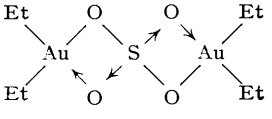
## 647. *The Organic Compounds of Gold. Part XIII. Some Dialkylgold Compounds containing Phosphorus and Arsenic.*

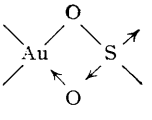
By M. E. Foss and C. S. Gibson.

The diethylgold derivatives of phenyl phosphates and phenylarsonic acid have been prepared, and found to resemble the previously fully described tetraethylsulphatodigold (*J.*, 1941, 102, 109). The constitution of these derivatives and of diethyl(diphenyl phosphato)gold is in keeping with the known instability of four-membered rings containing a large gold atom and three smaller atoms. On account of their sparing solubility, the structure of the tri(dialkylgold) phosphates could not be ascertained, but it is probable that they are polymers.

One of the results emerging from the study of dialkylgold derivatives of dibasic acids (Part VIII, *J.*, 1941, 102; Part IX, *J.*, 1941, 109) was the apparent instability of four-membered rings containing one large gold atom and three smaller atoms. Thus, it was found that tetraethylsulphatodigold did not assume the form (I), but had a molecular weight requiring four gold atoms per molecule, in which the co-ordinate link to each univalent $Et_2Au$ group is provided by an oxygen in a sulphate group other than the sulphate group involved in the formation of the covalent link. The most probable structure, deduced by Ewens and Gibson (Part IX), is represented diagrammatically in (III).




(I.)

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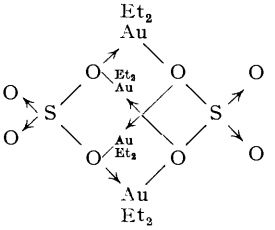
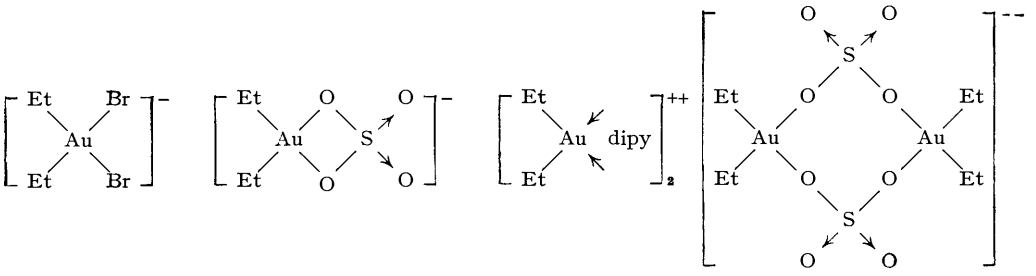



(III.)

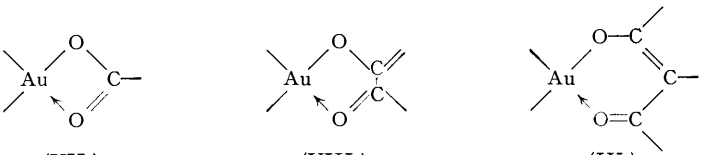
Further evidence in support of this formulation of tetraethylsulphatodigold, and of the instability of the ring system (II), was obtained by an investigation of the dipyridyl complex of (III). It has recently been shown (Foss and Gibson, Part XII, this vol., p. 3063) that this complex is a salt (cf. Gibson and Weller, Part VIII) which gives rise to three ions in nitrobenzene



(IV.) (V.) (VI.)

solution. Hence the anion corresponding to (IV), found in certain diamine complexes of diethylbromogold, is not (V) as one might at first suppose, but the tetraethyl-μ-disulphatodiaurate anion of (VI). In water, the gold–oxygen links of both (III) and (VI) are broken, with the formation of diaquodiethylauric ions and sulphate ions.

