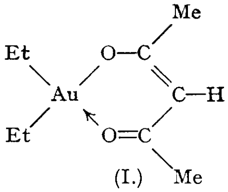
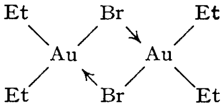
393. *The Organic Compounds of Gold. Part XI. Diethylthiocyanatogold.*

By W. L. G. Gent and C. S. Gibson.

Diethylthiocyanatogold (VI) has been prepared and its properties investigated. The molecule is dimeric, containing a four-membered ring of two gold and two sulphur atoms, and resembles, therefore, the diethylbromogold dimer and not the diethylcyanogold tetramer previously described. The compound is chiefly remarkable for the resistance of the sulphur–gold linkages to the co-ordinating action of nitrogenous bases, no complexes of which could be isolated, but thiourea and thioacetamide both react easily. Thermal decomposition of (VI) in the liquid state and in solution leads to the formation of *aurous thiocyanate*. Some complexes of this compound are described.

The properties of organic compounds of gold having the formula $(R_2AuX)_n$ (R = alkyl; X = acetylacetone, Br, CN, etc.; n = 1, 2, 4, etc.) and derived co-ordination complexes with ammonia, pyridine, and ethylenediamine have been described by Gibson *et al.* (*J.*, **1930**, 2531; **1931**, 2407; **1934**, 860; **1935**, 217, 1024; **1939**, 762). As in all auric compounds, the gold atom is 4-covalent and the number of gold atoms in the molecule it would seem, if we compare diethylacetylacetonylgold monomer (I), diethylbromogold dimer (II), and diethylcyanogold tetramer (III), is determined by the co-ordinating direction of the negative group and the intervalency angle of gold.


(I.)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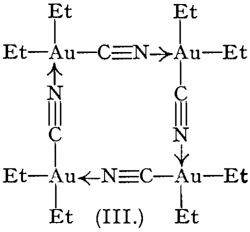
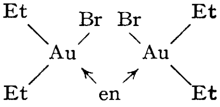
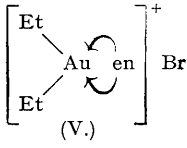

(III.)

The co-ordinate linkages holding the $(R_2AuX)_n$ molecules together are easily replaced by those with ammonia, pyridine, or ethylendiamine, resuling in the formation of covalent and then ionic compounds such as monoethylenediaminotetraethyldibromodigold (IV) and monoethylenediaminodiethylgold bromide (V). A remarkable property of the substances is the low temperature (*ca.* 100°) at which alkyl groups are lost as the hydrocarbon R_2, leaving finally the polymeric aurous compound of empirical formula AuX, but often passing through the stage of a definite auroso-auric compound.

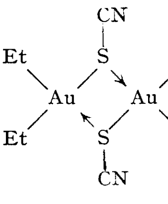

(IV.)


(V.)

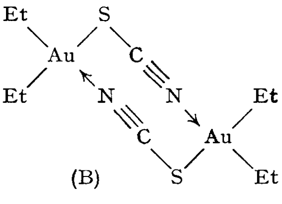
The substances $(R_2AuX)_n$ in which X = halogen are generally similar to one another in behaviour and there is little difference between them and that of the cyano-compound. The thiocyanato-group allows linkage of gold to a bivalent sulphur atom which might be expected to impose a more marked effect than the carbon atom of the cyanide group.

Diethylthiocyanatogold (VI) is readily prepared from the corresponding bromo-compound. It is a colourless, crystalline non-electrolyte, the molecular weight of which in freezing *cyclo*hexane indicates it to be dimeric.

Since the thiocyanato-group is linear, either of the structures (A) or (B) might be proposed. The fact that by the action of ammonia, ethylenediamine, or dipyridyl no derivative could be isolated in a solid or crystalline state is in sharp contrast to the behaviour of the cyano-compound and must be ascribed to the very strong co-ordination affinity between sulphur and gold which cannot be effectively broken by a co-ordinating nitrogen atom. Sulphur compounds, however, such as thiourea form complexes with (VI) fairly readily. The form (A) is preferable so far as chemical evidence is concerned; in dimensions it resembles the structure of diethylbromogold and might be expected to show a greater stability than the eight-membered heterocyclic ring of (B).

