

**646.** *The Organic Compounds of Gold. Part XII. The Constitution of Co-ordination Complexes of Dialkylgold Compounds with Diamines containing the N-C-C-N Grouping.*

By M. E. FOSS and C. S. GIBSON.

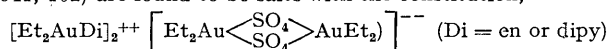
A re-examination of the physical (molecular weight and conductivity measurements) and chemical properties of co-ordination compounds containing the 2-covalent dialkylgold group ( $R_2Au$ ), has given important information concerning the constitution of the ethylenediamine and 2 : 2'-dipyridyl derivatives.

In the case of ethylenediamine, two types of derivative have been described, *viz.*, (a) salts,  $[R_2Auen]^+X^-$  ( $X = \text{halogen}$ ,  $R = \text{alkyl}$ ,  $en = \text{ethylenediamine}$ ), soluble in water, and (b) compounds previously considered as  $R_2XAuenAuXR_2$  ( $X = \text{halogen}$ ,  $CN$ ), with ethylenediamine bridging the two gold atoms, but now shown to be electrolytes having the constitution,  $[R_2Auen]^+[R_2AuX_2]^-$ .

Whereas earlier attempts to prepare 2 : 2'-dipyridyl complexes with both nitrogen atoms linked to the same gold atom were reported as being unsuccessful, evidence is now given for the existence in aqueous solution of the compound  $[Et_2Audipy]^+X^-$  ( $X = Br$ ), and compounds have been obtained, analogous to type (a), in which the halogen is replaced by the less powerfully co-ordinating nitrate and picrate groups. Moreover, the dipyridyl derivatives hitherto regarded as non-electrolytes,  $R_2XAudipyAuXR_2$  ( $X = Br$ ) are, like the corresponding ethylenediamine complexes, salts of the form  $[R_2Audipy]^+[R_2AuX_2]^-$  with the base linked to the gold atom through both nitrogen atoms. The properties of these type-(b) derivatives, and in particular the readiness with which they lose half their alkyl groups in low-boiling solvents, are readily explained in the light of their revised constitution.

The fact that *o*-phenanthroline yields complexes of both types (a) and (b) confirms the constitution of type-(b) compounds, since the rigid structure of the *o*-phenanthroline molecule eliminates any possibility of bridging.

The complexes formed by tetraethylsulphatodigold, previously thought to be non-electrolytes (*J.*, 1941, 102) are found to be salts with the constitution,



The inability to assume the simpler form  $[Et_2AuDi]^+[Et_2AuSO_4]^-$  is additional evidence that the four-membered ring in the anion  $[Et_2AuSO_4]^-$ , comprising a gold atom, two oxygen atoms, and a sulphur atom, is not permissible (*J.*, 1941, 109).

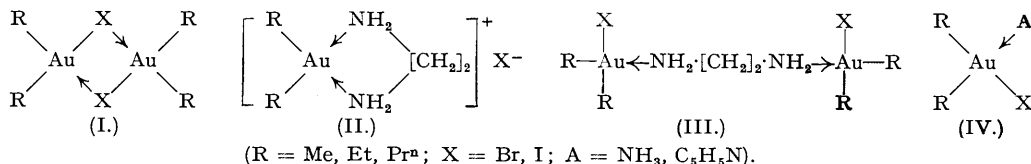
THE complexes formed by diamines such as ethylenediamine are, in general, characterised by a stability considerably greater than that of the corresponding complexes formed by monoamines (*e.g.*, ammonia, pyridine). This is to be ascribed largely to chelation involving the formation of 5-membered rings. The N-C-C-N grouping from a diamine is necessarily more restricted in the number of possible configurations, which may arise owing to flexibility, than a larger diamine, *i.e.*,  $NH_2[CH_2]_nNH_2$  where  $n = >2$ , and this accounts for the observation of Bailar and Work (*J. Amer. Chem. Soc.*, 1946, **68**, 232) that ethylenediamine (*en*) forms complexes with the transitional metals more rapidly than does trimethylenediamine. Further evidence for the greater stability of the 5-membered ring is provided by the experiments of Pfeiffer and Haimann (*Ber.*, 1903, **36**, 1064) with chromium and trimethylenediamine, and by the investigations of Mann (*J.*, 1927, 1224) in resolving the externally compensated tetrachloro-(1 : 2 : 3-triaminopropane 3-monohydrochloride)platinum, a result only possible if co-ordination takes place through the 1- and 2-positions.

Both ethylene- and trimethylene-diamine, however, give rise to chelate rings with metals having co-ordination numbers of 4 or 6, and it is only higher members of the diamine series ( $n = >3$ ) which act preferentially as bridges, with the two amino-groups linked to different metal atoms (Drew and Tress, *J.*, 1933, 1335). Examples of this type of bridging involving ethylenediamine are very rare (Chernyaev, *Ann. Inst. Plat.*, 1926, **4**, 243; 1928, **6**, 23; Brintzinger and Plessing, *Z. anorg. Chem.*, 1939, **42**, 193; O'Brien, *J. Amer. Chem. Soc.*, 1948, **70**, 2771), and in the few cases known it is often possible to suggest alternative constitutions. Clearly, however, *en* complexes of 2-covalent ions, such as  $Ag^+$  and  $Au^+$ , are almost certainly not chelates in view of the linear arrangement of the two valency bonds (Elliott and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846; Gibson, *Proc. Roy. Soc.*, 1939, *A*, **173**, 160; West, *Z. Krist.*, 1935, **90**, 555).