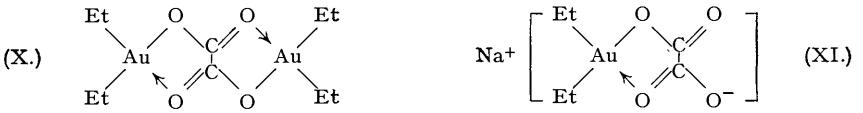
Similarly, in the dialkylgold derivatives of the dicarboxylic acids, four-membered rings of the type (VII) are not possible, and the co-ordinate link is provided by an oxygen from a second carboxyl group. In tetraethyloxalatodigold (X) and sodium diethyloxalatoaurate (XI), this is achieved by the formation of a five-membered ring (VIII). The six-membered



(VII.) (VIII.) (IX.)

ring system (IX) also is known to exist in the compound diethylgoldacetylacetone (Part I, *J.*, 1930, 2531).

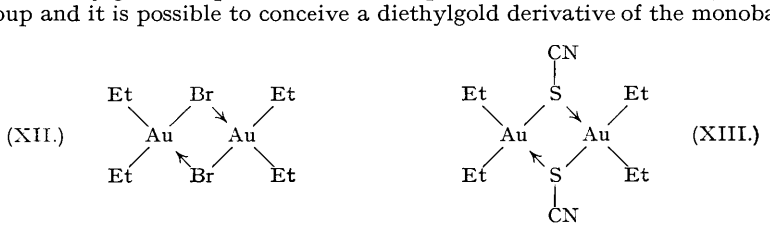
In all the systems (II), (VII), (VIII), and (IX), there is the possibility of resonance within the ring, but the formation of the four-membered rings (II) and (VII) requires considerable deviation from the natural valency angles of the constituent atoms. By contrast, the four-membered



(X.) (XI.)

rings in diethylbromogold (XII) and diethylthiocyanatogold (XIII) consisting of two large gold atoms bridged by halogen and sulphur atoms, respectively, are stable.

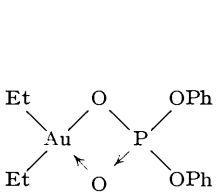
Gent and Gibson (Part XI, this vol., p. 1835) observed that the number of gold atoms in a molecule of a dialkylgold compound seems to depend on the co-ordinating direction of the negative group and it is possible to conceive a diethylgold derivative of the monobasic diphenyl



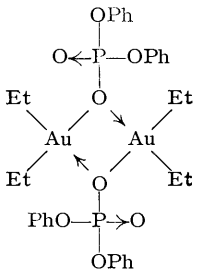
(XII.) (XIII.)

hydrogen phosphate, having the constitution (XIV). Bearing in mind, however, that the sulphate and phosphate groups are stereochemically similar, and the S–O and P–O bonds have approximately the same magnitude (see Pauling, " Nature of the Chemical Bond," 1940, p. 240), such a formulation is unlikely. In confirmation of this, *diethyl(diphenyl phosphato)gold* was

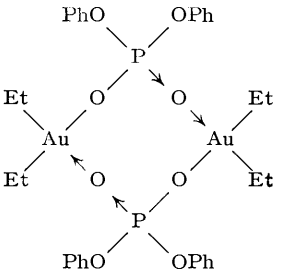
prepared by shaking diethylbromogold with silver diphenyl phosphate, and a cryoscopic determination of the molecular weight in benzene showed the compound to be dimeric. Of the



(XIV.)



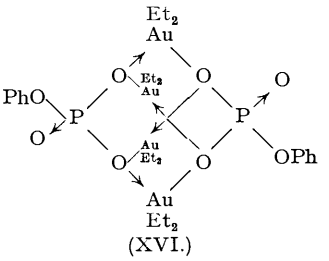
(XV*a*.)



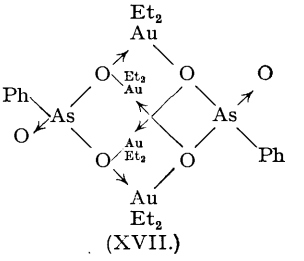
(XV*b*.)

two possible formulæ (XV*a*) and (XV*b*), the latter is preferable, since it contains an eight-membered ring similar to that already known to exist in (VI).

