I) in the anion,[12] as inferred from an incomplete *X*-ray examination. This is most unexpected as one might expect that four-covalent gold(I) complexes would be tetrahedral as are those of univalent copper and silver. It is obvious that four-covalent Au(I) complexes offer an interesting field for study.

The use of the ditertiary arsine chelate group favours the formation of four-covalent structures since the attachment of one molecule of the chelate compound, owing to its shape, prevents the use of linear *sp* bonds, and so favours the addition of a second molecule

[1] Chatt and Mann, *J.*, 1939, 1622.
[2] Harris and Nyholm, *J.*, 1956, 4375.
[3] Harris, Nyholm, and Stephenson, *Rec. Trav. chim.*, 1956, **75**, 687.
[4] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.
[5] Harris, Ph.D. Thesis, 1955, New South Wales.
[6] Nyholm, *Nature*, 1951, **168**, 705.
[7] Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, 1st Edn., 1947, p. 504; 2nd Edn., 1950, p. 614.
[8] Cox, Wardlaw, and Webster, *J.*, 1936, 775.
[9] Wells, *Z. Krist.*, 1937, **94**, 447.
[10] Meyer, *Compt. rend.*, 1936, **143**, 280.
[11] Levi-Malvano, *Atti. R. Accad. Lincei*, 1908, **17**, 857.
[12] Dothie, Llewellyn, Wardlaw, and Welch, *J.*, 1939, 426.

which could result in the formation of four sp^3 tetrahedral bonds. By using this ligand a series of univalent gold complexes, similar to those of univalent copper,[13] has been prepared. Compounds of the general formula $[Au(as)_2]X^-$ (where $X^- = ClO_4$, Br, I, CuI_2, AuI_2, and picrate) have been isolated by double decomposition from alcoholic solutions of the very soluble chloride $[Au(as)_2]Cl$ prepared by adding sodium tetrachloroaurate(III) to a mixture of *o*-phenylenebis(dimethylarsine) and hypophosphorous acid in alcohol. All of these compounds are uni-univalent electrolytes in nitrobenzene solution (see Table 1) with molecular conductivities of the order 22—27 mho in 10^{-3}—$2{\cdot}5 \times 10^{-4}$M-solutions in nitrobenzene at 20°; and this, together with the formation of the perchlorate $(Au(as)_2]ClO_4$, provides good evidence for the existence of the four covalent cation $[Au(as)_2]^+$. The molecular weight of the bromide in freezing nitrobenzene also supports this hypothesis. The complexes are stable in boiling water and are not reduced to metallic gold in boiling alcoholic hypophosphorous acid, showing the remarkable stability of the cation.

TABLE 1. *Molecular conductivities of univalent gold complexes in nitrobenzene at* 20°.

Compound	Molar concn.	Molar conductivity (mho)	Compound	Molar concn.	Molar conductivity (mho)
$[Au(as)_2]ClO_4$	$0{\cdot}82 \times 10^{-3}$	25·3	$[Au(as)_2]$ picrate	$2{\cdot}50 \times 10^{-4}$	22·1
$[Au(as)_2]Br$	$1{\cdot}20 \times 10^{-3}$	24·1	$[Au(as)_2][AuI_2]$ ...	$4{\cdot}60 \times 10^{-4}$	25·3
$[Au(as)_2]I$	$5{\cdot}70 \times 10^{-4}$	26·0	$[Au(as)_2][CuI_2]$ ...	$3{\cdot}44 \times 10^{-4}$	27·4

Evidence for the expected tetrahedral configuration of the four arsenic atoms about the gold is provided by the fact that the iodide $[Au(as)_2]I$ has been shown by *X*-ray powder photographs to be isomorphous with the corresponding copper(I) complex $[Cu(as)_2]I$.[13] This *X*-ray structural work has also shown that Au(I) is tetrahedrally co-ordinated in gold(I) iodide, as will be shown later.[14]

