230. *The Constitution of Complex Metallic Salts. Part XIII. The Stability of the 4-Covalent Auric Complex.*

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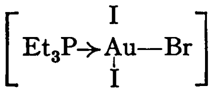
2-Covalent aurous compounds such as $[Et_3P \rightarrow AuBr]$ combine readily with a further molecule of halogen to give 4-covalent auric compounds such as $[Et_3P \rightarrow AuBr_3]$, which should have the uniplanar configuration. If the two halogen atoms enter the *trans*-position in the linear aurous molecule, two isomeric forms of a compound such as $[Et_3P \rightarrow AuBrI_2]$ should be obtained by (*a*) the addition of iodine to $[Et_3P \rightarrow AuBr]$, (*b*) the addition of iodine monobromide to $[Et_3P \rightarrow AuI]$. Several such dual preparations have been made, but each pair gave only one compound. It is concluded that the groups around the 4-covalent gold have considerable mobility, and only the more stable isomeride occurs; in this respect the 4-covalent auric complex resembles the 4-covalent palladous complex.

EVIDENCE for the configuration of the gold complexes in all the known valency states of the metal has been obtained during recent years. The 2-covalent aurous complex is linear: considerable (although not decisive) evidence for this configuration in $[Et_3P \rightarrow AuX]$ and $[Et_3As \rightarrow AuX]$, where $X = Cl$ and I, was obtained by Mann, Wells, and Purdie (J., 1937, 1828). The 4-covalent aurous complex, present in the αα'-dipyridyl and the phenanthroline compound, $K[Au(CN)_2dipy]$ and $K[Au(CN)_2,C_{12}H_8N_2]$, has been shown by Dothie, Llewellyn, Wardlaw, and Welch (J., 1939, 426) to be uniplanar. The 4-covalent auric complex, present in the bridged compound $[Et_2AuBr_2AuEt_2]$, has also been shown to be uniplanar by Burawoy, Gibson, Hampson, and Powell (J., 1937, 1690). Confirmation of the above results for the 2-covalent aurous and the 4-covalent auric complexes has been obtained by Elliott and Pauling (*J. Amer. Chem. Soc.*, 1938, **60**, 1846) by an investigation of the black crystals of cæsium aurous auric chloride, $Cs_2Au_2Cl_6$, which consists essentially of molecules of $Cs[AuCl_2]$ and $Cs[AuCl_4]$, in which the complex ions have the linear and the planar configuration respectively.

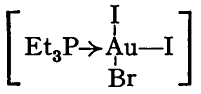
All the above results were obtained by *X*-ray crystal analysis. We have now attempted to obtain chemical evidence for the uniplanar configuration of the 4-covalent auric complex. It is known that phosphine compounds such as $[Et_3P \rightarrow AuBr]$ are extremely stable and can be distilled at low pressures (Mann, Wells, and Purdie, *loc. cit.*); we now find that these compounds readily combine with halogens at room temperature to form the corresponding auric derivatives, *e.g.*, *tribromo(triethylphosphine)gold*, $[Et_3P \rightarrow AuBr_3]$. These compounds crystallise excellently, have sharp m. p.'s, and are soluble in many organic solvents, in which their molecular weights, so far as they have been determined, are normal. Some of them possess great stability (see later).

The aurous compounds also combine readily with mixed halogens, such as iodine monochloride and monobromide, and it will be seen that, if the additional halogen atoms enter the *trans*-position in the linear aurous complex, *cis-trans*-isomeric forms of the resulting auric derivative should arise. For instance, if 1 mol. of iodine is added to $[Et_3P\rightarrow AuBr]$, the bromo-*trans*-di-iodo(triethylphosphine)gold (I) should result; if, however, iodine monobromide is added to $[Et_3P\rightarrow AuI]$, the *cis*-isomer (II) should be formed. We find, however, that the products from these two reactions are identical. The following mixed halogen derivatives have also been prepared in two ways :



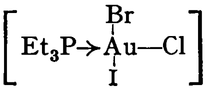
$$\left[Et_3P\rightarrow \overset{I}{\underset{I}{Au}}—Br\right]$$

(I.)



$$\left[Et_3P\rightarrow \overset{I}{\underset{Br}{Au}}—I\right]$$

(II.)



$$\left[Et_3P\rightarrow \overset{Br}{\underset{I}{Au}}—Cl\right]$$

(III.)