The colourless crystalline compound obtained by the interaction of the disilver phenyl phosphate and diethylbromogold has a molecular weight in benzene indicating four gold atoms per molecule, and, by analogy with tetraethylsulphatodigold (III), is described as *tetraethyl(monophenyl phosphato)digold* (XVI). In this molecule the four gold atoms form a square lying in a vertical plane, and the phenyl phosphate groups are oriented so that their planes of symmetry are mutually at right angles. The molecule as a whole, therefore, possesses no plane or centre of symmetry. The same is true of *tetraethylphenylarsonatodigold* (XVII) which was prepared from silver phenylarsonate and diethylbromogold. These two compounds serve as models for similar compounds containing potential diastereoisomeric-salt-forming groups.



(XVI.)



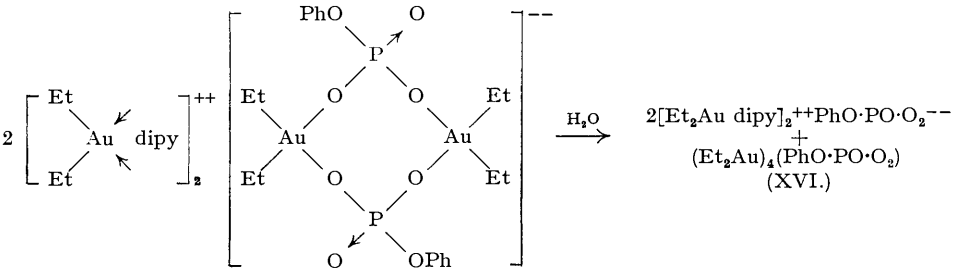
(XVII.)

The dipyridyl complexes of (XVI) and (XVII) resemble (VI), and may be named 2 : 2′-*dipyridyldiethylauric tetraethyl-μ-bis(monophenyl phosphato)diaurate* (XVIII), and 2 : 2′-*dipyridyldiethylauric tetraethyl-μ-bis(phenylarsonato)diaurate* (XIX). In water the large anions disrupt to give phenyl phosphate and phenylarsonate ions, with the simultaneous separation of the parent compounds (XVI) and (XVII), which unlike tetraethylsulphatodigold are sparingly soluble. 2 : 2′-Dipyridyldiethylauric ions may be precipitated from the resulting aqueous solutions, either as the picrate (see Part XII) or as the *dichromate*.

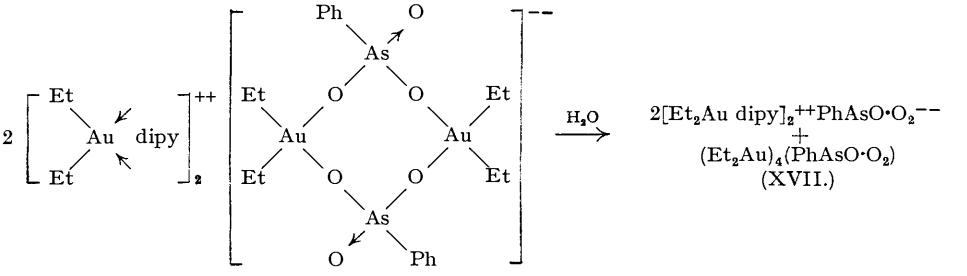
In extending the series of dialkylgold compounds to derivatives of the tribasic phosphoric acid, it was considered that such compounds might also possess interesting structural features. Clearly they cannot be simply $(R_2Au)_3PO_4$, which is formulated only by introducing inadmissible four-membered rings comprised of a large gold atom, two oxygen atoms, and the phosphorus atom. However, both *tri(diethylgold) phosphate* and *tri(di-*n*-butylgold) phosphate*, prepared from the appropriate dialkylbromogold compounds and silver orthophosphate, proved to be very sparingly soluble in all the usual solvents, whether hot or cold, with the exception of boiling methanol and ethanol. A cryoscopic determination of the molecular weight was therefore ruled out, and the boiling-point method was also impracticable since the elevation to be expected even for $(R_2Au)_3PO_4$ is too small for accurate measurement.