In the light of these facts, we have reconsidered the published data concerning the ethylenediamine complexes in the dialkylgold series, and have compared the behaviour of these complexes with that of the corresponding 2 : 2'-dipyridyl and *o*-phenanthroline complexes in which the possibility of bridging two gold atoms is respectively reduced and eliminated.

Gibson *et al.* (*J.*, 1930, 2531; 1931, 2407; 1935, 219; 1939, 762) have shown that, when

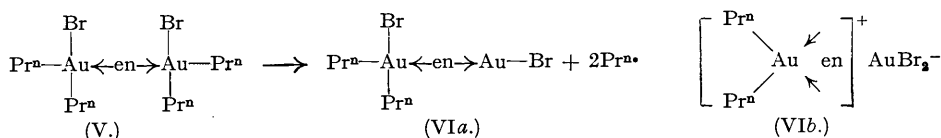
dialkylhalogenogold compounds (I) are treated with ethylenediamine, derivatives of two types may be isolated : (i) water-soluble salts, having the general formula (II) ; and (ii) compounds insoluble in water, to which was assigned the structure (III) by analogy with the non-electrolytes (IV) formed from monoamines (*J.*, 1930, 2531).



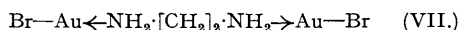
Whilst the first type (II) of compound is formed readily in the presence of excess of ethylenediamine, rather more care must be exercised in order to obtain the second type, because of the latter's tendency to pass into (II) in concentrated solution, according to the following equilibrium (Part IV, *J.*, 1935, 219) :



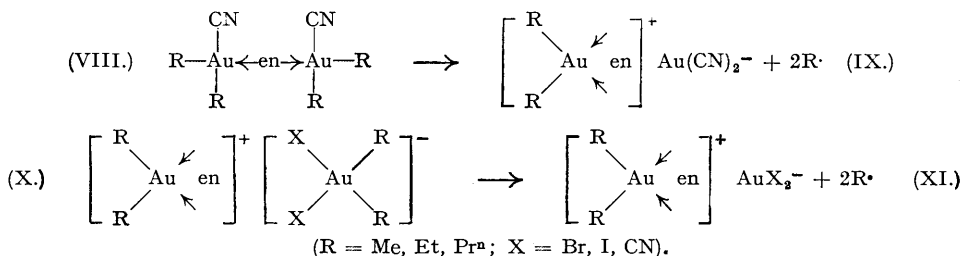
A characteristic feature of the bridged compounds thus formulated is the ease with which they undergo decomposition in boiling chloroform, benzene, or ethanol with the loss of *two* alkyl groups. In the case of the di-*n*-propyl bromo-compound, this decomposition was studied in some detail by Burawoy and Gibson (Part IV, *loc. cit.*), and the change was represented as follows :



It is immediately apparent that all four propyl groups in (V) are equivalent, and such a scheme fails to explain why the two remaining propyl groups are not lost with the same ease to give a final product (VII) :



A cryoscopic determination of the molecular weight of the dealkylated product  $\text{Pr}^a_2\text{Au}_2\text{Br}_2$  in nitrobenzene (by the technique of Roberts and Bury, *J.*, 1923, 2037, in order to avoid the influence of atmospheric moisture) has now shown that the compound is an electrolyte, since the values obtained approach half the formula weight, with increasing dilution. Moreover, the nitrobenzene solutions are found to be conducting, and we therefore believe that the compound (VIa) is more correctly formulated as (VIb) and accordingly may be renamed *ethylenediaminodi-*n*-propylauric bromoaurite*.\* There is a close parallel in the case of ethylenediamine complexes of the dialkylmonocyanogold compounds. Here salts of the type (II; X = CN) have not been isolated; but the supposed bridged complexes (VIII) are already known to give rise to cyanoaurites (IX) on dealkylation (Part V, *J.*, 1935, 1024) :

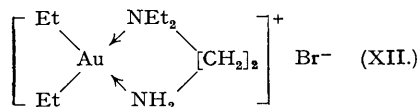


Arising from this, it seemed not unlikely that the parent ethylenediamine complexes might themselves be electrolytes formulated generally as (X). Previously, Burawoy and Gibson had found values of 791 and 753 for the molecular weight of the di-*n*-propylbromo-compound, in two different concentrations in nitrobenzene, and concluded that it must have the constitution

\* Compounds marked \* are renamed, having been previously described under a different name in keeping with the constitution then accepted.

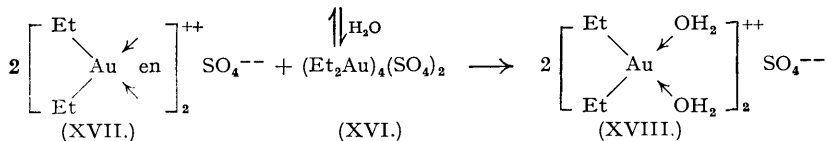
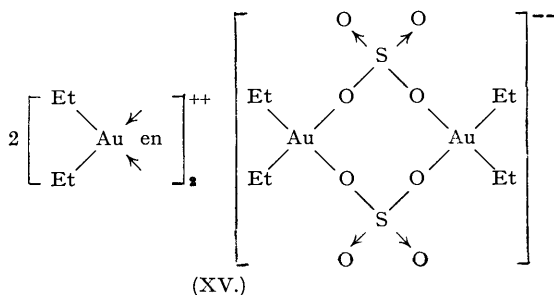
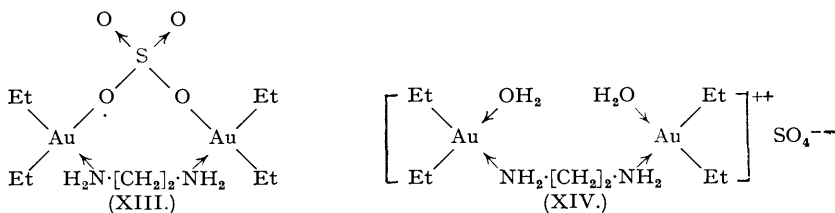
(V) (Requires *M*, 786). For the diethylcyano-compound they quote 599 and 625 compared with 623 for the non-electrolyte (VIII; R = Et).