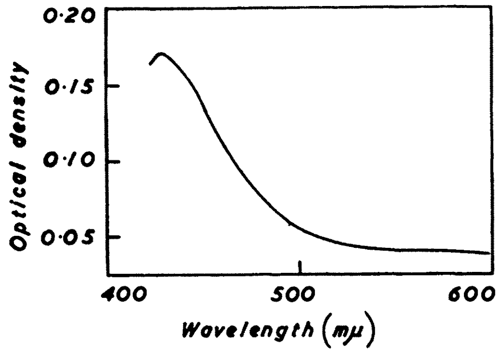
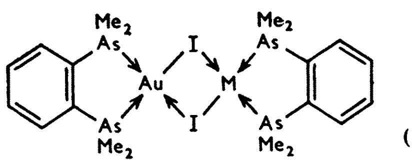


FIG. 1. *Absorption spectrum of* $[Au(as)_2I_2]I$ ($2{\cdot}44 \times 10^{-4}$M) *in nitrobenzene.*

It was pointed our earlier [6] that the use of an unsymmetrical chelate group, *e.g.*, a ditertiary arsine with a methyl group attached to one of the carbon atoms of the benzene ring, should yield complexes of Au(I) which could theoretically exist in optically active forms. Provided that these are reasonably· stable, this provides another method of establishing that the four bonds to the Au(I) atom are arranged tetrahedrally. Some work on these lines is proceeding. It is interesting also that a similar unsymmetrical ditertiary phosphine prepared by Hart and Mann [15] should be ideal for this purpose. Compounds of the empirical formulæ AuI,diarsine, show no evidence for the formation of halogen-bridged structures as in (I), at least in nitrobenzene solution because the molecular conductivities in this solvent indicate that they are salts of the type $[Au(as)_2][MI_2]$ (where M = Cu, Au), similar to the copper compounds $[Cu(as)_2][CuX_2]$ (X = Cl, Br, I).[13]



(I)

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

[14] Harris, Nyholm, and Stephenson, unpublished work.

[15] Hart and Mann, *Chem. and Ind.*, 1956, 574.

Tervalent gold complexes were prepared directly from sodium tetrachloroaurate(III) and the diarsine in alcohol and by the oxidation of the univalent complexes. Treatment of the univalent complex $[Au(as)_2]I$, with one mol. of iodine in boiling alcohol gave fine orange crystals of the empirical formula $AuI_3(as)_2$. This diamagnetic complex could be the polyiodide,$[Au^I(as)_2]^+I_3^-$, of univalent gold, or, a tervalent gold derivative. The view that the gold is tervalent is supported by the fact that the same compound can be prepared directly from sodium tetrachloroaurate(III) in alcohol by adding two mols. of the diarsine and treating the resulting yellow solution with sodium iodide. The product is of a slightly darker orange-red colour but the difference is apparently due to crystal size since the *X*-ray powder photographs of the two are identical. The absorption curves of these two compounds in nitrobenzene solution (see Fig. 1) are also similar. The deep colour of this iodide suggested that, as in the case of the deep red bivalent palladium(II) iodide complex,[2] $Pd(as)_2I_2$, some of the iodine atoms might be covalently bound within the complex ion. The molecular conductivity of the compound in nitrobenzene, in which this complex is sparingly soluble (see Table 2), is of the order expected for a uni-univalent electrolyte. This suggests that only one iodine atom is ionised and that the compound should be formulated as $[Au(as)_2I_2]I$. The corresponding perchlorate $[Au(as)_2I_2]ClO_4$ is readily prepared by iodine oxidation of the univalent perchlorate $[Au(as)_2]ClO_4$ and it also exhibits a molecular conductivity indicating a uni-univalent electrolyte (see Table 2). The bromo-complex $[Au(as)_2Br_2]ClO_4$ was also prepared but its low solubility precluded its investigation in solution.

TABLE 2. *Molecular conductivities of tervalent gold complexes in nitrobenzene at 20°.*

Compound	10^4 × Molar concn.	Molecular conductivity at 20° (mho)	Compound	10^4 × Molar concn.	Molecular conductivity at 20° (mho)
$[Au(as)_2I_2]I$	2·0	28·0	$[Au(as)_2I][ClO_4]_2$	1·82	40·8
$[Au(as)_2I_2]ClO_4$	2·26	27·9	$[Au(as)_2(NO_3)][NO_3]_2$	2·9	40·1 (25°)

The di-iodo-complex iodide $[Au(as)_2I_2]I$ dissolves in boiling water to a limited extent forming a golden solution. Treatment of this solution with perchloric acid yields a pink perchlorate $[Au(as)_2I][ClO_4]_2$ in which the gold atom appears to be five-covalent. The molecular conductivity (~41 mho) in nitrobenzene solution supports this formulation as a di-univalent electrolyte, since it is similar to that expected for electrolytes of this type, *e.g.*, $[Pd(as)_2][ClO_4]_2$.