It is likely that the sparing solubility of the compounds is caused by polymerisation. The first fraction of tri(diethylgold) phosphate obtained by evaporation of the cold reaction medium of ligroin and methanol redissolved only in hot alcohol. This suggests that the compound when first produced in solution is simple and of low molecular weight, but that in the process of isolation it polymerises. The polymers must have a repeating unit $(R_2Au)_3PO_4$, and every three gold atoms require six links provided by the four oxygen atoms in order to preserve the four-

covalency of gold. There are four ways of distributing six links between four oxygen atoms : one oxygen unbonded, and three doubly linked; two unbonded, and two triply linked; two




(XVIII.)




(XIX.)

singly linked, and two doubly linked; and three singly linked, and one triply linked. Since for each method of distribution several possible structures may be suggested, speculation as to the way in which the units are actually linked is not justified.

## Experimental.

*Disilver Phenyl Phosphate.*—Phenoxyphosphoryl dichloride (10·9 g.) (Hoeflake, *Rec. Trav. chim.*, 1917, **36**, 26) was added to a well-stirred solution of potassium carbonate (14·4 g.) in water (20 c.c.). The temperature was maintained at 40—50° during the addition of the chloride, and later was raised to 65° to complete the hydrolysis. The aqueous solution was evaporated to dryness, and the solid residue containing dipotassium phenyl phosphate was dissolved in water. This solution was acidified with hydrochloric acid, and barium phenyl phosphate (5·4 g.) was precipitated with barium chloride. Silver phenyl phosphate was obtained as a precipitate, by adding silver nitrate to a solution of the barium salt in a large volume of water (Found : Ag, 55·4. Calc. for $C_6H_5O_4PAg_2$ : Ag, 55·5%).

*Tetraethyl(monophenyl phosphato)digold* (XVI).—Diethylbromogold (1·74 g.), dissolved in ligroin (b. p. 40—60°; 35 c.c.), was shaken for 3 hours with finely powdered disilver phenyl phosphate (1·02 g.). The insoluble residue, consisting of silver bromide and the (phenyl phosphato)-compound, was collected by filtration, washed free from any unchanged diethylbromogold with ligroin, and extracted thoroughly with benzene. The benzene solution was evaporated *in vacuo* at room temperature, and *tetraethyl(monophenyl phosphato)digold* was obtained in the form of colourless rectangular prisms (1·57 g.), m. p. 130°, decomposing at 160° [Found : C, 25·0; H, 3·9; Au, 57·9%; *M* (in benzene), 1310, 1340. $C_{28}H_{50}O_8P_2Au_4$ requires C, 24·6; H, 3·7; Au, 57·8%; *M*, 1364]. The compound was sparingly soluble in water, alcohol, acetone, and ligroin, but soluble in chloroform and benzene. It was recovered unchanged from pyridine.

2 : 2′-*Dipyridyldiethylauric Tetraethyl-μ-bis(monophenyl phosphato)diaurate* (XVIII).—2 : 2′-Dipyridyl (0·083 g., 2 mols.) was mixed with tetraethyl(monophenyl phosphato)digold (0·36 g.) in benzene (15 c.c.). The benzene solution was evaporated at room temperature *in vacuo*, to give a syrup which crystallised on storage. The colourless solid *product* was washed thoroughly with benzene to remove unchanged reactants, and, after drying, melted with decomposition at 120° (0·44 g.) (Found : C, 34·7; H, 4·2; N, 2·5; Au, 46·3. $C_{48}H_{66}O_8N_4P_2Au_4$ requires C, 34·4; H, 4·0; N, 3·3; Au, 47·0%).

When the above preparation was repeated using an excess of dipyridyl (4 mols.), the same product resulted and half the dipyridyl was recovered from the benzene washings.

Owing to the sparing solubility of the compound in all the usual solvents except water—which causes decomposition—it was not possible to determine the molecular weight.