We have made a fresh series of measurements over a wider range of concentrations, on the same cyano-compound and on the diethylbromo-compound, which was considered as being similarly constituted to the propyl analogue (V) although its molecular weight was not determined (Part VIII, *J.*, 1941, 102). The results, represented graphically in the figure indicate that in dilute solution the apparent molecular weight in nitrobenzene approaches half the formula weight in each case, and that in more concentrated solution multiple ionic association occurs so that the apparent molecular weight may, in certain concentrations, approximate to, and even exceed, the formula weight. This is reminiscent of the behaviour in organic solvents of certain tetra-alkylammonium halides, and of the unsymmetrical diamine complex (XII) upon which comment is made in Part X (*J.*, 1949, 431):



The existence of ions in nitrobenzene is confirmed by the marked increase in conductivity when either of the compounds  $\text{Et}_4\text{Au}_2(\text{CN})_2\text{en}$  or  $\text{Et}_4\text{Au}_2\text{Br}_2\text{en}$  is added to pure nitrobenzene. Under the same conditions, diethylmonocyanogold (tetramer) which is known to be a non-electrolyte (Part V, *loc. cit.*) produced no such change in conductivity.

It is therefore beyond doubt that all the supposedly bridged complexes so far examined are in fact electrolytes, having ethylenediamine chelated as in structure (X). This being so, the four alkyl groups are no longer equivalent and, since the alkyl groups in the cation show no tendency to be eliminated in low-boiling solvents [ethylenediaminediethylgold bromide (II; R = Et, X = Br) may be recrystallised unchanged from boiling alcohol], it must be the

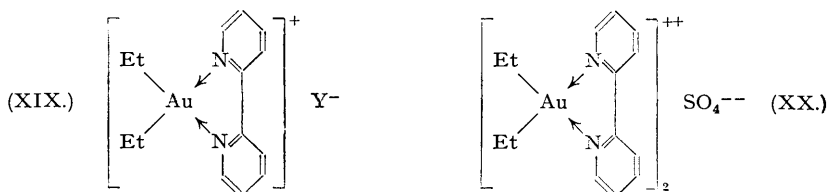


two alkyl groups in the anion which are split off the more readily to give a compound (XI) having one gold atom in the aurous state.

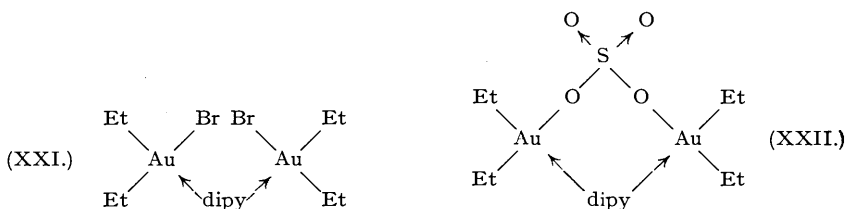
Tetraethylsulphatodigold (XVI) resembles diethylmonocyanogold, in that only one ethylenediamine complex can be isolated. To this also was assigned a bridged structure (XIII) and it was necessary to postulate an ionic form (XIV) in water, in order to account for the presence of sulphate ions.

On account of the sparing solubility of the complex in all solvents except water—in which it disproportionates—and ethyl or methyl alcohol—from which it may be recrystallised unchanged—it has not been possible to determine the molecular weight cryoscopically. The ebullioscopic method is also impracticable because the maximum elevation to be expected is too small for convenient measurement. However, a methanolic solution is conducting, and therefore by analogy with ethylenediaminodiethylauric dibromodiethylaurate (X; R = Et, X = Br), a constitution (XV) is suggested. This implies a molecular formula of twice the empirical formula  $\text{Et}_4\text{Au}_2\text{SO}_4\text{en}$  and dissociation to give three ions. In water, *ethylenediaminodiethylauric tetraethyl- $\mu$ -disulphatodiaurate* \* (XV) probably exists in equilibrium with ethylenediaminodiethylauric sulphate (XVII) and tetraethylsulphatodigold (XVI), the latter actually existing as the aquo-salt (XVIII) (see Part VIII, *loc. cit.*). This is strictly comparable with the behaviour of complexes  $[\text{R}_2\text{AuEn}]^+[\text{R}_2\text{AuBr}_2]^-$  mentioned above. Further evidence in support of these views regarding the ethylenediamino-sulphato-complex, is obtained from a study of the corresponding 2 : 2'-dipyridyl complex, discussed later.

