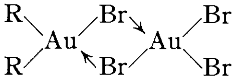
50. *The Organic Compounds of Gold. Part IV.* n-*Propyl Compounds.*

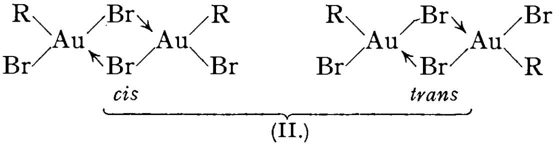
By Abraham Burawoy and Charles S. Gibson.

THE chemical properties of monoethyldibromogold (discussed in Part III; Burawoy and Gibson, J., 1934, 860) and its molecular weight in freezing bromoform indicate that the constitution of this type of compound can be either (I) or (II) (R = Et).



(I.)

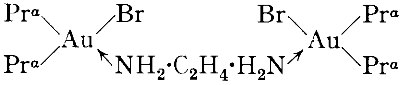
or



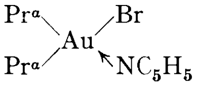
(II.)

Whatever be the configuration of the atoms and groups attached to the 4-covalent gold atoms, the *cis*- and the *trans*-forms (II) are theoretically possible. The spontaneous and quantitative decomposition of monoethyldibromogold into ethyl bromide and aurous bromide is easily explained on that constitutional formula; on the other hand, its chemical properties, its formation from diethylmonobromogold and tribromogold (auric bromide), and its colour are more in keeping with constitution (I). It has too low a solubility in carbon tetrachloride (it is decomposed in benzene) to permit of a measurement of its dipole moment which would throw additional light on its constitution; so, to complete the investigation of this type of gold compound, a detailed study has been made of its homologue, *mono*-n-*propyldibromogold.*

Di-*n*-propylmonobromogold (Kharasch and Isbell, *J. Amer. Chem. Soc.*, 1931, **53**, 2701) was obtained from pyridinotrichlorogold and *n*-propylmagnesium bromide and isolated in the form of *monoethylenediaminotetra*-n-*propyldibromodigold* (III), a colourless crystalline compound which is a non-electrolyte. No corresponding derivative of diethylmonobromogold has been obtained, but the compound is analogous to the monoammino- and monopyridino-diethylmonobromogold compounds of Gibson and Simonsen (J., 1930, 2531) and also to the *monopyridinodi*-n-*propylmonobromogold* (IV) now to be described.



(III.)



(IV.)

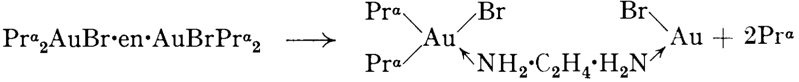
Monoethylenediaminotetra-*n*-propyldibromodigold (III) is insoluble in water and ligroin, soluble in alcohol, chloroform, and nitrobenzene, and sparingly soluble in benzene, bromoform, and *cyclo*hexane. In a melting-point tube, it has m. p. 110—111°, gas being evolved; the product (often slightly discoloured) then solidifies and decomposes at about 140°, frequently with explosion. The action of heat on compound (III) is further described below.

A solution of (III) in chloroform after a while deposits colourless needles of ethylenediaminodi-*n*-propylgold bromide (Gibson and Colles, J., 1931, 2413), more rapidly when concentrated than when dilute; the formation takes place as follows,

$$2Pr^{a}_{2}AuBr\cdot en\cdot AuBrPr^{a}_{2} \rightleftharpoons 2[Pr^{a}_{2}Au\ en]Br + Pr^{a}_{2}AuBr\cdot AuBrPr^{a}_{2}$$

the salt being insoluble and di-*n*-propylmonobromogold (an oil at the ordinary temperature) being readily soluble in chloroform. Owing to this behaviour, the purification of (III) by solution in chloroform and addition of ligroin until crystallisation commences must be carried out in not too concentrated solution and as rapidly as possible. A similar decomposition takes place when (III) is repeatedly washed with small quantities of water; the aqueous filtrate contains a small but quite recognisable amount of ethylenediaminodi-*n*-propylgold bromide.

