98. *The Organic Derivatives of Gold. Part X. Diethylgold Cyclic Derivatives containing the* N–C–C–S *System.*

By (the late) R. V. G. EWENS and C. S. GIBSON.

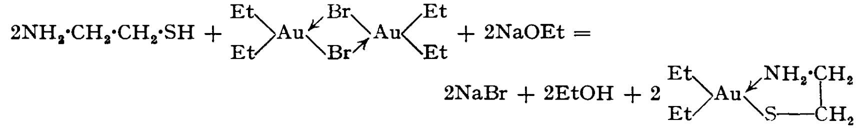
Diethylmonobromogold reacts quantitatively with 2-aminoethanethiol to give the non-electrolyte (2-*aminoethylthio*)*diethylgold* (I), in which the sulphur atom displays the reactivity typical of an organic sulphide. This compound yields a *sulphilimine* (VIII) and alkylates to yield a sulphonium cation, isolated as the *picrate* (as V). The constitution of the non-crystalline bromide is shown to be similar.

The stable (*dithio-oxamido*)*tetraethyldigold* (X), which contains a heterocyclic system similar to (I), has also been prepared.

THE well-known affinity of the transitional metals for nitrogen and sulphur, as in the complexes with amines and sulphides, suggested that suitable aminothiols ought to form chelate complexes of considerable stability. The simplest monoacidic chelating compound of this class, 2-aminoethanethiol, does not appear to have been investigated from this point of view, though a few complexes of cysteine—the carboxylated analogue—have been described (for the cobalt–cysteine complexes, see Schubert, *J. Amer. Chem. Soc.*, **1933**, **55**, 3336).

Among the metals, nickel, palladium, copper, and particularly cobalt form well-defined complexes with 2-aminoethanethiol which will be described later. The dialkylgold derivative, however, is unique in containing only one organic residue and thus a single chelate ring. This characteristic feature (which is a normal one for the dialkylgold derivatives of bidentate compounds), arises because the univalent R_2Au group requires two further covalencies to satisfy the electronic requirements of the gold atom, and these links are disposed at an angle of approximately 90°. Simple univalent cations with a co-ordination number of two (*e.g.*, Ag^+, Cu^+) on the other hand have a normal valency angle of 180° and are thus not particularly suited to ring formation with a single molecule of a mono-chelating compound.

2-Aminoethanethiol and diethylmonobromogold react in the presence of sodium ethoxide according to the equation :



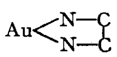
(I.)

The change proceeds so rapidly that the hydrobromic acid liberated by the interaction of the thiol and diethylmonobromogold may be titrated with the sodium ethoxide, phenolphthalein being used as indicator. If the reaction is carried out in chloroform–ethanol the sodium bromide is precipitated and (2-*aminoethylthio*)*diethylgold* (I) can readily be isolated from the filtrate. The colourless crystals are unaffected by light over a long period, and this unusual stability among organic gold compounds is further shown by the high melting point (172—173°), the highest yet recorded for a mononuclear non-electrolyte in this series. The compound (I) is very soluble in chloroform, soluble in ethanol and other organic solvents mentioned below, but almost insoluble in acetone and ether; surprisingly it is, however, somewhat soluble in hot water.

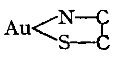
The difficulty in establishing the molecular weight of the compound in solution affords a curious contrast when set against the stability in the solid state. In benzene, in which the complex is but sparingly soluble, the value first obtained indicates that the substance is monomeric (*M*, found: approx. 300. Calc.: 331), but the freezing-point depression rapidly decreases and oily material accumulates on the walls of the vessel. The change is probably due to oxidation, and the use of an inert atmosphere would have determined this; but because of the limited solubility the attainable depressions are in any case so low that a change of solvent appeared to be a more advantageous step; experiments in benzene were therefore abandoned. In pure bromoform the reactivity is obvious; the solution rapidly becomes turbid through the separation of a colourless amorphous product. This behaviour is not surprising in view of the reaction of the compound with alkyl halides (see below), but it makes even the initial freezing-point depressions unreliable and the apparent molecular weights are in fact always high (*e.g.*, 438, 443), but lie between the values for the monomeric and the dimeric formula. In nitrobenzene, in which the solubility is again limited, the immediate production of a bright yellow colour clearly indicates the formation of a molecular compound, and recalls the well-known behaviour of polynitro-compounds, such as tetranitromethane, with unsaturated substances. The complex (I) is readily recovered unchanged from the nitrobenzene solution by precipitation with ether. The apparent molecular weight in nitrobenzene (363) is little more than that of the monomer. In a fourth solvent, glacial acetic acid, the behaviour appears to be normal (*M* 322), but the complex is nevertheless slowly decomposed by the acid and on standing the solution deposits a colourless amorphous substance. While none of these results alone is thus completely satisfactory, the weight of evidence in favour of the monomeric formula is cumulatively strong.