Whereas ethylenediamine has long been known to chelate with gold in such compounds as (II), attempts to prepare 2 : 2'-dipyridyl complexes, in which both nitrogen atoms are attached to the same gold atom, were reported as being unsuccessful (Part VIII). Certainly, in studies

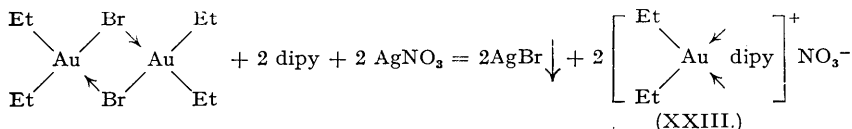


of the reaction of 2 : 2'-dipyridyl (dipy) with diethylbromogold (Part VII, *J.*, 1939, 762) and with tetraethylsulphatodigold (Part VIII) it had not been possible to isolate (XIX; Y = Br) or (XX). Even with a large excess of dipyridyl, the products contained only one dipyridyl group per two gold atoms, *viz.*,  $\text{Et}_4\text{Au}_2\text{Br}_2\text{dipy}$  and  $\text{Et}_4\text{Au}_2\text{SO}_4\text{dipy}$ , and were considered to be non-electrolytes (XXI) and (XXII), with dipyridyl bridging the two gold atoms. In view of



the well-known tendency for 2 : 2'-dipyridyl to form chelate compounds with univalent, bivalent, and tervalent metals [*e.g.*,  $(\text{Ag}, 3\text{dipy})^{++}$ ,  $(\text{Ni}, 3\text{dipy})^{++}$ ,  $(\text{Fe}, 3\text{dipy})^{++}$ ,  $(\text{Pt}, 2\text{dipy})^{++}$ ; Morgan and Burstall, *J.*, 1930, 2594; 1931, 2213; 1932, 20; 1934, 965], it seemed somewhat surprising that it should not chelate with the bivalent  $\text{R}_2\text{Au}$  group, and we therefore decided to investigate this possibility more thoroughly.

That  $\text{R}_2\text{Au}$  is able to form such ring complexes was shown by treating diethylbromogold

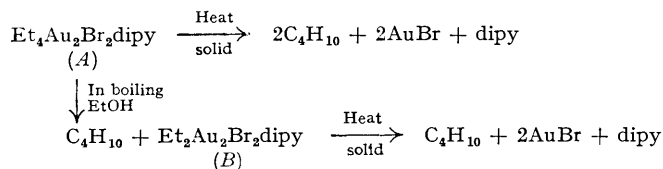


(I; R = Et, X = Br) with dipyridyl and silver nitrate. The halogen was replaced in this way, in order to create conditions more favourable for ring formation, because it is known that a nitrate group becomes linked to gold less firmly than the more polarisable halogen (Weitz, *Annalen*, 1915, 410, 117). The product is the complex salt, 2 : 2'-dipyridyldiethylauric nitrate (XXIII).

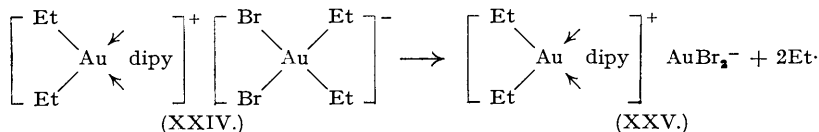
An aqueous solution of (XXIII) has the properties of a strong electrolyte; the limiting value of the equivalent conductivity is 101 mhos at 25°, and with an allowance of 71 mhos

for the mobility of the nitrate ion the mobility of the complex cation is 30 mhos (the mobility of the triethylbutylammonium ion, a cation with the same number of atoms, is 29 mhos). When the aqueous solution is treated with picric acid, the sparingly soluble 2 : 2'-dipyridyldiethylauric picrate (XIX;  $Y = C_6H_2(NO_2)_3 \cdot O^-$ ) is precipitated. This picrate dissolves readily in nitrobenzene, and cryoscopic measurements show that it is dissociated.

Having demonstrated the existence of a 2 : 2'-dipyridyldiethylauric cation, we re-examined the reaction between dipyridyl and diethylbromogold in benzene, and in agreement with Brain and Gibson (Part VII) have succeeded in isolating only one product (*A*) with a composition  $Et_4Au_2Br_2dipy$ . The melting point of 169° (decomp.), previously quoted, however, is erroneous. The correct melting point is 121°, but we have observed that in a few instances no very obvious change has occurred at this temperature; and final decomposition has taken place at 169°. The reason for this became evident when, in attempting a recrystallisation of the substance *A* from boiling alcohol, a vigorous gas evolution took place, accompanied by the separation of very sparingly soluble colourless needles, having the composition  $Et_2Au_2Br_2dipy$  and melting at 169°. This new compound (*B*) has been formed by elimination of two ethyl groups from *A* in solution, and a similar change may take place in a melting-point tube if the rate of heating is slow. When either *A* or *B* is heated rapidly in the solid state, at or just below its melting point, complete dealkylation occurs to give two molecules and one molecule, respectively, of *n*-butane, leaving a residue of aurous bromide, dipyridyl, and a trace of gold. The mode of decomposition resembles that of diethylthiocyanatogold, for which a chain mechanism has been suggested (Gent and Gibson, Part XI, this vol., p. 1835).