It has not been possible to control the decomposition of pure monoethylenediaminotetra-*n*-propyldibromodigold (III) in quantity by heat, which may proceed explosively even below 100°; but the action of heat on solutions of the compound can be investigated conveniently. When clear solutions of (III) in benzene, *cyclo*hexane, and chloroform are heated on the water-bath, colourless needles separate (those from the first two solutions, when dilute, are generally discoloured owing to slight reduction of the gold compound). The product, which is best obtained by gently boiling the chloroform solution for a few minutes, and is insoluble in water and ligroin, sparingly soluble in chloroform, and easily soluble in alcohol, is *monoethylenediaminodi*-n-*propyldibromodigold* (V), in which one gold atom is univalent and 2-covalent and the other is tervalent and, as in all other cases of tervalent gold compounds, 4-covalent. This compound decomposes at about 140° with explosive violence and it must be identical with the product formed when gas is evolved from (III) in a melting-point tube :



$$\mathrm{Pr^{\alpha}_2AuBr{\cdot}en{\cdot}AuBrPr^{\alpha}_2} \longrightarrow \mathrm{(Pr^{\alpha})_2Au(Br){\leftarrow}NH_2{\cdot}C_2H_4{\cdot}H_2N{\rightarrow}Au{-}Br} + 2\mathrm{Pr^{\alpha}}$$

(III.) (V.)

Whether free *n*-propyl radicals are actually evolved during the decomposition of (III) has not been determined, but their production would seem to be the correct explanation of the action of heat on monoethylenediaminotetra-*n*-propyldibromodigold. The further decomposition of monoethylenediaminodi-*n*-propyldibromodigold has not been investigated.

When compound (III) is shaken with carbon tetrachloride and dilute hydrobromic acid, it yields a carbon tetrachloride solution of di-*n*-propylmonobromogold. This solution, of known concentration (1 mol.), is mixed with a carbon tetrachloride solution containing rather less than the calculated quantity of bromine (2 mols.) and, after some hours, allowed to evaporate to dryness. The crystalline residue after purification as described later, is *mono*-n-*propyldibromogold*, which is obtained in dark red, doubly refracting prisms. Its molecular weight in freezing bromoform indicates the formula $[\mathrm{Pr^{\alpha}AuBr_2}]_2$; unlike the corresponding ethyl compound, it has a melting point (54°) and it is much more highly soluble in such solvents as chloroform, bromoform, and carbon tetrachloride. In its chemical properties it is exactly analogous to the ethyl compound. Although it is more stable than its ethyl analogue, it decomposes quantitatively, very slowly at the ordinary temperature and rapidly above its melting point, into *n*-propyl bromide and aurous bromide :

$$[\mathrm{Pr^{\alpha}AuBr_2}]_2 \longrightarrow 2\mathrm{Pr^{\alpha}Br} + 2\mathrm{AuBr}$$

When it is shaken with aqueous potassium bromide, a solution of potassium bromoaurate is obtained and di-*n*-propylmonobromogold separates as a colourless oil. Mono-*n*-propyldibromogold is decomposed by solvents which are easily brominated or oxidised, yielding solutions of di-*n*-propylmonobromogold and precipitates of aurous bromide, which may be partly reduced to gold. Like its ethyl analogue, it does not form derivatives of itself : when solutions of the compound and pure pyridine in carbon tetrachloride are mixed, monopyridinodi-*n*-propylmonobromogold (see above), soluble in carbon tetrachloride, and a scarlet precipitate of pyridinotribromogold are obtained, the solution becoming practically colourless; theoretical quantities of both compounds are obtained according to the equation

$$[\mathrm{Pr^{\alpha}AuBr_2}]_2 + 2\mathrm{Py} \longrightarrow \mathrm{Pr^{\alpha}_2AuBrPy} + \mathrm{PyAuBr_3}$$

The dipole moments of organic gold compounds have not been previously measured, and that of diethylmonobromogold was first investigated: * a zero dipole moment would confirm the symmetrical constitution already assigned to the compound (J., 1930, 2531). The dipole moment was measured in benzene solution at 25°, the dielectric constant being determined by Sugden's method (J., 1933, 768) with a silver condenser. The results are tabulated below (f_2 = molar fraction of the solute, d, e, and n = density, dielectric constant, and refractive index of the solution, $p_{1,2}$ = specific polarisation,

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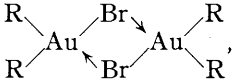
* The authors are indebted to Professor S. Sugden, F.R.S., for kindly affording them facilities for carrying out this determination.