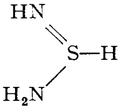

(A)

(VI.)

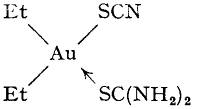

(B)

It followed naturally from the assumption of the sulphur-bridged structure that isolation of complexes with sulphur compounds should be attempted. Dibenzyl sulphide was found to be without action. Whereas the sulphur of the thiocyanate group is of a negative character, that of dibenzyl sulphide is more neutral. On the principle " like displaces like " aqueous sodium sulphide was used and gave rise to a colourless substance insoluble in all common organic solvents. This suggested that the material is polymeric, but the empirical formula could not be determined since, on drying, a black substance of indefinite composition was formed. This had such a high gold content as to imply that a large proportion of the alkyl groups had been lost.

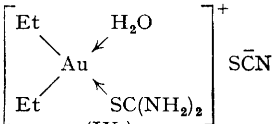
Thiourea is known to contain a proportion of *iso*thiourea (VII) which it was deemed might allow the sulphur atom to be a competitor with that in (VI). *Diethylthioureidothiocyanatogold*



(VII.)



(VIII.)

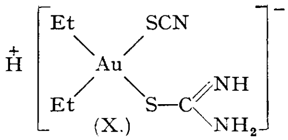


(IX.)

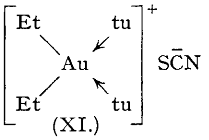
(VIII) is readily isolated as a stable compound and is unexpectedly somewhat soluble in water (*ca.* 0·5% w/v) to give an acid solution which develops a distinctive red-brown colour, different from that of ferric thiocyanate, with ferric chloride.

Formation of a hydrated complex (IX) is thereby excluded and the simplest assumption is that of an *iso*thiourea *derivative* (X).

The thiourea complex (VIII) was found to be soluble with difficulty in aqueous thiourea solution which, however, gives a reaction for thiocyanate ion indicating that diethyldithioureidogold thiocyanate (XI) is present in solution. From such solutions a picrate and a chromate can be precipitated; the latter compound was not investigated. It was to be expected that the picrate would have a composition ($Et_2Au\ tu_2$)pic (tu = thiourea; pic = picrate ion) analogous to (XI) but, in fact, this was associated with an extra molecule of thiourea, *i.e.*, it had the empirical formula Et_2Autu_3pic. The method of purification of the *complex* ruled out the possibility that the extra molecule is contained in the crystal lattice apart from the gold complex, so that the odd thiourea molecule is associated either with the complex cation or with the picrate ion. All evidence points to the former being the point of attachment. The *dithioureidoaurous thiocyanate* (XII), described later, when precipitated with picric acid



(X.)



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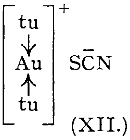

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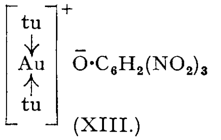
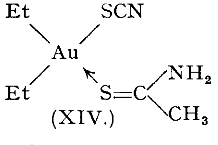


(XIII.)

gave a normal *picrate* (XIII), and Dixon's observation (*J.*, 1917, **111**, 185) that only one complex is formed between thiourea and picric acid was confirmed. This complex is evidently not completely dissociated in water, since it gives a deep red colour with sodium hydroxide, but a saturated solution of the gold complex does not show this reaction until after boiling with dilute acid. Since in aurous compounds the two covalencies are at an angle of 180° to one another (Elliott and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846), it follows that the association of the extra thiourea molecule must be related to the square configuration of the two ethyl groups and the two co-ordinated thiourea molecules.

Of other sulphur compounds with an enolic disposition, thioacetamide was used to prepare *diethylthioacetamidothiocyanatogold* (XIV), which is soluble in an excess of thioacetamide, the solution showing a reaction for thiocyanate ion due presumably to the formation of diethyldithioacetamidogoldthiocyanate (XV) of which the isolation was not attempted.



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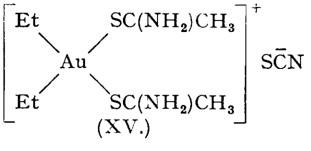


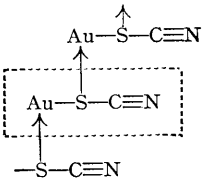
(XV.)