The dealkylation of *A* in boiling alcohol, to give *B*, is analogous to the behaviour of the ethylenediamine complexes (X) and is to be interpreted in the same way, so that *A* is 2 : 2'-dipyridyldiethylauric dibromodiethylaurate\* (XXIV) instead of (XXI) suggested by Brain and Gibson, and *B* is 2 : 2'-dipyridyldiethylauric bromoaurite (XXV). These structures were confirmed by



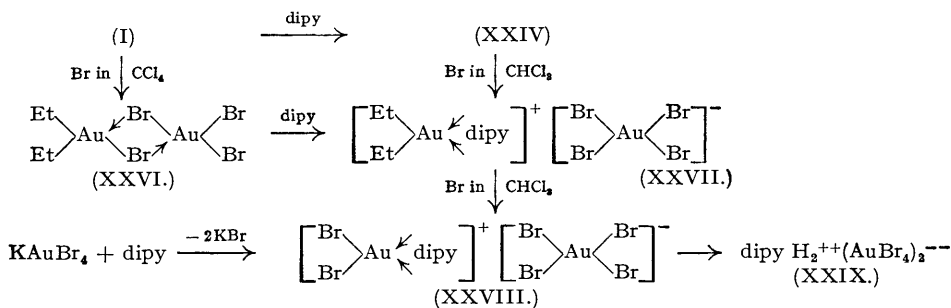
a study of physical and chemical properties. In nitrobenzene the values of the ratio (*i*) of the observed freezing-point depressions ( $\Delta t_{obs.}$ ) to the depressions calculated for molecular weights of 826 and 678 ( $\Delta t_{calc.}$ ) approaches 2 at infinite dilution. The law of mass action is obeyed and, further, the nitrobenzene solutions are conducting.

The bromoaurite (XXV) is de-ethylated only in high-boiling solvents such as toluene or xylene. The solids separating from boiling toluene and xylene are very sparingly soluble reddish-brown substances of variable constitution. Because of their sparing solubility, it was not possible to purify or identify them completely, but they are typical bromoaurates. Such products admixed with gold are to be expected from the decomposition of a bromoaurite (Brain, Gibson, and I.C.I. Ltd., B.P. 497,746).

A further indication of the non-equivalence of the four ethyl groups of (XXIV) is afforded by its reaction with bromine in chloroform to give an immediate precipitate of 2 : 2'-dipyridyldiethylauric bromoaurate (XXVII). It is interesting to note that (XXVII) is also obtained when monoethylbromogold (XXVI) is treated with dipyridyl, so that the result of treating diethylbromogold with bromine and 2 : 2'-dipyridyl is independent of the order in which these two reactants are used.

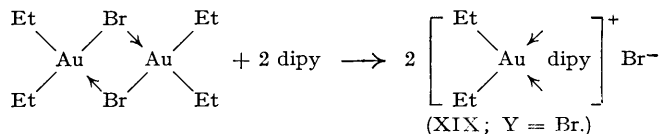
If an excess of bromine is used, the initial reaction with (XXIV) is followed by a slower reaction yielding 2 : 2'-dipyridyl dibromoaurate (XXIX) as the ultimate product. This subsequent reaction probably goes through the intermediate 2 : 2'-dipyridyldibromoauric bromoaurate (XXVIII), hydrobromic acid arising from bromination of the solvent. It was not possible to isolate (XXVIII), because the sparing solubility of both (XXVII) and (XXIX)

makes it difficult to stop the reaction at the appropriate stage; however, it has been prepared from 2 : 2'-dipyridyl and potassium bromoaurate, using the method of Gibson and Colles

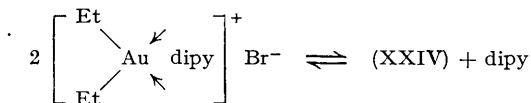


(Part II, *J.*, 1931, 2407) and shown to give dipyridyl dibromoaurate (XXIX) with hydrobromic acid.

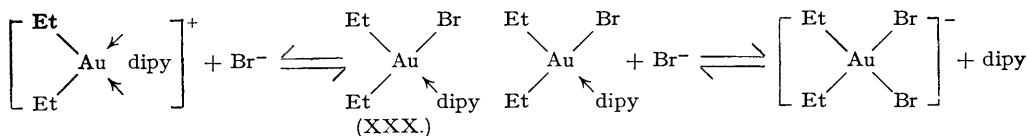
Whereas the reaction between dipyridyl and diethylbromogold in benzene appears to take the same course, however large an excess of dipyridyl is used, there is evidence that 2 : 2'-dipyridyldiethylauric bromide (XIX; Y = Br) exists in aqueous solution. Both 2 : 2'-dipyridyl and diethylbromogold are, separately, sparingly soluble in water, but when shaken together in the molar proportions of 2 : 1 they dissolve readily. From the resulting aqueous solution



the picrate (XIX; Y = picrate) may be precipitated with picric acid. This indicates the presence of dipyridyldiethylauric ions, and since dipyridyldiethylauric dibromodiethylaurate (XXIV) is sparingly soluble in water the dissolved complex must be the bromide (XIX; Y = Br). On concentration of the solution in order to isolate the bromide, however, an oil remains (cf. the behaviour of diethylbromogold and 2-ethylthioethylamine; Ewens and Gibson, Part X, *loc. cit.*). This cannot be induced to crystallise, save by washing with benzene, which extracts half the dipyridyl, leaving the crystalline complex (XXIV) :



Two equilibria are postulated in order to explain this observation :

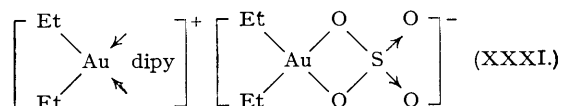


It has previously been noted that when dipyridyl links to gold it does so through both its nitrogen atoms, and there is a little tendency for one of the nitrogen atoms to co-ordinate alone. The first equilibrium must lie almost entirely to the left. However, when once a nitrogen-gold link is severed, 2 : 2'-dipyridyldiethylbromogold (XXX) is produced, and the dipyridyl is held only as firmly as any monoamine and should be displaced very easily by a further bromide ion to give the dibromodiethylaurate ion. The second equilibrium must therefore lie predominantly to the right.