The dipyridyl complex, when stirred in water, underwent decomposition with the separation of an insoluble solid. This was collected, washed with water, and dried, and shown to be tetraethyl(phenyl phosphato)digold, from its m. p. alone and mixed with an authentic specimen. Phenyl phosphate ions were detected in the aqueous filtrate, and the addition of picric acid to the filtrate gave an immediate precipitate of 2 : 2′-dipyridyldiethylauric picrate, m. p. 190—191° (decomp.) (Found : Au, 30·4. Calc. for $C_{20}H_{20}O_7N_5Au$ : Au, 30·8%).

*Tetraethylphenylarsonatodigold* (XVII).—Silver phenylarsonate was prepared by converting phenyl-

arsonic acid into its diammonium salt with aqueous ammonia, and adding silver nitrate. The precipitated silver salt was collected, washed with water, and dried (Found: Ag, 52·1. Calc. for $C_6H_5O_3AsAg_2$: Ag, 51·9%).

Diethylbromogold (2·0 g.) in ligroin (b. p. 40—60°; 35 c.c.) was shaken with silver phenylarsonate (2·5 g., 2 mols.) for 4 hours. The mixture was filtered, and the solid washed with ligroin. The filtrate and washings were evaporated *in vacuo* at room temperature, and tetraethylphenylarsonatodigold crystallised as colourless rectangular prisms (0·68 g.). A further quantity of product was obtained by extracting the insoluble solid with benzene (30 c.c.) and evaporating the extract. The combined fractions were recrystallised by dissolving them in benzene and evaporating the solution *in vacuo* to give a product (1·95 g.) melting at 128°, and decomposing at 133°. The *compound* dissolved readily in benzene and chloroform but less readily in ligroin, and was almost insoluble in alcohol, acetone, and water (Found: C, 23·8; H, 3·6; Au, 55·3%; *M*, 1300, 1330. $C_{28}H_{50}O_6As_2Au_4$ requires C, 23·7; H, 3·5; Au, 55·5%; *M*, 1420).

2 : 2′-*Dipyridyldiethylauric Tetraethyl-μ-bis(phenylarsonato)diaurate* (XIX).—2 : 2′-Dipyridyl (0·28 g., 4 mols.) was mixed with the foregoing arsonato-compound (0·65 g.) in benzene (15 c.c.). The benzene solution was evaporated *in vacuo* at room temperature, and the colourless crystals which separated were washed with ligroin and recrystallised by careful evaporation of a chloroform solution to which a little ligroin had been added. The dipyridyl *complex* (0·64 g.) separated in colourless plates, m. p. 138° (decomp.), sparingly soluble in ligroin and benzene but readily soluble in chloroform and alcohol (Found: C, 32·8; H, 4·15; N, 3·6; Au, 45·2. $C_{48}H_{66}O_6N_4As_2Au_4$ requires C, 33·3; H, 3·85; N, 3·2; Au, 45·2%).

When the complex (0·6 g.) was stirred in water, it underwent a definite change in appearance, with the separation of a sparingly soluble solid. This product was collected, dried, and shown to be tetraethylphenylarsonatodigold (0·37 g.) (m. p. 128—129°). Addition of picric acid to a portion of the aqueous filtrate precipitated 2 : 2′-dipyridyldiethylauric picrate, m. p. 190° (decomp.) (Found: Au, 30·3. Calc. for $C_{20}H_{20}O_7N_5Au$: Au, 30·8%).

From a second portion of the filtrate, 2 : 2′-*dipyridyldiethylauric dichromate* was precipitated with sodium dichromate. This salt crystallised from hot water in orange-yellow needles, m. p. 186° (decomp.) (Found: Au, 37·6. $C_{28}H_{36}O_7N_4Cr_2Au_2$ requires Au, 38·0%).