The thermal decomposition of diethylthiocyanatogold differs from that of the corresponding tetrameric cyano-compound in that no substance similar to diethyldicyanodigold was isolated, the products of decomposition being always *aurous thiocyanate* (XVI) and butane. On heating the compound in bulk above 100° aurous thiocyanate is not formed, but gold and an orange polymer of thiocyanogen are produced.

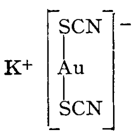
The compound (VI) melts to a clear liquid at 63° and below about 80° there is little decomposition even if the substance is kept at such temperatures for some time. Above 80° there is an induction period, which shortens as the temperature rises, during which butane is evolved at an increasing rate until finally the decomposition becomes explosive. The reaction is clearly not unimolecular and probably involves a chain mechanism. The simplest explanation is that thermal activation results in the ejection of an ethyl radical, and to become stable in the aurous state the gold atom releases the other radical of its pair. These may either terminate the chain by combining to form butane or may attack another diethylgold group to remove one ethyl group as butane and release the other as a radical :

$$(\mathrm{Et_2AuSCN})_2 \longrightarrow (\mathrm{Et_2AuSCN})_2{}^* \longrightarrow \mathrm{Et_2AuSCN,AuSCN} + 2\mathrm{Et}$$
$$\mathrm{Et} + (\mathrm{Et_2AuSCN})_2 \longrightarrow \mathrm{C_4H_{10}} + \mathrm{Et_2AuSCN,AuSCN} + \mathrm{Et}$$
$$\mathrm{Et} + \mathrm{Et_2AuSCN,AuSCN} \longrightarrow \mathrm{C_4H_{10}} + 2\mathrm{AuSCN} + \mathrm{Et}$$

Diethylthiocyanatogold decomposes in hydrocarbon solvents to give aurous thiocyanate; careful purification of the liquids is necessary to avoid reduction of some of the compound to gold. The preparation of pure aurous thiocyanate (XVI) by decomposition of the parent substance in xylene enabled the preparation of *potassium aurothiocyanate* (XVII) to be made. Like diethylthiocyanatogold, the aurothiocyanate ion is resistant to the attack of co-ordinating agents. Both dipyridyl and pyridine are without action on this ion and no evidence was obtained of 4-covalent aurous compounds such as were isolated from the action of dipyridyl and *o*-phenanthroline on potassium aurocyanide (Dothie, Llewellyn, Wardlaw, and Welch, *J.*, 1939, 426). Thiourea, however, gives an immediate precipitate of *thioureidothiocyanatogold* (XVIII) which is soluble in thiourea solution to give dithioureidoaurous thiocyanate (XII). This substance was easily isolated and is a stable compound. From its solution picric acid precipitates dithioureidoaurous picrate (XIII), and the same substance is precipitated in excess of thiourea, there being no molecular association as with the corresponding diethylgold compound.

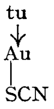


(XVI.)



$$\mathrm{K^+}\left[\mathrm{SCN{-}Au{-}SCN}\right]^-$$

(XVII.)



$$\mathrm{tu}\rightarrow\mathrm{Au{-}SCN}$$

(XVIII.)

EXPERIMENTAL.

Diethylthiocyanatogold (VI).—Silver thiocyanate was prepared by double decomposition of silver nitrate and potassium thiocyanate.

Preliminary experiments were carried out in acetone to prepare diethylthiocyanatogold, but it was found that ligroin (b. p. 40—60°) caused less reduction to metallic gold. A five-fold molecular excess of silver thiocyanate was used, the concentration of diethylbromogold being about M/150. Upon adding the silver salt there appeared to be almost immediate formation of silver bromide. The mixture was shaken for 3 hours, filtered, and the residue extracted twice with ligroin. The solution was then evaporated under reduced pressure and the compound appeared in the form of colourless needle-shaped crystals (90% of theoretical yield). Without further purification the compound is stable for some months when stored in the absence of light.