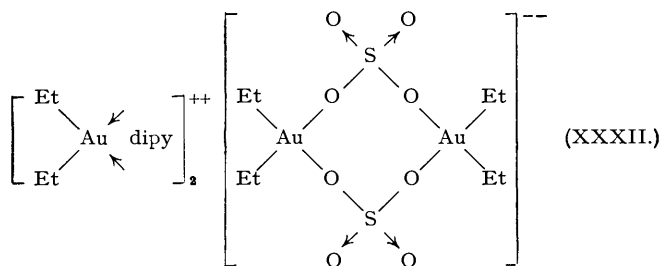
In the process of concentrating the aqueous solution of (XIX; Y = Br), the bromide ion concentration is increased. This, in itself, is insufficient to bring about appreciable conversion of 2 : 2'-dipyridyldiethylauric ions into dibromodiethylaurate ions, but the addition of benzene to the oil, by removing dipyridyl, assists the displacement of both equilibria to the right, and dibromodiethylaurate ions are precipitated as (XXIV), with unchanged dipyridyldiethylauric ions. That this is essentially the course of events is clear, because the same equilibria may be

demonstrated in dilute aqueous solution. If a dilute solution of 2 : 2'-dipyridyldiethylauric bromide is treated with an excess of potassium bromide, the equilibrium is not displaced sufficiently to cause precipitation of (XXIV). If a similar aqueous solution is extracted with benzene, this also is insufficient, but, when the solution containing added bromide ions is thus extracted, a precipitate of (XXIV) is formed.

By investigating the properties of the 2 : 2'-dipyridyl complex from tetraethylsulphatodigold, the base is again shown to be chelating, and the constitution (XXXI) assigned to the



complex by Gibson and Weller should be modified. The most obvious alternative (XXXI) readily accounts for the fact that 2 : 2'-dipyridyldiethylauric ions may be precipitated from aqueous solution, as the picrate (XIX; Y = picrate), but the existence of the four-membered ring in the anion, containing a large gold atom and three smaller atoms, is known to be highly improbable (Part IX, *J.*, 1941, 109). Further evidence in support of this is provided by cryoscopic measurements of the molecular weight of the complex in nitrobenzene. The apparent molecular weight at infinite dilution is 515, which is almost exactly two-thirds of the value (762) required by the empirical formula  $\text{Et}_4\text{Au}_2\text{SO}_4\text{dipy}$ . Clearly, this is not the value to be expected from (XXXI), which would dissociate into two ions, and the more satisfactory interpretation is that the undissociated compound has a formula  $\text{Et}_8\text{Au}_4(\text{SO}_4)_2\text{dipy}_2$ —twice the empirical formula—and that it dissociates to give three ions. We therefore infer that the complex in nitrobenzene solution has the constitution (XXXII) and can be renamed 2 : 2'-dipyridyldiethylauric tetraethyl- $\mu$ -disulphatodiaurate.\*