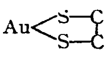
The instability in solution may be due partly to ring strain, because heterocyclic systems containing one or more relatively large atoms must necessarily be distorted. The ring type (II) is familiar in ethylenediaminediethylgold bromide ($(Et_2Au\ en)Br$. We have obtained evidence (unpublished) that the ring system (IV) is unstable; hence the ring system (III) is obviously strained.

(II.)



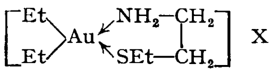
(III.)

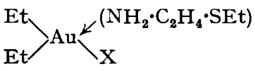


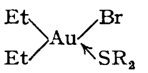


(IV.)

The sulphur atom in (2-aminoethylthio)diethylgold shows a reactivity akin to that of organic sulphides. The solid complex reacts vigorously with methyl iodide—explosively on a 0·5 g. scale—while in solution the methylation proceeds so rapidly and so far that no definite compound can be isolated. With ethyl bromide in ethanol the reaction proceeds much more smoothly, but the syrup obtained on evaporation cannot be induced to crystallise. Nevertheless we show (i) that alkylation takes place at the sulphur atom and (ii) that the product is essentially the salt (V) rather than a compound having the alternative covalent structure (VI), where X = Br. Our proof is as follows. When diethylmonobromogold is treated with ethyl 2-aminoethyl sulphide, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SEt$, an oil resembling that obtained by direct alkylation of the complex (I) is produced. Both are freely soluble in most organic solvents other than hydrocarbons, and also to some extent in water. Since our inability to obtain a crystalline bromide by either route might have been due to the presence of an equilibrium mixture of (V) and (VI), especially if (VI) had a low enough melting point (cf. the acetylacetonate of m. p. 10°; Gibson and Simonsen, *J.*, **1930**, 2531), it was clearly desirable to introduce an alternative anion of lower co-ordinating power so that the salt form (V) would be favoured. Treatment of an ethanolic solution containing diethylmonobromogold and ethyl 2-aminoethyl sulphide with silver nitrate or perchlorate readily eliminates the halogen, but the resulting salts are too soluble and deliquescent to be suitable for further study. The ion in (V) should be resolvable because of the asymmetry at the sulphur atom; but the (+)-α-bromocamphor-π-sulphonate, prepared in the same way, showed no sign of crystallisation.


(V.)

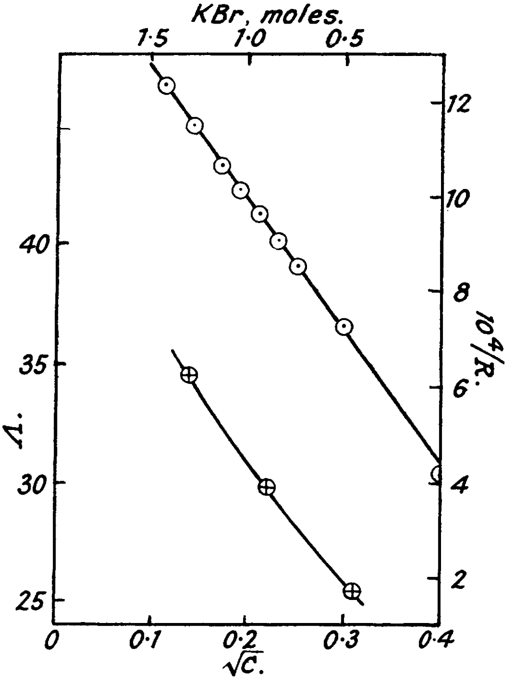

(VI.)


(VII.)