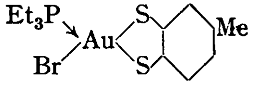
$[Et_3P\rightarrow AuClI_2]$ from (*a*) $[Et_3P\rightarrow AuCl] + I_2$ and (*b*) $[Et_3P\rightarrow AuI] + ICl$
$[Et_3P\rightarrow AuICl_2]$ from (*a*) $[Et_3P\rightarrow AuI] + Cl_2$ and (*b*) $[Et_3P\rightarrow AuCl] + ICl$
$[Et_3P\rightarrow AuIBr_2]$ from (*a*) $[Et_3P\rightarrow AuI] + Br_2$ and (*b*) $[Et_3P\rightarrow AuBr] + IBr$

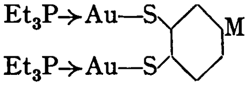
Again, each pair of reactions gave identical products. We have also prepared the *chlorobromoiodo*-compound (III) from (*a*) $[Et_3P\rightarrow AuCl]$ and BrI and (*b*) $[Et_3P\rightarrow AuBr]$ and ICl : this compound could theoretically exist in three isomeric forms, but only one was obtained. As cyanogen bromide would not combine with the aurous compounds, the possibility of isomeric compounds of type $[Et_3P\rightarrow AuBr_2(CN)]$ could not be investigated.

This apparent non-existence of *cis-trans*-isomerides of type (I) and (II) may be due to one of two causes. These trihalide compounds may have the tetrahedral configuration and thus be quite distinct from the auric compound investigated by Gibson and his co-workers (*loc. cit.*). It is, however, very unlikely that such a radical difference should exist, and an *X*-ray investigation of these phosphine compounds will be made to decide their configuration when circumstances permit. Alternatively, it is more probable that, whilst the auric complex maintains a uniplanar configuration, the groups joined to the metal have a certain mobility and thus adopt the most stable orientation around the metallic atom.* In this case, the less stable of the *cis-trans*-isomerides, if formed at all, would rapidly pass over into the more stable form. A precisely similar position occurs with the 4-covalent palladium complex, where compounds of the type $[a_2Pd\,b_2]$ exist almost invariably only in the more stable *trans*-form. Even when two forms can be isolated, as in $[(NH_3)_2Pd(NO_2)_2]$ (Mann, Crowfoot, Gattiker, and Wooster, J., 1935, 1642), one form readily passes over into the other—an apparently irreversible change. If the non-existence of two forms of, *e.g.*, the bromodi-iodo-compound is due to the ready conversion of the less into the more stable form, it is probable that the latter is the symmetric form (I). We have sought chemical evidence for this by treating the compound with sodium oxalate (1 mol.) ; if two *cis*-halogen atoms had been replaced by the oxalate group (a common reaction with complex palladium and platinum compounds), the compound (I) could give only one derivative, the iodo-oxalate, whereas (II) could give two derivatives, the bromo- and the iodo-oxalate. These experiments failed, however, as sodium oxalate did not react at room temperature and caused considerable reduction at higher temperatures.

It is clear, however, that interconversion of the two possible isomerides might be considerably suppressed by the use of a suitable chelate group. We have therefore treated tribromo(triethylphosphine)gold with 1 mol. of the disodium salt of toluene-3 : 4-dithiol, in order to prepare the compound (IV), which should also exist in *cis-trans*-forms. The product proved, however, to be amorphous and insoluble in all the usual solvents. In

(IV.)





(V.)

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* It should be emphasised, moreover, that in this case only one compound would ultimately be formed, irrespective of the mode of addition of the halogen molecule to the aurous complex.

these properties it is in marked contrast to the colourless crystalline aurous compound, *toluene*-3 : 4-*bis*(*thiotriethylphosphinegold*) (V), readily prepared by the action of the sodium salt of the dithiol on 2 mols. of the compound $[Et_3P\rightarrow AuCl]$, and which was readily soluble in several solvents. In view of the difficulty in preparing suitable chelated auric derivatives of type (IV), however, work on these lines has been temporarily abandoned.