The absorption curve for this five-covalent compound $[Au(as)_2I][ClO_4]_2$ (see Fig. 2) is clearly different from that of the six-covalent complex $[Au(as)_2I_2]I$ (Fig. 1). The five-covalent ion readily passes into the six-covalent ion in nitrobenzene solution on the addition of iodide ions, according to the equation :

$$[Au(as)_2I]^{++} + I^- \longrightarrow [Au(as)_2I_2]^+$$

as shown by the change in the absorption curve when $[Au(as)_2I][ClO_4]_2$ is shaken in nitrobenzene with solid sodium iodide (see Fig. 2). This was confirmed by a conductometric titration in this solvent (Fig. 3). When one titrates an approximately M/7000-solution of the compound $[Au(as)_2I][ClO_4]_2$, in nitrobenzene, with M/100-methyltriphenylarsonium iodide a sharp end-point is obtained after the addition of one g.-ion of iodide per mole of complex.

The colourless four-covalent complex ion $[Au(as)_2]^{+++}$ was isolated as its perchlorate by adding a mixture of one mol. of sodium tetrachloroaurate(III) and two mols. of the diarsine in alcoholic solution to concentrated aqueous perchloric acid. The dry compound explodes with great violence when heated and is sparingly soluble in cold water and acetone. The triperchlorate is not sufficiently soluble even in hot nitrobenzene to permit of conductivity measurements or to allow one to carry out conductometric titrations with iodide.

Further confirmation that the compound contains tervalent gold is provided by its preparation from the nitrate $Au(NO_3)_3(as)_2$. The latter is obtained by refluxing the di-iodo-iodide with alcoholic silver nitrate, the colourless nitrate being obtained from the filtrate. This nitrate also appears to be five-covalent in nitrobenzene solution since its molecular conductivity in this solvent is 40 mho, which is the value expected for a di-univalent electrolyte, but the co-ordination number in the solid state is unknown. In aqueous solution the nitrate groups are completely ionised and the compound functions as a ter-univalent electrolyte (see Experimental section) in which the co-ordination number of the gold atom is four.

Thus, three different types of diarsine complexes have been prepared containing tervalent gold. These are: (*a*) the colourless, and presumably, four-covalent triperchlorate $[Au(as)_2][ClO_4]_3$; (*b*) the five-covalent * salt $[Au(as)_2I][ClO_4]_2$; and (*c*) the six-covalent dihalogeno-complexes $[Au(as)_2I_2]X$ ($X = I$ and ClO_4) and $[Au(as)_2Br_2]ClO_4$. Since all gold(III) compounds investigated previously appear to be of the four-covalent type, and in many cases have been shown to possess a square-planar arrangement, it is of interest to examine the possible bonds involved in these five-and six-covalent complexes.

FIG. 2. *Absorption spectrum of* $[Au(as)_2I](ClO_4)_2$ ($1{\cdot}82 \times 10^{-4}$M) *in nitrobenzene* (0·5 *cm. cell*). *I, Immediate. II, After the solution had been shaken with anhydrous sodium iodide.*