The gold content of *diethylthiocyanatogold* was found by direct ignition (Found : Au, 62·7. $\mathrm{C_5H_{10}NSAu}$ requires Au, 63·0%). The compound is readily soluble in *cyclo*hexane, and the molecular weight was determined by depression of the freezing point of this substance (Found : *M*, 628, 618. $\mathrm{C_{10}H_{20}N_2S_2Au_2}$ requires *M*, 626).

A carefully purified specimen of (VI) had m. p. 62—64° without decomposition. The changes occurring on further heating are described below.

Reaction with nitrogen compounds. A solution of the parent compound (0·5 g.) in ligroin (10 ml.) was treated with ethylenediamine (0·1 g.) in alcohol (5 ml.). No precipitation was observed, and the solution was evaporated under reduced pressure over concentrated sulphuric acid. An oily residue remained which crystallised on treatment with a small quantity of methyl alcohol. The crystals after purification by solution in ligroin and evaporation (0·4 g.) had m. p. 59°, not depressed by admixture with the parent compound. Evidently, no compound is formed with ethylenediamine under these conditions. A similar experiment with an aqueous solution of ethylenediamine also gave a negative result.

Equimolecular amounts of the parent substance and pyridine dissolved in ligroin precipitated a small quantity of an oil. A portion of this oil on treatment with methyl alcohol crystallised, the solid being found to be (VI) as before. The main bulk of the solution was evaporated under reduced pressure over concentrated sulphuric acid. Small needle-shaped crystals appeared, but disappeared after a short time, leaving oily drops. On standing overnight these again crystallised, the residue being the parent compound.

Similar experiments with ammonia, dipyridyl, and quinoline gave negative results.

Reaction with dibenzyl sulphide. Equimolecular amounts of the parent substance and dibenzyl sulphide were dissolved in ligroin, and the solution evaporated under reduced pressure. A crystalline non-homogeneous mass remained. It was extracted with ethyl alcohol and this solution evaporated. The solid recovered was shown to be dibenzyl sulphide, 95% of that used being recovered.

Reaction with sodium sulphide. The parent substance (0·2 g.) was dissolved in ligroin and treated with a five-fold excess of sodium sulphide (0·1 g.). A creamy precipitate was formed on shaking; this was separated and extracted twice with ligroin. The combined volumes of ligroin contained no gold nor did the aqueous layer, but this showed a strong thiocyanate-ion reaction. The solid is extremely water-repellent and insoluble in any of the common solvents. On drying in a vacuum, it changed to a black powder (Found: Au, 83·3%).

Thioureidodiethylthiocyanatogold (VIII).—Equimolecular proportions of diethylthiocyanatogold and thiourea were dissolved in ligroin and water, respectively, and mixed. On shaking, a white precipitate formed which was separated and dried. Recrystallisation from acetone failed, the compound being too highly soluble. Dilution of acetone solutions with either water or ligroin precipitated the *compound* in a pure state. Alternatively, it was crystallised from chloroform to give small colourless needles having m. p. 88° (Found: Au, 50·7. $C_6H_{14}N_3S_2Au$ requires Au, 50·6%).

Saturated aqueous solutions of (VIII) or filtrates from the purification process of precipitation from acetone showed a characteristic red-brown coloration on treatment with ferric alum solution. On treatment with a few drops of mineral acid the colour of ferric thiocyanate appeared. Furthermore, these solutions were found to be acidic. A small quantity of the complex dissolved in acetone (2 ml.) and precipitated by water showed a pH of *ca.* 4·5. A control experiment indicated a pH of 5·5. A similar effect was shown by a saturated aqueous solution. The amount dissolved was about 0·05%.

Diethyldithioureidogold Thiocyanate (XI).—When the parent substance and thiourea in a molecular ratio of 1 : 2 were dissolved in ligroin and water respectively, and shaken together, a quantity of diethylthioureidothiocyanatogold was precipitated, the aqueous layer showing an intense thiocyanate ion reaction. On increasing the ratio of thiourea to (VI) to 3 and 4 : 1, the precipitation was not completely inhibited. It was assumed that the ionic complex might be isolated if the anion were changed, but clearly, silver or barium salts of the common anions could not be used since both of these metals would remove thiourea from the solution also. Picric acid and potassium chromate were used, both giving yellow precipitates.