The above trihalogeno(triethylphosphine)gold compounds form a complete and unique series of fusible non-ionic complex compounds and their properties are therefore summarised in the following table, in which R represents the co-ordinated Et_3P molecule.

	M. p.	Colour.
(1) $[RAuCl_3]$	121°	Pale yellow needles
(2) $[RAuCl_2Br]$	119—120	Golden needles
(3) $[RAuClBr_2]$	128—129	Dark orange needles
(4) $[RAuBr_3]$	129	Deep red needles
(5) $[RAuCl_2I]$	105—106	Purple-brown plates
(6) $[RAuClBrI]$	107—108	Black needles
(7) $[RAuBr_2I]$	109	Brownish-black needles
(8) $[RAuClI_2]$	94—95	Black needles and plates
(9) $[RAuBrI_2]$	90—91	Black needles and plates
(10) $[RAuI_3]$	77	Black needles

The comparative stability of the above compounds is of great interest. The *trichloro*-compound (1) decomposes within a few days on standing at room temperature, even if kept in the dark, with deposition of gold; the *dichloro*-compounds (2) and (5) also decompose on standing, but not so rapidly. The *tri-iodo*-compound (10) decomposes to a black liquid mass within a few weeks if kept at room temperature in the dark, and the *di-iodo*-compounds (8) and (9) similarly decompose on standing for a few months. All the remaining compounds are stable indefinitely under these conditions. It is noteworthy that the gold content of all these auric compounds can be accurately determined by direct ignition; this proves that the first stage of thermal decomposition is not loss of two halogen atoms with formation of the corresponding aurous compound, since the latter would then undergo considerable volatilisation and a low value for gold would result. The auric compounds can, however, be reduced smoothly to the corresponding aurous compounds by passing sulphur dioxide into their alcoholic solutions even at room temperature. In these circumstances, the compound (4) gave [RAuBr], and the compound (5) gave [RAuI]. Similarly, the compound (6) on treatment with cold acetone was reduced also to [RAuI]. These results indicate that the more electronegative halogen atoms are preferentially removed from the complex by both reducing agents.

The introduction of acid radicals other than halides into the auric molecule has proved very difficult. Attempts to prepare the compound $[Et_3P\rightarrow AuBr_2NO_2]$ by the action of aqueous-alcoholic sodium nitrite on the tribromo-compound failed, as reduction to metallic gold readily ensued. Indirect attempts to prepare this compound by the formation of $[Et_3P\rightarrow AuNO_2]$ and subsequent addition of bromine also failed, as the aurous compounds, *e.g.*, $[Et_3P\rightarrow AuBr]$, proved surprisingly resistant to the action of sodium nitrite, and prolonged heating ultimately gave only reduction to gold.

EXPERIMENTAL.

The names of solvents used for recrystallisation are given in parentheses after the compounds concerned. All molecular weights were determined cryoscopically in ethylene dibromide solution.

The following two aurous compounds are new: *Monobromo*(*trimethylphosphine*)*gold*. An aqueous solution of chloroauric acid was diluted with a saturated solution of potassium bromide (6 mols.) and the mixture cooled in ice-water and diluted with a few c.c. of alcohol. A stream of trimethylphosphine, generated by the thermal decomposition of $[Me_3P,AgI]_4$, was passed into the cooled and gently shaken mixture until the latter had developed a pale reddish-brown colour. The mixture was set aside overnight, and the colour had then disappeared and the white *monobromo*-compound separated. It was collected, washed with water, dried, and obtained as fine crystals (acetone), m. p. 225° (partial decomp.) (Found: C, 10·3; H, 2·7. C_3H_9BrPAu requires C, 10·2; H, 2·55%). The compound can be recrystallised from a large volume of boiling alcohol.