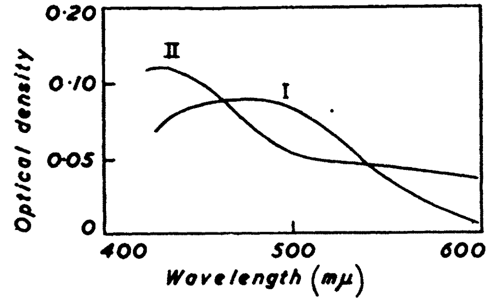
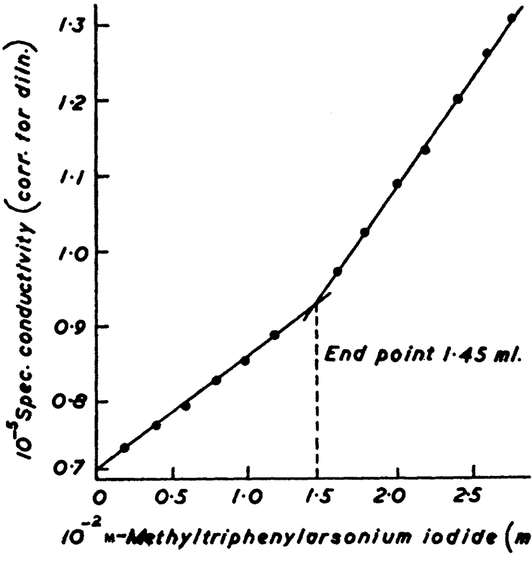


FIG. 3. *Conductometric titration of* 2×10^{-4}M-$[Au(as)_2I](ClO_4)_2$ (100 *ml.*; *factor* 0·74) *with* 10^{-2}M-*methyltriphenylarsonium iodide in nitrobenzene at* 26°.



In a previous paper [2] we suggested that the formation of five-covalent Pd(II) complex ions in nitrobenzene solution by the reaction $[Pd(as)_2]^{++} + Hal^- \longrightarrow [Pd(as)_2Hal]^+$ could be explained on the following grounds: (*a*) the existence of a vacant 5*p* orbital on the palladium atom capable of utilising a lone pair of electrons on the donor atom of the ligand (here Hal^-); (*b*) the possession of a positive charge on the palladium atom, presumably owing to the formation by the arsenic atoms of dative d_π–d_π bonds with the palladium atom, using 4*d* electron pairs of the latter. An alternative explanation involving a purely electrostatic $[(as)_2Pd]^{++} \cdots Hal^-$ bond was considered unlikely in view of the colour changes and sharpness of the end-point accompanying titration with a halogen ion.

It is obvious that, since the $[Au(as)_2]^{+++}$ ion has an even higher positive charge, a

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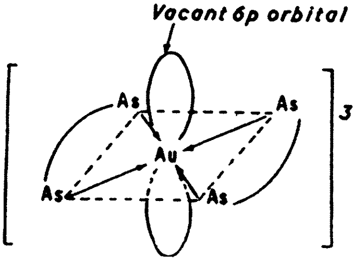
* It must be emphasised that the five-covalency refers to the ions in nitrobenzene solution, for the compounds may well be polymerised to form a six-covalent gold atom in the solid state. It is also possible that a molecule of nitrobenzene completes the six-fold co-ordination in complexes of the type $[Au(as)_2I][ClO_4]_2$ in nitrobenzene solution, but there is no evidence to support this.

similar explanation for the formation of five-covalent Au(III) complexes is likely. If we take a value of 2·0 for the electronegativity of the gold atom and 2·0 for the arsenic atom,[*] then the charge on the gold atom in the $Au(as)_3^{+++}$ ion would be −1·0 unit if all four As→Au links were single σ co-ordinate bonds. As with the palladium compounds, however, double-bond formation utilising *5d* electron pairs of the gold atom in d_π–d_π bond formation would lead to a final charge on the gold atom of +1·0 unit. These approximate values are intended, of course, to indicate changes of charge on the central atom. No absolute significance should be attached to them. This positive value is higher than with the palladium compounds and so formation of five-covalent complexes might be expected to occur even more readily.

It is of interest that Malatesta and Vallarino [16] have explained the formation of solvates of Rh(I) in which the rhodium atom appears to reach a co-ordination number of five by a similar hypothesis. This leads us to consider the more difficult problem of why it is possible to add a second halogen ion to the Au(III) atom to form a six-covalent complex cation.[†] The higher positive charge on the gold atom than on the palladium atom might at first sight offer an obvious explanation. However, when a five-covalent ion is formed the bond orbitals are $5d6s6p^3$ and unless we invoke the use of a *6d* orbital there are only *five* bond orbitals ($5d6s6p^3$) of the metal available to attach the ligands. It is assumed that the formation of six equivalent $5d^26s6p^3$ bonds involving promotion of two electrons is most improbable. The formation of six *equivalent* bonds using a $5d6s6p^36d$ combination is energetically unlikely as shown by Craig, Maccoll, Nyholm, Orgel, and Sutton.[17]

FIG. 4.