Sodium picrate on the other hand precipitates (*ethyl 2-aminoethyl sulphide*)*diethylgold picrate* from the aqueous-alcoholic solution, and the new compound crystallises readily in the form of large lemon-yellow lustrous and transparent prisms. The picrate is definitely a salt and conducts well in ethanol. For a 0·0193M-solution at 25·5°, Λ is 34·5 $ohms^{-1}$ (compare $\Lambda = 32{\cdot}35$ for 0·01M-tetraethylammonium picrate in ethanol at 25°; Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1925, **114**, 275) (see also the Figure). Further, the oil obtained by the action of ethyl bromide on the parent complex (I) yields in similar fashion a picrate of identical crystalline form, having the same m. p. and mixed m. p.; hence the alkylation must have taken place on the sulphur atom. The picrate, like compound (I), is stable to light. It is slightly soluble in water, moderately so in chloroform, and readily in ethanol.

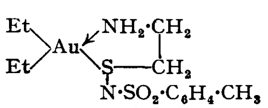
The hypothesis that the uncrystallisable bromide might be partly or wholly the covalent compound (VI) is superficially attractive. It is well known that the halides in general are better co-ordinating groups than less polarisable oxy-anions, and it was observed by Weitz (*Annalen*, 1915, **410**, 117) that *tetra*ammines of tervalent gold $[Au(NH_3)_4]X_3$ could readily be made when $X = NO_3, ClO_4$, etc., but not when X is a halide ion. It may be remarked that in the dialkylgold series the stability of the M–X link appears to increase with the atomic number (and polarisability) of the halogen; for instance, dimethyl*iodo*gold is formed when methylmagnesium iodide acts on pyridinetri*chloro*gold (Brain and Gibson, *J.*, 1939, 762). The same order is frequently observed in the complexes of the more noble metals, though it is by no means universal and is frequently upset by oxidation–reduction phenomena or for steric reasons. The commonest cases of co-ordination through sulphur occur with thiourea and with alkyl sulphides, of which only the latter concern us here. Brain and Gibson (*loc. cit.*) observed that only one molecule of dibenzyl sulphide could be introduced into diethylmonobromogold as in (VII; $R = CH_2Ph$), whence we infer that the Br^- ion co-ordinates more strongly than the sulphide. (The complex derived from the more volatile diethyl sulphide is even less stable.) Finally, these authors prepared a complex analogous to (V) using *as*-*N*-diethylethylenediamine (*i.e.*, with NEt_2 in place of SEt) and isolated it as the bromide, though here the crystallisation offered some difficulty. In water the compound behaved as a salt, the molecular weight indicating the presence of two ions. Since the solubility in organic solvents was appreciable, the conversion into the covalent form analogous to (VI) was proposed under these conditions, and to explain the observed polymerisation in bromoform a structure involving 5-covalent gold was postulated.

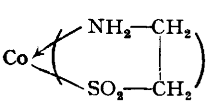
All these arguments may be adduced in favour of the possible existence of structure (VI). On the other hand, if the covalent form of (ethyl 2-aminoethyl sulphide)diethylgold bromide were of any importance in aqueous-alcoholic solution, then on adding potassium bromide the conductivity of a picrate solution should not increase steadily but should show some sort of inflexion of the type commonly observed in conductometric analysis, owing to the formation of some covalent complex. As indicated in the figure, however, no such effect is observed. It must therefore be concluded that the co-ordination of the sulphur is *stronger* than that of the bromide ion, notwithstanding the possible ring strain, because of the stabilising effect of the chelate ring. The stability constants of a number of ammonia and ethylenediamine complexes determined by Bjerrum ("Complex Ammine Formation in Aqueous Solution", Copenhagen, 1941) afford numerous examples of this effect. Further, it is not necessary to assume a covalent form to explain the solubility of such complexes in organic solvents since many alkylammonium halides with considerable hydrocarbon content, and of undoubted salt-like character, behave thus. Moreover, the solutes display multiple ion association at all but the lowest concentrations, and Brain and Gibson's molecular-weight observations on the unsymmetrical diamine complex are no doubt explicable in this way.

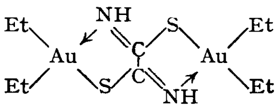


Upper curve, axes top and right: conductometric titration of complex picrate with potassium bromide. Lower curve, axes left and bottom: conductivity of complex picrate in ethanol at 25·5°.

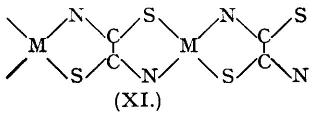
Among other properties of 2-aminoethylthiodiethylgold characteristic of an organic sulphide is its behaviour with chloramine-T, which reacts to give the crystalline sulphilimine (VIII). Qualitatively, it was found that (I) decolourised halogen solutions, yielded amorphous and unstable precipitates with the mercuric halides, and underwent oxidation easily. No "sulphoxide" or "sulphone" could be isolated, however, though the complex of tervalent cobalt with the aminothiol does yield the corresponding $M{-}SO_2^-$ compound (IX) (Ewens, unpublished result).