Diethyldithioureidogold Picrate–Thiourea.—A solution of diethylthioureidothiocyanatogold in a ten-fold molecular excess of thiourea dissolved in water was precipitated by adding an excess of picric acid in aqueous solution. The precipitate was separated and dried. It was highly soluble only in acetone and in ethanol. Evaporation of these solutions gave only powdery residues; dilution with water or ligroin yielded small canary-yellow needles, decomposing at 214° (Found: Au, 27·7; C, 21·8; H, 3·37; S, 13·5; N, 17·6. $C_{13}H_{24}N_9O_7S_3Au$ requires Au, 27·7; C, 21·9; H, 3·37; S, 13·5; N, 17·8%). The *complex* was not sufficiently soluble in any suitable solvent to allow determination of molecular weight.

A saturated solution of the compound in water showed no change in colour on addition of a drop of sodium hydroxide, but after boiling with a drop of dilute hydrochloric acid followed by addition of sodium hydroxide a deep golden-yellow colour was developed.

Picric Acid–Thiourea Complex.—Equimolecular amounts of picric acid and thiourea were dissolved in hot glacial acetic acid. On cooling, the solution was diluted with ligroin, and a bright yellow precipitate appeared. After purification, this compound had m. p. 125—127° and is clearly the same substance as that prepared by Dixon (*loc. cit.*). Similar experiments with 2 and 3 molecular proportions of thiourea yielded mixtures of the compound and thiourea, so only one molecular complex is formed.

It was reported by Dixon that the complex breaks up in aqueous solution, but on dissolving equimolecular amounts of the complex and picric acid in equal volumes of water and adding an equal volume of sodium hydroxide to each, the picric acid solution precipitated its sodium salt whilst the solution of the complex showed a deep red coloration. Addition of more thiourea to this solution caused no further colour change, indicating that only the 1 : 1 molecular ratio is significant and that an equilibrium between complex and components is not involved.

Diethylthioacetamidothiocyanatogold (XIV).—The parent substance (0·2 g.) and thioacetamide (0·05 g.), dissolved in ligroin and water respectively, precipitated a colourless *compound* on being shaken together (Found: Au, 50·5. $C_7H_{15}N_2S_2Au$ requires Au, 50·7%). This compound was soluble in excess of thioacetamide, thiocyanate ion being detected in an aqueous solution, but the ionic complex could not be isolated.

Thermal Decomposition of Diethylthiocyanatogold.—On rapidly heating a specimen of (VI) in an ignition tube, decomposition takes place explosively, gold being left and an orange substance condensing in the cool parts of the tube. This appeared to be a polymer of thiocyanogen. More gentle heating in a melting-point apparatus indicated that decomposition begins at about 80° increasing until at 110° visible outgassing takes place. By 120° this had ceased and a colourless compound remained which at 140° decomposed, leaving gold and the orange compound.

For studying the decomposition quantitatively a modified Victor Meyer's apparatus was constructed, the decomposition tube of which was immersed in a thermostatically controlled oil-bath. The gaseous product of the reaction is butane as the following experiments show: (*a*) The compound (0·2813 g.), heated at 100°, decomposed explosively after 2 minutes. Volume of gas at N.T.P., 19·8 ml. Expected volume, 20·2 ml. (calculated as butane). (*b*) The compound (0·1547 g.), heated at 89·3°, decomposed explosively after 7 minutes. Volume of gas at N.T.P., 11·0 ml. Expected volume, 11·1 ml. (calculated as butane).

An attempt was made to follow the rate of evolution of butane, the results being shown in graphical form in the figure for temperatures of 89·3° and 79·8° respectively.

On rapidly heating a solution of diethylthiocyanatogold in xylene or toluene to its boiling point a colourless precipitate was formed. This substance is aurous thiocyanate (see below). Decomposition in benzene and tetralin gave the same product. All of these solvents needed careful purification, otherwise reduction of the compound to metallic gold took place to a greater or lesser extent.