The $[Au(as)_2]^{+++}$ ion can be represented as in Fig. 4 with one lobe of the vacant *6p* orbital above and one below the plane. Addition of a halogen ion with the formation of a five-covalent complex utilises this *p* orbital on the one side, reducing the other lobe almost to vanishing point. The addition of a second halogen could be accounted for simply by proposing that an electrostatic dipole $Au^+ \cdots Hal^-$ bond is formed; but this is not supported by the colour change or by the sharpness of the end-point observed when titrating with a halogen (see I^- titration in Fig. 3). Another possible explanation is to assume that the *p* orbital is shared between the two halogen atoms occupying positions on opposite sides of the square. This would mean that two " half bonds " were formed (*not* one electron bond). This idea was suggested by Rundle and Sturdevant [18] and later by Fyfe [19] to explain the type of bond in ammines of bivalent transition metals. Such bonds would be fairly ionic—a situation met in $[Au(as)_2Hal_2]^+$. We prefer to regard $[M^{II}(NH_3)_6]^{++}$ complex ions as involving $4s4p^34d^2$ hybrid bond orbitals for reasons discussed elsewhere,[17] and we do not favour the idea for these compounds.

Dr. L. E. Sutton [20] has suggested to us that the two halogen atoms (*e.g.*, the iodine atoms in the $[Au(as)_2I_2]^+$ ion) might be bound by collinear *6p6d* hybrid bonds in a hybridisation distinct from and additional to the $5d6s6p^2$ hybrids which hold the four arsenic atoms in a square. This explanation is consistent also with what one would expect on the basis of ligand (crystal) field theory.[21] Of the eight non-bonding *5d* electrons of the gold atom

[*] The values of percentage ionic character involved in these estimates are taken from Coulson " Valence," Clarendon Press, Oxford, 1952, p. 135.

[†] *X*-Ray analysis of the iodide $[Au(as)_2I_2]I$ by Mr. Stephenson [14] has established a *trans*-octahedral structure for the complex gold(III) ion.

[16] Malatesta and Vallarino, *J.*, 1956, 1867.

[17] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[18] Rundle and Sturdevant, *J. Amer. Chem. Soc.*, 1947, **69**, 1561.

[19] Fyfe, *J.*, 1952, 2018.

[20] L. E. Sutton, 1955, personal communication, see ref. 3.

[21] Orgel, *J.*, 1952, 4756.

six are located in a filled, electrically symmetrical $5d_{\epsilon}$ sub-shell. The remaining two-paired non-bonding electrons are in a $5d_{\gamma}$ orbital. The $5d_{x^2-y^2}$ orbital combines with the $6s$ and two $6p$ orbitals to give four square $5d_{x^2-y^2}6s6p^2$ bonds. Now the *filled* $5d_{z^2}$ orbital points towards the remaining two positions of the octahedron, *i.e.*, is normal to the plane of the square. Thus any ligands along this z axis are expected to suffer a repulsion and hence the bond lengths should be longer than usual. Preliminary X-ray results establish this as correct. Moreover the proposal that the bonding orbitals for these two iodine atoms along the z axis are $5p6d$ hybrids leads to the same conclusion as ligand field theory in regard to lengths, namely, that these two bonds should be longer than normal covalent bonds using $5d$ orbitals. A simple illustration of the effect of using an outer d orbital with two sets of non-equivalent bonds is given by gaseous phosphorus pentachloride in which the two co-axial $3p3d$ bonds are longer than the three $3s3p^2$ bonds in the plane. These ideas will be elaborated in a forthcoming [14] paper dealing with the crystal structure of $[Au(as)_2I_2]I$.