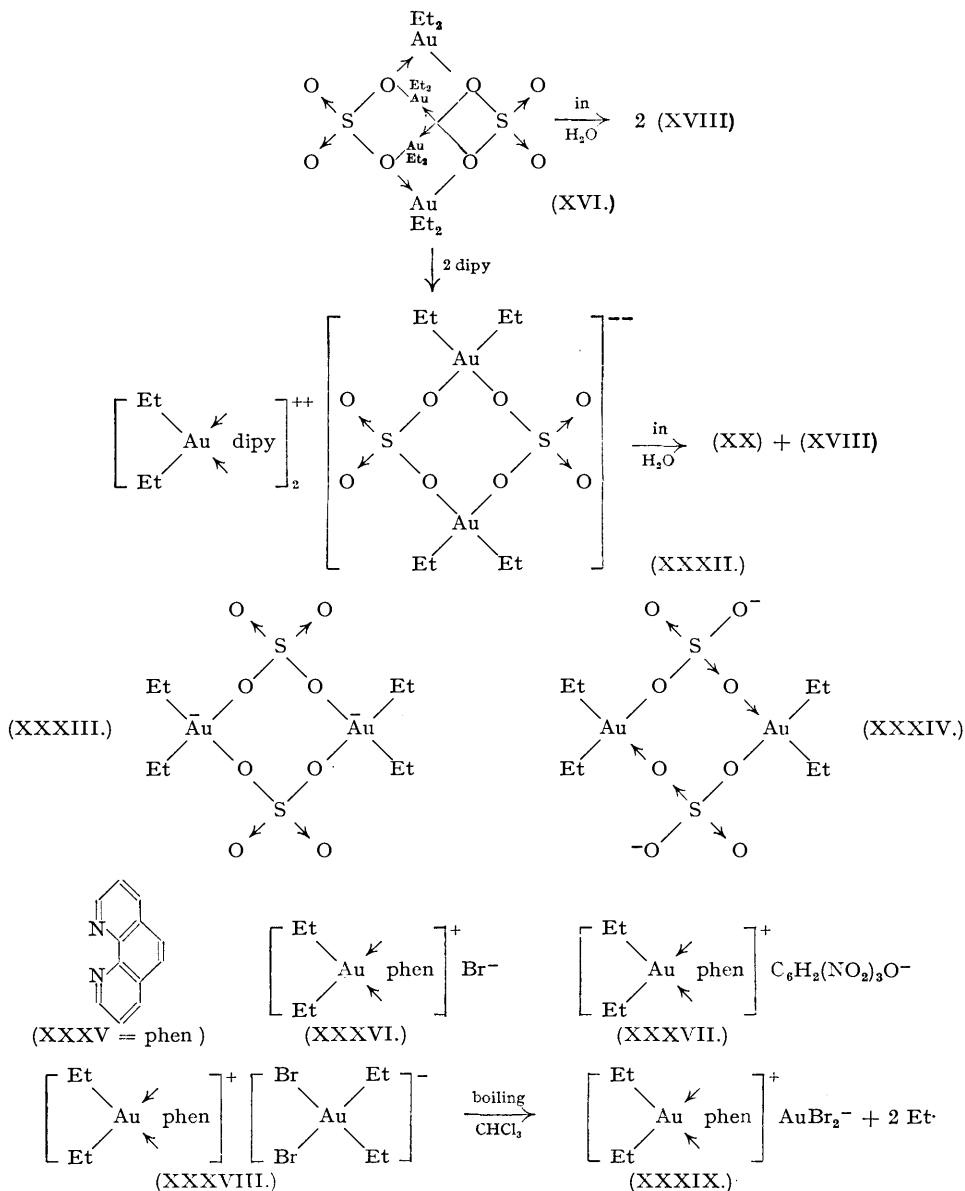


The tetraethyl- $\mu$ -disulphatodiaurate ion, comparable with the dibromodiethylaurate ion occurring in (XXIV), can arise from tetraethylsulphatodigold (XVI) as shown below.

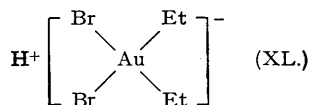
The relative stability of the large anion, containing an eight-membered ring, is undoubtedly associated with the possibility of various resonance forms, of which the two main types are illustrated in (XXXIII) and (XXXIV). In water, however, as with tetraethylsulphatodigold (XVI) which exists as (XVIII) (Part VIII, *loc. cit.*), the gold-oxygen links are broken and (XXXII) is then converted into diaquodiethylauric sulphate (XVIII) and 2 : 2'-dipyridyldiethylauric sulphate (XX). The existence of (XX) in aqueous solution is interesting in view of the failure to isolate it in the solid state, and accounts for the detection of sulphate ions by Gibson and Weller (Part VIII).

Although there is no inherent objection, on steric grounds, to ethylenediamine and 2 : 2'-dipyridyl forming bridged complexes, provided that the two co-ordinating nitrogen atoms are separated sufficiently to allow space for the two large gold atoms, no evidence of such bridging exists. In *o*-phenanthroline (XXXV) the position of the two nitrogen atoms is rigidly fixed and their co-ordination with separate gold atoms becomes sterically impossible. The two compounds,  $\text{Et}_4\text{Au}_2\text{Br}_2\text{phen}$ , and  $\text{Et}_2\text{AuBrphen}$ , formed when *o*-phenanthroline reacts with diethylbromogold in the appropriate proportions, must therefore be *o*-phenanthroline-diethylauric dibromodiethylaurate (XXXVIII) and *o*-phenanthroline-diethylauric bromide (XXXVI). The latter is sparingly soluble in all solvents except methyl and ethyl alcohol, from which it may be recovered unchanged after 30 minutes' boiling, thus demonstrating the stability of the complex cation under these conditions. The addition of picric acid to a solution of (XXXVI) precipitates *o*-phenanthroline-diethylauric picrate (XXXVII). The complex (XXXVIII) resembles its ethylenediamine (X; X = Br) and 2 : 2'-dipyridyl analogues (XXIV)

in properties, particularly in decomposing in boiling chloroform with the loss of two ethyl groups to yield *o*-phenanthrolinodiethylauric bromoaurite (XXXIX).



The isolation of *o*-phenanthrolinodiethylauric dibromodiethylaurate, which has only one possible formulation, is confirmation of the existence of the dibromodiethylaurate ion previously encountered in (X; X = Br) and (XXIV). This same ion may be present in hydrobromic

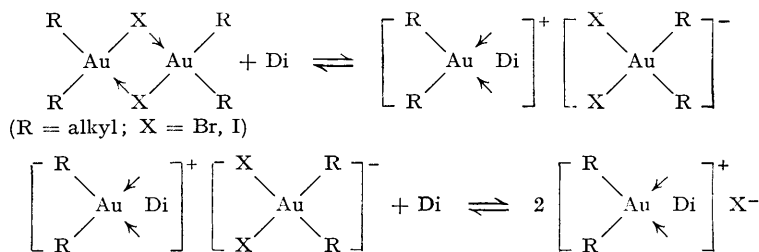


acid solutions of diethylbromogold. Diethylbromogold dissolves to a definite but limited extent in hydrobromic acid solution (0.104 g. per 100 c.c. of *n*-HBr; 0.174 g. per 100 c.c. of



2N-HBr: whereas its solubility in water is 0.01 g. per 100 c.c.); it is not reprecipitated when the acid is neutralised with sodium hydroxide. The compound probably dissolves as hydrogen dibromodiethylaurate (XL) which in the process of neutralisation is converted into its sodium salt.