Monobromo(triethylphosphine)gold. Similarly prepared from an alcoholic solution of triethylphosphine, the reaction being complete after *ca.* 1 hour's standing, this *compound* can be recrystallised from alcohol, or by diluting a hot solution in benzene with *cyclo*hexane and allowing the mixture to cool slowly; colourless crystals, m. p. 87° (Found: C, 18·2; H, 3·8. $C_6H_{15}BrPAu$ requires C, 18·2; H, 3·4%). (The m. p. of $[Et_3P \rightarrow AuCl]$, previously given as 78°, has now been found to be 84—85°.)

The Auric Compounds.—These were all prepared in the same way, and a general description suffices for all. A cold solution of the corresponding aurous compound in chloroform was treated with a solution of the requisite halogen, simple or mixed (1 mol.), dissolved in chloroform or carbon tetrachloride. Combination to form the auric compound was rapid. If only chloroform had been used, the auric compound remained at first in solution, and, on spontaneous evaporation of the solvent, separated ultimately in large crystals. If, however, much carbon tetrachloride had been used, the auric compound crystallised rapidly from the mixed solvents, and the initial separation of the crystals was thus dependent on the relative proportion of solvents used.

Tribromo(trimethylphosphine)gold. This *compound* was much less soluble than the following ethyl compounds and separated rapidly even from pure chloroform solutions; beautiful orange-red crystals (chloroform or benzene), m. p. 162° (Found: C, 7·05; H, 1·6. $C_3H_9Br_3PAu$ requires C, 7·0; H, 1·75%).

Trichloro(triethylphosphine)gold, pale yellow needles (alcohol), m. p. 121° (Found: H, 3·5; Au, 46·9. $C_6H_{15}Cl_3PAu$ requires H, 3·6; Au, 46·8%. Low and variable carbon values were always obtained), is easily soluble in acetone and chloroform, and sparingly soluble in alcohol and carbon tetrachloride. The *dichlorobromo*-compound, golden needles (alcohol), m. p. 119—120° (Found: C, 15·15; H, 3·3; Au, 42·2. $C_6H_{15}Cl_2BrPAu$ requires C, 15·45; H, 3·2; Au, 42·3%). The *chlorodibromo*-compound, dark orange needles (alcohol), m. p. 128—129° (Found: C, 14·3; H, 3·1; Au, 38·5. $C_6H_{15}ClBr_2PAu$ requires C, 14·1; H, 3·0; Au, 38·6%). The *tribromo*-compound, deep red needles (alcohol or benzene), m. p. 129° (Found: C, 13·05; H, 2·5; *M*, in 0·628% solution, 594; in 1·000% solution, 613. $C_6H_{15}Br_3PAu$ requires C, 13·0; H, 2·7%; *M*, 555).

The *dichloroiodo*-compound formed dark purple-brown plates (alcohol), m. p. 105—106° (Found: H, 2·8, 3·1; Au, 38·4, 38·5. $C_6H_{15}Cl_2IPAu$ requires H, 2·9; Au, 38·4%. Consistent carbon values could not be obtained, but the duplicate analyses identify the compound). Alternative methods of preparation are given: (*a*) A 1% (wt./vol.) solution of chlorine in carbon tetrachloride (7·0 c.c.; *i.e.*, 1 mol. of Cl_2) was added to a solution of $(Et_3P \rightarrow AuI]$ (0·44 g.) in chloroform (5 c.c.), the mixture immediately becoming dark brown and all odour of chlorine disappearing. Crystals of the dichloroiodo-compound separated and were purified as indicated above. (*b*) A 5% (wt./vol.) solution of iodine monochloride in carbon tetrachloride (6·44 c.c.; 1 mol. of ICl) was added to a solution of $[Et_3P \rightarrow AuCl]$ (0·70 g.) in chloroform (5 c.c.). The solution behaved precisely as in (*a*), and the crystals had the same m. p., either alone or when mixed with the (*a*) crystals. In all these dual preparations, the m. p. of the initial crystals which separated spontaneously at room temperature from the mother-liquor was always determined before and after recrystallisation, and was seldom changed by this process. No question of an undetected conversion of a less into a more stable isomeride during recrystallisation could therefore arise.