In connection with this stabilisation of tervalent gold when tervalent arsenic is in the ligand it is of interest that Mann and Purdie [22] have shown that two-covalent gold(I) complexes of the type $Et_3P\rightarrow AuCl$ may also be oxidised to tervalent gold derivatives. They have shown that the univalent complexes take up a molecule of bromine or iodine to give four-covalent molecules of the type $[Et_3P\rightarrow AuCl(Hal)_2]^0$. The crystal structure of the trimethylphosphine complex $[Me_3P\rightarrow AuBr_3]^0$ reveals that the arrangement round the gold is square-planar,[23] as expected for $5d6s6p^2$ bonds.

Rundle [24] has recently examined the structure of the gold complex $[Au^{III}(DMG)_2]$ $[Au^{I}Cl_2]$ (where DMG = dimethylglyoxime) and shown that the gold(III) atom is square-co-ordinated with the two chelate groups. The packing in the crystal is such, however, that there are linear gold chains with Au–Au 3·26 Å. The chains contain alternate gold(I) and gold(III) atoms and the configuration around the gold(III) atom is octahedral, metal bonds being included. It has been postulated that these weak metal bonds arise from the presence of a vacant p orbital on the gold atom (Rundle [24] and references quoted by him). The configuration about the gold(I) atom is square-planar, the two weak metal bonds being included which are also thought to result from the presence of vacant p orbitals on the gold(I) atoms.

EXPERIMENTAL

Yields quoted refer to vacuum-dried material.

*Di-(*o*-phenylenebisdimethylarsine)gold*(I) *Bromide.*—A solution of sodium tetrachloroaurate dihydrate (0·20 g.) in ethanol (5 ml.) was added with stirring to *o*-phenylenebis(dimethylarsine) (0·31 g.) in alcohol (10 ml.) containing 30% hypophosphorous acid (2·5 ml.). The light yellow precipitate that momentarily appeared dissolved to a red solution which rapidly became colourless. Towards the end of the addition, the red colour of the solution persisted. The solution was boiled for a few minutes and on filtration was colourless. It was treated with 7N-hydrobromic acid (5 ml.) followed by water (15 ml.) and to the turbid solution ammonium bromide (2 g.) in water (20 ml.) was added. After standing, the white crystalline *compound* which was deposited was filtered off and washed with water and ether (yield 0·28 g.) [Found: C, 27·9; H, 4·0; Au, 22·9%; *M* (cryoscopic, 0·19% in nitrobenzene), 530. $C_{20}H_{32}BrAs_4Au$ requires C, 28·3; H, 3·8; Au, 23·2%; *M*, 850]. The compound melted at 201° with the deposition of metallic gold. It is readily soluble in acetone, soluble in nitrobenzene, and can be recrystallised from ethanol and boiling water.

*Di-(*o*-phenylenebisdimethylarsine)gold*(I) *Iodide.*—The diarsine (0·70 g.) and 30% hypophosphorous acid (2 ml.) in alcohol (10 ml.) were treated with sodium tetrachloroaurate dihydrate (0·40 g.) in ethanol (5 ml.), as above, and the mixture was boiled and filtered. The colourless filtrate was diluted with water (10 ml.) and heated to boiling, sodium iodide (1·0 g.) in alcohol (15 ml.) being then slowly added with stirring. The white crystalline complex was

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[22] Mann and Purdie, *J.*, 1940, 1235.
[23] Perutz and Weiss, *J.*, 1946, 438.
[24] Rundle, *J. Amer. Chem. Soc.*, 1954, **76**, 3101.

washed with cold water by decantation, and recrystallised from ethanol (yield 0·58 g.) (Found : C, 26·6; H, 3·5; Au, 22·1. $C_{20}H_{32}IAs_4Au$ requires C, 26·8; H, 3·6; Au, 22·0%). The compound is sparingly soluble in cold ethanol, nitrobenzene, and boiling water.

Di-(o-*phenylenebisdimethylarsine*)*gold*(I) *Perchlorate.*—This compound was obtained by treating hot alcoholic solutions of the previous compounds with 60% perchloric acid. The white crystalline *salt* was washed and dried as before (Found : C, 27·6; H, 3·8; Au, 22·8. $C_{20}H_{32}IAs_4Au$ requires C, 27·6; H, 3·7; Au, 22·6%); it is slightly soluble in ethanol and nitrobenzene.