P_2 = total polarisation of the solute, P_E = the electron polarisation calculated from the refractive index, and $P_\mu = P_2 - P_E$ when P_E = 102·2) :

f_2.	$d^{25°}$.	$\epsilon^{25°}$.	$p_{1,2}$.	P_2.	$n^{22·5°}_{5780}$.	P_E.	P_μ.
—	0·8732	2·2730	0·3412	—	1·4992	—	—
0·001849	0·8815	2·2745	0·3383	106·7	—	—	4·5
0·004199	0·8949	2·2855	0·3354	118·4	1·5021	102·1	16·2
0·006893	0·9087	2·2960	0·3321	120·8	—	—	18·6
0·010140	0·9225	—	—	—	1·5049	102·2	—

Regarding the accuracy of the results, (1) the infra-red term is neglected, (2) since the compound has a high molecular weight, comparatively dilute solutions are used, and (3) diethylmonobromogold is not completely stable in benzene, in which it is conveniently soluble, and though during the determinations very little decomposition takes place, such solutions show considerable decomposition after two days. The actual values consequently may not be appreciably different from zero and, in any case, the actual dipole moment is certainly less than 1·0 × 10^{-18} e.s.u. This is in agreement with the symmetrical constitution, , for the dialkyl compounds. The simple constitution, AuR_2Br, is excluded (as, indeed, it is also excluded by the known molecular weight in the case of the diethyl compound); it would also require a comparatively high dipole moment, and the polarisation calculated with half the value of the true molecular weight would be still lower than the above, confirming a zero dipole moment.

Owing to the immediate reaction between mono-*n*-propyldibromogold in carbon tetrachloride solution and silver, it was impossible to use a silver condenser for the determination of the dipole moment of this compound. This has been carried out on the freshly prepared substance in carbon tetrachloride solution by Mr. G. C. Hampson, M.A., in the Dyson Perrins Laboratory of the University of Oxford, using a platinum condenser at 25°.* The results are :

	f_2.	$d^{25°}$.	$\epsilon^{25°}$.	P_2.	μ (assuming a value of P_E = 108 c.c., calcd. from $[Et_2AuBr]_2$).
	0·0	1·5853	2·2272	—	—
A	0·008091	1·6200	2·5407	664	5·2 × 10^{-18} e.s.u.
B	0·004617	1·6038	2·3906	634	5·0 ,,
C	0·006872	1·6152	2·5337	752	5·6 ,,
D	0·003463	1·6009	2·3914	813	5·8 ,,

Owing to the deep violet colour of the solutions the refractive index could not be determined; it was calculated from that of diethylmonobromogold.

In these determinations there are slight inconsistencies. Determination (B) (lower concentration) indicates a lower dipole moment than (A), both carried out on the same day; whereas determinations (C) and (D) give results in the right order. Platinum has a very slight action on these gold compounds and some slight action was noticed during the determinations. The solutions themselves were fairly stable, though the dielectric constant fell slightly when they were left in the condenser for some time. The deposit (very small) could be removed and the replaceable capacity of the condenser did not change during the measurements, as was shown by the agreement between the calibrations for air and pure carbon tetrachloride before and after the experiments. It is possible that less reaction (which was small in any case) took place during the second determinations (C and D) than during the first two and hence the greater consistency of the former. The determinations, however, show clearly that the order of magnitude of the dipole moment is not lower than 5 × 10^{-18} and may be as high as 6 × 10^{-18} e.s.u. Such a high dipole moment indicates an unsymmetrical structure for mono-*n*-propyldibromogold in particular and analogous compounds in general. The possible unsymmetrical constitutions are (I) and the *cis*-form of (II). The compound as obtained in the many preparations is always homogeneous