*Silver Diphenyl Phosphate.*—Freshly distilled phenol (25 g.) and phosphorus oxychloride (25 c.c.) were refluxed for 12 hours, in a dry atmosphere. The reaction mixture was well cooled in a freezing mixture, while ice-cold water (100 c.c.) was run in slowly. The aqueous solution was extracted with ether, and the ether extract was washed with cold water and treated carefully with a saturated solution of potassium carbonate. The potassium salt which separated was recrystallised from water and converted into silver diphenyl phosphate (4·3 g.) by treatment with silver nitrate (Found: Ag, 30·3. Calc. for $C_{12}H_{10}O_4PAg$: Ag, 30·2%).

N.B. This preparation was carried out repeatedly, according to the method of Iwatsura (*Biochem. Z.*, 1926, **173**, 348, 350), in order to obtain disilver phenyl phosphate required for the work outlined above, but in all cases silver diphenyl phosphate was obtained.

*Diethyl(diphenyl phosphato)gold* (XV).—Diethylbromogold (0·67 g.) in ligroin (b. p. 40—60°; 15 c.c.) was shaken for 3 hours with silver diphenyl phosphate (0·9 g.). The undissolved solid was then collected and washed well with ligroin, and the filtrate and washings were evaporated to dryness *in vacuo* at room temperature. The residue (0·41 g.) was combined with a further fraction (0·63 g.) obtained similarly from a second extraction of the solid with benzene, and the whole recrystallised by careful evaporation of a benzene solution *in vacuo* at room temperature. The *product* (0·95 g.) crystallised in colourless prisms, m. p. 70—71° (decomp.) [Found: C, 38·2; H, 4·2; Au, 39·0%; *M* (in benzene), 974, 985. $C_{32}H_{40}O_8P_2Au_2$ requires C, 38·1; H, 4·0; Au, 39·1%; *M*, 1008].

*Tri(diethylgold) phosphate.*—Diethylbromogold (3 g.) was shaken in a mixture of ligroin (b. p. 40—60°; 15 c.c.) and methanol (5 c.c.) with silver orthophosphate (1·9 g.) for 3 hours. A small volume of methanol was found to be essential for reaction. The undissolved solid was filtered off, and the filtrate was evaporated to dryness *in vacuo* to give a colourless solid (0·58 g.). The insoluble material was extracted successively with hot methanol and hot ethanol. Evaporation of these extracts gave a further quantity of product (0·62 g.). The inability to extract the product completely may have been due to progressive polymerisation, with a simultaneous decrease in solubility.

The combined fractions, recrystallised from methanol, gave colourless needles (1·08 g.), m. p. 123° (decomp). The *phosphate* was very sparingly soluble in all solvents, hot or cold, except hot alcohol, and for this reason it was not possible to determine its molecular weight [Found: C, 16·5; H, 3·7; Au, 68·1. $(C_{12}H_{30}O_4PAu_3)_n$ requires C, 16·7; H, 3·5; Au, 68·6%].

*Tri(di-n-butylgold) Phosphate.*—Ethylenediaminodi-*n*-butylgold bromide (2·5 g.) (Gibson and Colles, *J.*, 1931, 2413) was dissolved in the minimum quantity of cold water, and the solution was filtered from undissolved impurities. The filtrate was treated with 5N-hydrobromic acid (2 equivs.) in order to liberate di-*n*-butylbromogold as an oil, which was then extracted with ligroin (b. p. 40—60°; 4 × 50 c.c.). The extract, after being dried ($Na_2SO_4$) and evaporated *in vacuo* to about 70 c.c., was shaken for 3 hours with silver phosphate (1·2 g.) in the presence of methanol (5 c.c.). The resulting solution was filtered, and the solvent was then evaporated off in a dry atmosphere at reduced pressure. The residue was recrystallised from ethanol, yielding colourless needles (1·0 g.), m. p. 114° (decomp.). *Tri(di-n-butylgold) phosphate*, although slightly more soluble than its ethyl analogue, was still insufficiently soluble to permit a molecular-weight determination [Found: C, 28·3; H, 5·7; Au, 57·0. $(C_{24}H_{54}O_4PAu_3)_n$ requires C, 28·0; H, 5·3; Au, 57·5%].

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GUY'S HOSPITAL MEDICAL SCHOOL,
(UNIVERSITY OF LONDON), S.E.1.

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