Di-(o-*phenylenebisdimethylarsine*)*gold*(I) *Picrate.*—A solution of the previous bromide (0·10 g.) in hot water (50 ml.) was treated with a hot solution (10 ml.) of picric acid (0·03 g.). A yellow precipitate was formed at once. The mixture was kept warm until the precipitate had coagulated and settled, then the *compound* was filtered off and washed with warm water and dry ether (yield 0·10 g.) (Found : C, 31·4; H, 3·5; N, 4·3. $C_{26}H_{35}O_7N_3As_4Au$ requires C, 31·3; H, 3·55; N, 4·2%) ; it dissolves in ethanol, acetone, and chloroform to yellow solutions.

Di-(o-*phenylenebisdimethylarsine*)*gold*(I) *Di-iodoaurate*(I).—A solution of the iodide, $[Au(as)_2]I$ (0·090 g.), in hot ethanol (5·0 ml.) was treated with gold(I) iodide (0·050 g.) dissolved in a hot alcoholic solution (5 ml.) of sodium iodide (1·0 g.). The slight yellow colour of this solution was discharged by the dropwise addition of 0·1N-sodium thiosulphate, and any gold was filtered off. The warm mixture of the two solutions deposited white crystals when stirred. The solution was cooled to room temperature and the filtered *compound* was washed with cold ethanol and dry ether (yield 0·1 g.) (Found: C, 19·8; H, 2·5. $C_{20}H_{32}I_2As_4Au_2$ requires: C, 19·7; H, 2·6%). The compound was very sparingly soluble in nitrobenzene.

Di-(o-*phenylenebisdimethylarsine*)*gold*(I) *Di-iodocuprate.*—Colourless crystals of this *compound* were obtained by treating the iodide $[Au(as)_2]I$ with copper(I) iodide and sodium iodide as in the previous preparation (Found : C, 22·3; H, 3·0. $C_{20}H_{32}I_2As_4AuCu$ requires C, 22·1; H, 3·0%). This compound was very sparingly soluble in nitrobenzene.

Di-(o-*phenylenebisdimethylarsine*)*gold*(III) *Perchlorate.*—A solution of sodium tetrachloroaurate dihydrate (0·80 g.) in ethyl alcohol (20 ml.) was treated all at once with a solution of *o*-phenylenebisdimethylarsine (1·14 g.) in alcohol (40 ml.). The yellow solution was filtered from sodium chloride into 72% perchloric acid (10 ml.), and the cream microcrystalline *salt* was filtered off and washed with alcohol, cold water, and hot acetone (yield 1·14 g.) (Found: C, 22·4; H, 3·2; Au, 18·5. $C_{20}H_{32}O_{12}Cl_3As_4Au$ requires C, 22·5; H, 3·0; Au, 18·4%). The gram susceptibility of this compound (χ_g) is $-0{\cdot}07 \times 10^{-6}$ at 19°, whence $\mu = 0$.

Di-(o-*phenylenebisdimethylarsine*)*di-iodogold*(III) *Iodide.*—This compound was prepared directly from sodium tetrachloroaurate or by oxidation of the univalent gold compound $[Au(as)_2]I$.

(a) *Direct preparation.* Sodium tetrachloroaurate(III) dihydrate (0·20 g.) in ethanol (5·0 ml.) was added all at once to *o*-phenylenebisdimethylarsine (0·31 g.) in ethanol (10·0 ml.). The resulting orange-red solution was filtered into a hot aqueous-alcoholic (1 : 1) solution (10 ml.) containing sodium iodide (2·5 g.). A red crystalline iodide was deposited. The mixture was heated on the water-bath for some time, then filtered, and the *salt* washed with ethanol followed by ether (yield 0·47 g.) (Found : C, 20·8; H, 2·7; I, 32·6; Au, 16·9. $C_{20}H_{32}I_3As_4Au$ requires C, 20·9; H, 2·8; I, 33·1; Au, 17·15%). This compound is very sparingly soluble in nitrobenzene.

(b) *Iodine oxidation.* A boiling solution of di-(*o*-phenylenebisdimethymethylarsine)gold(I) iodide (0·18 g.) in absolute alcohol (10·0 ml.) was treated slowly with stirring with iodine (0·060 g.) in hot ethanol (5·0 ml.). The buff microcrystalline compound was filtered off from the warm solution and washed with warm ethanol and ether (yield 0·21 g.) (Found: C, 21·0; H, 2·7; I, 32·6%). The compound is diamagnetic.