The *chlorobromoiodo*-compound, obtained by two methods, formed black needles (alcohol), m. p. 107—108° (Found: C, 12·6; H, 2·8; Au, 35·4; *M*, in 0·782% solution, 543. $C_6H_{15}ClBrIPAu$ requires C, 12·9; H, 2·8; Au, 35·3%; *M*, 557·5). The *dibromoiodo*-compound, brownish-black needles (alcohol), m. p. 109° (Found: C, 12·1; H, 2·7; Au, 32·8; *M*, in 0·764% solution, 631. $C_6H_{15}Br_2IPAu$ requires C, 12·0; H, 2·5; Au, 32·8%; *M*, 602). The *chlorodi-iodo*-compound, obtained by two methods, black needles or plates having a green surface reflection (alcohol), m. p. 94—95° (Found: C, 12·0; H, 2·7; Au, 32·9. $C_6H_{15}ClI_2PAu$ requires C, 11·9; H, 2·5; Au, 32·6%). The *bromodi-iodo*-compound, obtained by two methods, black needles (alcohol), m. p. 90—91° (Found: C, 10·9; H, 2·1; Au, 30·0. $C_6H_{15}BrI_2PAu$ requires C, 11·1; H, 2·3; Au, 30·4%). The *tri-iodo*-compound, black needles (alcohol), m. p. 77° (Found: C, 10·05; H, 1·9. $C_6H_{15}I_3PAu$ requires C, 10·35; H, 2·15%).

*Chlorodibromo(tri-*n*-propylphosphine)gold,* similarly prepared by the addition of bromine to $[Pr_3P \rightarrow AuCl]$, formed deep orange leaflets (alcohol), m. p. 145° (Found: C, 19·6; H, 3·9; Au, 35·8; *M*, in 0·697% solution, 588. $C_9H_{21}ClBr_2PAu$ requires C, 19·5; H, 3·8; Au, 35·7%; *M*, 553).

Toluene-3 : 4-bis(thiotriethylphosphinegold) (V). A solution of $[Et_3P \rightarrow AuCl]$ (0·582 g., 2 mols.) in warm alcohol (15 c.c.) was added rapidly to a solution of the dithiol (0·129 g., 1 mol.) in alcohol (10 c.c.) to which a standard alcoholic solution of sodium ethoxide (2 mols.) had been added. The mixture was boiled gently for 1 minute, cooled, a small precipitate removed, and the filtrate taken to dryness in a desiccator. Large colourless plates formed as the evaporation proceeded. These were collected, washed with water, and twice recrystallised from alcohol. The above *compound* was thus obtained as colourless crystals, m. p. 124—125° (Found: C, 28·4; H, 4·4; Au, 50·8. $C_{18}H_{36}S_2P_2Au_2$ requires C, 29·0; H, 4·6; Au, 50·3%).

When the tribromo-auric compound was similarly treated with the disodium salt of the dithiol (1 mol.), both in cold alcoholic solution, the mixture became turbid, and a yellowish-green amorphous precipitate was formed. This was collected and washed with alcohol and water, but could not be purified owing to its minute solubility in all solvents tried.

Reduction.—(1) *With sulphur dioxide.* (*a*) An aqueous solution of sulphur dioxide was added with shaking to a solution of the tribromo-compound (0·5 g.) in warm alcohol (25 c.c.) until the mixture was colourless. On cooling, or on dilution with water, white needles of the monobromoaurous compound, m. p. 87°, separated. (*b*) A suspension of the dichloroiodo-compound (0·3 g.) in alcohol (25 c.c.) was similarly treated at room temperature until the solution was colourless. Dilution with water gave the monoiodo-aurous compound, m. p. 67—69°.

(2) *With acetone.* A solution of the chlorobromoiodo-compound (0·2 g.) in acetone (5 c.c.) was set aside for 24 hours, and had then become almost colourless. It was poured into water, and the precipitated monoiodo-aurous compound, when collected and recrystallised (alcohol), had m. p. 67—69°.

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