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* The authors are greatly indebted to Mr. Hampson for his willing co-operation and for the great care with which the determinations were made. The experience gained in this work shows that in the comprehensive study of the dipole moments of organic gold compounds an all-gold condenser should be used.

and it is unlikely that the *cis*-form is more stable than the *trans*-form of such a compound. The compound cannot be the *trans*-modification, which would have a low or zero dipole moment. The evidence, therefore, from the measurement of the dipole moment is in favour of constitution (I), which, as indicated above, is in keeping with the chemical and general physical properties of the substance.

Since a number of diverse types of organic gold compounds have become or are becoming available, it is to be hoped that a detailed investigation of the dipole moments of representative types will be undertaken, and a discussion of the origin of the high dipole moment of the monoalkyldibromogold compounds may be postponed until a larger number of gold compounds has been examined. In the meantime, the high dipole moment of mono-*n*-propyldibromogold may be compared with those of the triethylstannic chloride ($3{\cdot}44 \times 10^{-18}$) and diethylstannic dichloride ($3{\cdot}85 \times 10^{-18}$) recently investigated by Spaght, Hein, and Pauling (*Physikal. Z.*, **1933**, **34**, 212).

EXPERIMENTAL.

Monoethylenediaminotetra-n-*propyldibromodigold* (III).—To a mechanically stirred suspension of pyridinotrichlorogold (40 g., prepared as described by Burawoy and Gibson, J., **1934**, 860) in dry pyridine (300 c.c.), a filtered solution of *n*-propylmagnesium bromide [prepared from magnesium (5·6 g.), *n*-propyl bromide (28·4 g., 2·2 mols.), and ether (60 c.c.)] is added during 3 minutes while the mixture is cooled in a freezing mixture. After a further 10 minutes' stirring, water at 0° (100 c.c.) is added, followed by ligroin (b. p. 40—60°, 300 c.c.) and hydrobromic acid (*d* 1·49, 450 c.c.) at such a rate that the temperature does not rise above 30—40°. The mixture is stirred for a further 30 minutes and then filtered from precipitated gold and any unchanged pyridinotrichlorogold. The ligroin solution is separated, washed with water, and shaken with ethylenediamine until no further colourless precipitate of ethylenediaminodi-*n*-propylgold bromide, $[Pr_2Au\ en]Br$ (Gibson and Colles, *loc. cit.*), is produced. This precipitate is removed by extraction with water and the treatment of the ligroin solution with ethylenediamine is repeated until no further precipitate is formed. To the filtered aqueous solution, hydrobromic acid is carefully added until no further colourless precipitate is produced; it is important to avoid an excess of the acid. The compound is separated, washed with a small quantity of water and then with ligroin, and dried over phosphoric oxide. It may be purified by adding ligroin to a filtered chloroform solution until crystallisation takes place, the operation being carried out rapidly; yield, 6·4 g. or 15·6% of the theoretical amount, varying in different preparations from 12 to 21%. By using pyridinotribromogold (37 g.) and proceeding in a similar manner, the same compound (4 g.; yield, 14·5%) is obtained.

Monoethylenediaminotetra-n-*propyldibromodigold* is a colourless crystalline compound; its properties and behaviour on being heated are described on p. 219. The determination of the gold content is somewhat difficult, since the compound explodes not only when heated in bulk but also on treatment with bromine and with sulphuric acid. The bromine content was determined by treatment with sodium methoxide in methyl alcohol on the water-bath for 1 hour and subsequent titration with silver nitrate and potassium thiocyanate. The nitrogen was determined by microanalysis, and the molecular weight by the cryoscopic method [Found: N, 3·4; Br, 20·4, 20·5; Au, 49·6; *M*, 791, 753 (nitrobenzene). $C_{14}H_{36}N_2Br_2Au_2$ requires N, 3·6; Br, 20·35; Au, 50·1%; *M*, 786·5].