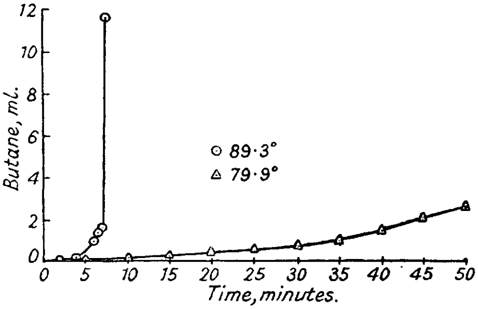
The time elapsing before appearance of aurous thiocyanate does not seem to depend on the solvent; *e.g.*, at 80°, benzene, toluene, and xylene all deposited the colourless thiocyanate after about 12 minutes at similar concentrations. The time before precipitation depends very markedly, however, on the temperature of the solvent as the following data indicate :

Temp.	80°	107°	114°	129°
Time, secs.	720	25	17	10

Aurous Thiocyanate (XVI).—Diethylthiocyanatogold (2 g.) was added in small portions with continual stirring to 100 ml. of carefully purified xylene kept at about 125° in an oil-bath. After a few seconds aurous thiocyanate is precipitated as a white flock. Usually there is a faint tinge of blue due to minute traces of colloidal gold. The suspension was allowed to stand for 5 minutes to allow the decomposition to reach completion, and then filtered off, and washed first with xylene and then with acetone. After drying in a vacuum, the *aurous thiocyanate* was a colourless powder insoluble in any solvent (Found : Au, 77·1. AuSCN requires Au, 77·3%). The compound decomposes at about 140° into metallic gold and a thiocyanogen polymer.

Potassium Aurothiocyanate (XVII).—Attempts to prepare this substance by addition of aurous thiocyanate to aqueous solutions of potassium thiocyanate failed. Although the aurous thiocyanate is freely soluble, the complex is unstable in aqueous solution and rapidly deposits gold.

A saturated solution of potassium thiocyanate was prepared in absolute alcohol, and aurous thiocyanate added with shaking until an excess was apparent. The solution was shaken for some time longer and then filtered and evaporated under reduced pressure. Potassium aurothiocyanate appeared in small, colourless, non-hygroscopic needles which show no signs of decomposition when kept dry during several months.



The compound was analysed by dissolving it in water, and rapidly adding a molecular proportion of thiourea to precipitate the gold as the thiourea–thiocyanate complex. This was separated, and the filtrate and washings titrated with standard silver nitrate [Found : KSCN, 27·4. $KAu(SCN)_2$ requires KSCN, 27·6%].

On dissolving the compound in water, a cloudy solution is formed which increases with dilution, indicating an equilibrium between the complex and its components.

Thioureidothiocyanatogold (XVIII).—Thiourea (0·048 g.) was added to an aqueous solution of potassium aurothiocyanate (0·223 g.). The new *complex* was precipitated as a heavy colourless powder; it was purified by dissolving the crude dried material in acetone and diluting with ligroin. Although it was soluble in both acetone and alcohol, neither of these solutions yielded crystalline material. The compound decomposes sharply at 132° (Found : Au, 59·2. $C_2H_4N_3S_2Au$ requires Au, 59·5%).

Dithioureidoaurous Thiocyanate (XII).—Thioureidothiocyanatogold was treated with one molecular proportion of thiourea in 1% aqueous solution in which the whole completely dissolved. On evaporation under reduced pressure small colourless needles appeared. These were dissolved in alcohol, and the *compound* precipitated by dilution with ligroin (Found : C, 9·05; H, 1·90; Au, 48·2. $C_3H_8N_5S_3Au$ requires C, 8·84; H, 1·97; Au, 48·4%).

In some preparations the initial evaporation of the aqueous solution yielded crystals in about equal proportions of needles and hexahedral platelets. Hand separation of these showed that both had the same m. p., 125—126°. Potassium aurothiocyanate was found to have no reaction with pyridine or with 2 : 2′-dipyridyl. On recrystallisation from water both forms yielded needles.

Dithioureidoaurous Picrate.—A solution of (XII) in water yielded a voluminous precipitate with picric acid. This was separated, dried, and recrystallised from acetone in which it is moderately soluble. This *picrate* crystallised in masses of long golden-yellow needles decomposing at 215° (Found : Au, 33·8. $C_8H_{10}N_7O_7S_2Au$ requires Au, 34·1%).

Precipitation of (XII) in the presence of a five-fold molecular excess of thiourea by picric acid yielded the same picrate.

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