The compounds obtained by these two methods are identical in nitrobenzene solution (see Fig. 1) and in the solid state. The latter similarity was shown by the identical diffraction patterns, registered with a Norelco self-recording Geiger spectrometer (these compounds were kindly measured for us by Mr. J. F. McConnell, M.Sc., of the School of Applied Physics, N.S.W. University of Technology).

Di-(o-*phenylenebisdimethylarsine*)*iodogold*(III) *Perchlorate.*—The gold(III) iodide complex $[Au(as)_2I_2]I$ was boiled with water (200 ml.), and the yellow solution was filtered off from the small amount of suspended matter resulting from partial decomposition. On addition of an excess of 72% perchloric acid a flocculent red *product* was deposited immediately; it was washed with cold water, acetone, and ether (yield 0·034 g.) (Found : C, 22·1; H, 3·04; I, 11·3; Cl, 6·7. $C_{20}H_{32}O_8Cl_2As_4Au$ requires C, 21·9; H, 2·95; I, 11·6; Cl, 6·5%) and is very sparingly soluble in nitrobenzene.

Di-(o*-phenylenebisdimethylarsine*)*di-iodogold*(III) *Perchlorate.*—A boiling solution of di-(*o*-phenylenebisdimethylarsine)gold(I) perchlorate (0·44 g.) in boling absolute·alcohol (150 ml.) was treated with iodine (0·12 g.) in boiling alcohol (35 ml.) with stirring. The reddish-brown *compound* which was deposited was filtered off and washed with hot alcohol and acetone (yield 0·45 g.) (Found: C, 21·6; H, 3·05; I, 23·2; Cl, 3·1. $C_{20}H_{32}O_4ClI_2As_4Au$ requires C, 21·4; H, 2·9; I, 22·6; Cl, 3·15%).

Di-(o*-phenylenebisdimethylarsine*)*dibromogold*(III) *Perchlorate.*—A boiling solution of di-(*o*-phenylenebisdimethylarsine)gold(I) perchlorate (0·87 g.) in boiling chloroform (300 ml.) was treated dropwise with stirring with 12·5 ml. of a carbon tetrachloride solution of bromine (0·88 g./100 ml.). The yellow precipitate was filtered from the hot solution and washed with chloroform and acetone (yield 0·38 g.) (Found: C, 23·2; H, 3·2; Br, 15·4; Cl, 3·4. $C_{20}H_{32}O_4ClBr_2As_4Au$ requires C, 23·35; H, 3·1; Br, 15·5; Cl, 3·4%). The *compound* was not sufficiently soluble in nitrobenzene for conductivity measurements.

Di-(o*-phenylenebisdimethylarsine*)*gold*(III) *Nitrate.*—A solution of silver nitrate (0·24 g.) in absolute alcohol (300 ml.) was refluxed with $[Au(as)_2I_2]I$ (0·46 g.) for some minutes, then filtered, and the colourless filtrate was cooled in ice. The crystals deposited on storage were washed with ethanol and acetone (yield 0·20 g.) (Found: C, 24·5; H, 3·3; N, 4·0; Au, 20·7. $C_{20}H_{32}O_9N_3As_4Au$ requires C, 25·1; H, 3·4; N, 4·4; Au, 20·6%). The *compound* becomes purplish, presumably owing to some decomposition to gold. It is very sparingly soluble in nitrobenzene. A sufficient concentration for conductivity measurements (see Table 1) was obtained by dissolving 2·8 mg. in 10·0 ml. of hot nitrobenzene by vigorous shaking for 15 min. This compound is soluble in cold water in which it functions as a tri-univalent electrolyte (Λ_M = 428 mho at 25°, 2·73 × 10^{-4}M). Hence in water all three NO_3^- groups are ionised.

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DEPARTMENT OF INORGANIC CHEMISTRY, SCHOOL OF APPLIED CHEMISTRY,
N.S.W. UNIVERSITY OF TECHNOLOGY, SYDNEY, AUSTRALIA.
WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET, LONDON.

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