Ethylenediaminodi-*n*-propylgold bromide produced from (III) in the manner described above was identical with an authentic specimen (Found: Au, 46·8; calc., 46·6%).

Monoethylenediaminodi-n-*propyldibromodigold* (V) is produced by the action of heat on (III). Its preparation and properties have been described above (Found: Br, 23·1, 23·0; Au, 56·6, 56·4. $C_8H_{22}N_2Br_2Au_2$ requires Br, 22·8; Au, 56·3%).

Mono-n-*propyldibromogold* (as I, R = $C_3H_7{}^a$).—Monoethylenediaminotetra-*n*-propyldibromodigold (11·6 g.) is shaken with an excess of hydrobromic acid, the liquid di-*n*-propylmonobromogold being liberated. This is extracted with a small quantity of carbon tetrachloride, the solution washed with water, dried with anhydrous sodium sulphate, and evaporated at the ordinary temperature under reduced pressure to about 15 c.c. To this filtered solution, bromine in carbon tetrachloride (1·63*N*, 34·0 c.c.; theo. for 2 mols., assuming the above constitution, 36·3 c.c.) is added, and the mixture kept in a glass-stoppered vessel for 24 hours. The deep red solution is allowed to evaporate spontaneously and the crystalline residue is recrystallised from carbon tetrachloride by obtaining a solution at a temperature not higher than 40°, filtering it through fine sintered glass, and cooling it in a freezing mixture (yield, 6 g., apart from about 1 g. obtained from the mother-liquor). The compound crystallises in dark red, doubly refracting prisms having a purple metallic lustre. It has m. p. 54°, above which it begins to decompose. Its molecular weight is determined in freezing bromoform (Found : Br, 39·95; Au, 48·8, 49·4; *M*, 777·5, 809. $C_6H_{14}Br_2Au_2$ requires Br, 39·95; Au, 49·3%; *M*, 800·2).

The greater stability of *mono*-n-*propyldibromogold* over the corresponding ethyl derivative is shown by the fact that a specimen kept for a month at 18—22° suffered a loss in weight of only 1·8%, but a slight rise in temperature causes a rapid increase in the rate of decomposition (compare Burawoy and Gibson, *loc. cit.*). When the compound is heated at 80—85°, its decomposition into *n*-propyl bromide and aurous bromide is complete in 30 minutes (Found : loss, 30·5. $[Pr^{\alpha}Br_2Au]_2$ requires for loss of $2Pr^{\alpha}Br$, 30·7%). The yellowish-green residue is pure aurous bromide (Found : Au, 71·2; calc., 71·1%).

To mono-*n*-propyldibromogold (2·62 g.) in carbon tetrachloride (20 c.c.), pyridine (0·52 g.; 2 mols.) is added. The violet colour is immediately destroyed and a red compound is precipitated. The latter, after separation and washing with carbon tetrachloride, is identified by comparison with an authentic specimen and by analysis as pyridinotribromogold (Found : Au, 38·2; calc., 38·2%). The slightly reddish filtrate from the pyridinotribromogold (obtained in almost quantitative amount) is evaporated, and the residue recrystallised from ligroin. It is obtained in colourless needles, m. p. 61—62°, soluble in benzene, chloroform, and carbon tetrachloride and almost insoluble in ligroin at the ordinary temperature. The same compound is prepared by allowing di-*n*-propylmonobromogold to react with pyridine in ligroin. It is *pyridinodi*-n-*propylmonobromogold* (IV), $PyPr^{\alpha}_2AuBr$ (Found : Au, 44·7, 44·6. $C_{11}H_{19}NBrAu$ requires Au, 44·6%).

The authors are greatly indebted to Mr. W. Morris Colles for his assistance and to the Government Grant Committee of the Royal Society and to Imperial Chemical Industries, Ltd., for grants. One of them (A. B.) is also indebted to the Academic Assistance Council for a maintenance grant.

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

[*Received, December 6th,* 1934.