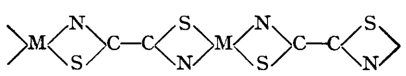

(VIII.)


(IX.)


(X.)

Lastly, to furnish additional evidence for the ring system (III), we prepared the diethylgold derivative of dithio-oxamide (rubeanic acid) by its interaction with diethylmonobromogold in the presence of alkali. *(Dithio-oxamido)tetraethyldigold* (X) forms yellow prisms from benzene or chloroform and has a molecular weight in benzene in agreement with the formula assigned to it. No doubt the ring system here is stabilised by the single–double bond resonance in the thiocarbamido-groups. Certainly this compound showed none of the reactivity associated with (I).


(XI.)


(XII.)

Structure (X), which resembles that for the corresponding oxalate complex (Gibson and Weller, *J.*, 1941, 102), is a model for the analytically well-known precipitates given by rubeanic acid with the bivalent nickel, copper, and cobalt ions; a co-ordination number of four requires infinite polymerisation as in (XI) and this formulation, with five-membered rings, is preferable to that of Jensen (*Z. anorg. Chem.*, 1944, **252**, 227), who proposed the alternative arrangement (XII) with four-membered rings.

EXPERIMENTAL.

(2-*Aminoethylthio*)*diethylgold*.—To diethylmonobromogold (6·7 g., 1 mol.) and freshly sublimed 2-aminoethanethiol (1·5 g., 1 mol.) in chloroform (80 ml.) was added 0·651M-sodium ethoxide (1 mol.). The solution was filtered from the precipitated sodium bromide, evaporated, and the residue recrystallised from ethanol to yield 5·76 g. (87%) of colourless needles of (2-*aminoethylthio*)*diethylgold*, m. p. 172—173° (decomp.) (Found : C, 21·9; H, 4·4; N, 4·5; Au, 59·4. $C_6H_{16}NSAu$ requires C, 21·7; H, 4·9; N, 4·2; Au, 59·5%). Molecular weight determinations (the concentrations C given are in g. of solute/1000 g. of solvent): (a) *In benzene*. $C = 3{\cdot}62$, $\Delta t = 0{\cdot}062°$, $M = 298$. ($C_6H_{16}NSAu$ requires M, 331.) The depression rapidly decreased to *ca.* 0·02° with obvious signs of decomposition. Initial depressions for solutions of higher concentration could not be determined because of the low solubility. (b) *In bromoform*. The results in this solvent were affected by reaction and the formation of an insoluble product. Two typical results are (i) $C = 2{\cdot}25$, $\Delta t = 0{\cdot}074°$, $M = 438$; (ii) $C = 3{\cdot}23$, $\Delta t = 0{\cdot}105°$, $M = 443$. (c) *In nitrobenzene*. The compound formed a bright yellow solution. For $C = 12{\cdot}64$, $\Delta t = 0{\cdot}240°$ (unchanged by the addition of anhydrous sodium sulphate; compare Roberts and Bury, *J.*, 1923, 2037), whence $M = 363$. On increase of the concentration to $C = 19{\cdot}78$, Δt rose to 0·347°, but was unchanged on the addition of further solute so that this solution presumably became saturated on cooling. Almost pure compound was recovered by precipitation with ether. (d) *In glacial acetic acid*. $C = 9{\cdot}09$, $\Delta t = 0{\cdot}110°$, $M = 322$. A steady decomposition set in and the solution deposited a colourless insoluble decomposition product which was not further examined.

(2-*Aminoethylthio*)*diethylgold sulphilimine*. To (2-aminoethylthio)diethylgold (0·5 g., 1 mol.) in ethanol (5 ml.) was added slowly chloramine-T (0·37 g. : 1·08 mols.) in water (7·5 ml.). The colourless *sulphilimine* rapidly separated, and after being washed with water was recrystallised from ethanol to form granular clusters of needles (0·53 g., 71%), m. p. 136° (decomp.) (Found : C, 30·7; H, 4·6; N, 5·7; Au, 39·3. $C_{13}H_{23}O_2N_2S_2Au$ requires C, 31·2; H, 4·6; N, 5·6; Au, 39·4%). The sulphilimine was readily soluble in chloroform, slightly in benzene, and slowly decomposed on keeping.

(*Ethyl 2-aminoethyl sulphide*)*diethylgold picrate*. (a) To finely divided diethylmonobromogold (3·35 g., 1 mol.) suspended in water were added ethyl 2-aminoethyl sulphide (1·05 g., 1 mol.) and then aqueous silver nitrate (1·70 g., 1 mol.) to make the total volume *ca.* 50 ml. Silver bromide immediately began to separate and, after a few hours' shaking to ensure complete reaction, was filtered off. (The filtrate contained the complex nitrate, which crystallised with great difficulty and was very soluble and deliquescent. The perchlorate and (+)-α-bromocamphor-π-sulphonate, produced similarly in water or other solvent, also crystallised poorly.) A slight excess of sodium picrate solution was added and precipitated (*ethyl 2-aminoethyl sulphide*)*diethylgold picrate*. A more convenient procedure, which avoided the elimination of the halogen, is as follows.

(b) Diethylmonobromogold (0·67 g., 1 mol.) and ethyl 2-aminoethyl sulphide (0·2 g., 1 mol.) were dissolved in ethanol (10 ml.)—from which the complex bromide could only be obtained as a syrup—and the solution diluted with an equal volume of water. Sodium picrate (0·55 g., 1·2 mols., in 15 ml.) gave a yellow crystalline precipitate, which was filtered off, washed with water, and recrystallised from aqueous ethanol to yield 0·87 g. (74%) of large lustrous yellow prisms; m. p. 120—121°, followed by rapid decomposition and gas evolution at *ca.* 134° (Found : C, 29·05; H, 4·4; N, 9·8; Au, 33·15. $C_{14}H_{23}O_7N_4SAu$ requires C, 28·6; H, 3·9; N, 9·5; Au, 33·5%). The compound was very slightly soluble in water, moderately so in chloroform. The conductivity in ethanol at 25·5°, measured in the usual manner, gave the following results. Concentration 0·0964M, $\Lambda = 25{\cdot}4$; 0·0482M, $\Lambda = 29{\cdot}8$; 0·0193M, $\Lambda = 34{\cdot}5$ ohms^{-1}.

Conductometric titration. For reasons already given, the effect of bromide ion on the conductivity was examined. To 25 ml. of a 0·00817M-solution of the picrate in 75% v/v aqueous ethanol at 25° was added in small portions 0·1009M-potassium bromide in the same solvent. The variation of the reciprocal resistance (plotted in the figure) was linear, and showed no sign of any inflexion which would have indicated the formation of a covalent complex.

Action of alkyl halides. Under a variety of conditions methyl iodide reacted to give mixtures of colourless and yellow products which could not be satisfactorily separated, of high iodide content. Ethyl bromide similarly furnished mixtures, mostly of a syrupy nature, as in the following experiment. A solution of (2-aminoethylthio)diethylgold (0·335 g.) and ethyl bromide (0·2 ml.) in ethanol (5 ml.) was allowed to stand overnight and then evaporated. The gummy residue, which contained a few ill-defined crystals but showed no signs over a long period of crystallising further, was redissolved in ethanol, and addition of an excess of aqueous sodium picrate gave a precipitate which, treated as before, furnished 0·14 g. of a picrate identical in crystalline form, melting point, and mixed melting point with the authentic product above.

(*Dithio-oxamido*)*tetraethyldigold*.—To a solution of diethylmonobromogold (2·24 g.) in ligroin (b. p. 40—60°; 20 ml.) was added a warm solution of dithio-oxamide (0·4 g., 1 mol. to 2 Au) and the calculated amount of potassium hydroxide (2 mols.) in ethanol (40 ml.). Potassium bromide was immediately precipitated and filtered off. The filtrate was evaporated down and the residue extracted with chloroform. On addition of ligroin (b. p. 60—80°), (*dithio-oxamido*)*tetraethyldigold* (1·62 g., 77%) crystallised in yellow prisms, m. p. 142—143° (decomp.) (Found: Au, 62·5. $C_{10}H_{22}N_2S_2Au_2$ requires Au, 62·5%). Molecular weight in benzene : $C = 8{\cdot}65$, $\Delta t = 0{\cdot}069°$, $M = 636$; $C = 19{\cdot}44$, $\Delta t = 0{\cdot}154°$, $M = 640$ ($C_{10}H_{22}N_2S_2Au_2$ requires M, 628).

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

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