The reaction between the dialkylhalogenogold compounds and diamines (Di) containing the N-C-C-N grouping may be represented generally as follows:



The diamine disrupts one of the four equivalent Au-X bonds and then, in view of its tendency to form chelate compounds, breaks a second such bond involving the same gold atom. As a result a positively charged  $[\text{R}_2\text{AuDi}]^+$  ion and a negatively charged  $[\text{R}_2\text{AuX}_2]^-$  ion are produced. The latter is then attacked further by the diamine, the Au-X bonds breaking to give two halide ions and another  $[\text{R}_2\text{AuDi}]^+$  cation. Similar schemes may be written to explain the reactions of the dialkylcyanogold and tetra-alkylsulphatodigold compounds with these diamines. Diethylthiocyanatogold, however, is not attacked by diamines, because the co-ordinating power of nitrogen is insufficient to break the strong gold-sulphur bond (Part XI, *loc. cit.*).

Chelation by a diamine increases the stability of the carbon-gold link, so that the alkyl groups in the  $[\text{R}_2\text{AuDi}]^+$  ion tend much less to be split off as the *n*-alkane, R-R, than do the alkyl groups in the parent dialkylhalogenogold compounds or in the  $[\text{R}_2\text{AuX}_2]^-$  anion. Thus, it is found that, of all dialkylgold compounds, those of the type  $[\text{R}_2\text{AuDi}]^+\text{X}^-$  are the most stable.

#### EXPERIMENTAL.

*Ethylenediaminodi-n-propylauric Bromoaurite* (VIb).—Known previously as monoethylenediaminodi-*n*-propylbromodigold, this was prepared as in Part IV (*loc. cit.*) (Found: Au, 56.1. Calc. for  $\text{C}_8\text{H}_{22}\text{N}_2\text{Br}_2\text{Au}_2$ : Au, 56.3%). The molecular weight was determined in nitrobenzene, in presence of  $\text{Na}_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (Roberts and Bury, *J.*, 1923, 2037); concentrations *c* are expressed as g. of solute per kg. of solvent.

$c = 3.02$ ,  $\Delta t = 0.055^\circ$ ,  $M = 378$ ;  $c = 6.03$ ,  $\Delta t = 0.099^\circ$ ,  $M = 420$ ;  $c = 8.21$ ,  $\Delta t = 0.130^\circ$ ,  $M = 435$ .  $\text{C}_8\text{H}_{22}\text{N}_2\text{Br}_2\text{Au}_2$  requires  $M$ , 700.

The nitrobenzene solutions are conducting.

*Ethylenediaminodiethylauric Dicyanodiethylaurate* \* (X; R = Et, X = CN).—Known previously as monoethylenediaminotetraethylidicyanodigold, this was prepared as in Part V (*loc. cit.*) (Found: C, 23.4; H, 4.8; N, 9.4; Au, 63.0. Calc. for  $\text{C}_{12}\text{H}_{28}\text{N}_4\text{Au}_2$ : C, 23.1; H, 4.5; N, 9.0; Au, 63.3%). The molecular weight in nitrobenzene varies as shown in the table below (see also figure) ( $\text{C}_{12}\text{H}_{28}\text{N}_4\text{Au}_2$  requires  $M$ , 623).

<i>c</i> .....	2.91	4.95	7.69	10.11	12.97	18.27	23.77	27.37
$\Delta t$ .....	0.051°	0.075°	0.111°	0.138°	0.174°	0.226°	0.273°	0.302°
<i>M</i> .....	393	455	477	505	514	557	600	625

When a little of the compound was added to pure nitrobenzene, there was a marked increase in conductivity. Under the same conditions, diethylmonocyanogold, a non-electrolyte, produced no change in conductivity.

*Ethylenediaminodiethylauric Dibromodiethylaurate* \* (X; R = Et, X = Br).—Known previously as ethylenediaminotetraethylidibromodigold, this was prepared from diethylbromogold as described in Part VIII (*loc. cit.*) (Found: C, 16.8; H, 3.9; N, 4.0; Au, 53.6. Calc. for  $\text{C}_{10}\text{H}_{28}\text{N}_2\text{Br}_2\text{Au}_2$ : C, 16.4; H, 3.8; N, 3.8; Au, 54.0%). The apparent molecular weight in nitrobenzene varies with concentration as shown (see also figure) ( $\text{C}_{10}\text{H}_{28}\text{N}_2\text{Br}_2\text{Au}_2$  requires  $M$ , 730).

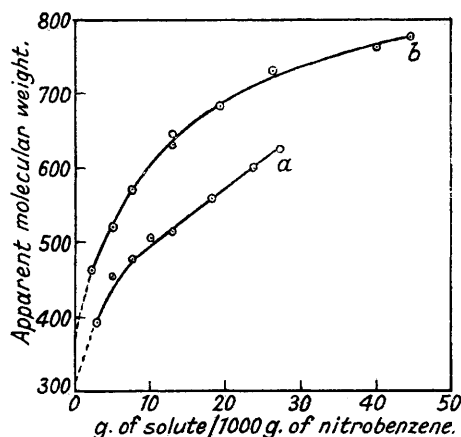
<i>c</i> .....	2.35	4.99	7.61	12.96	12.93	19.39	26.17	40.09	44.58
$\Delta t$ .....	0.035°	0.066°	0.092°	0.142°	0.138°	0.196°	0.247°	0.362°	0.397°
<i>M</i> .....	462	521	570	629	646	682	730	763	774

Addition of the compound to pure nitrobenzene produced a marked increase in conductivity.

*Ethylenediaminodiethylauric Tetraethyl- $\mu$ -disulphatodaurate* \* (XV).—This salt was prepared from tetraethylsulphatodigold, as described in Part VIII for ethylenediaminotetraethylsulphatodigold. It is recrystallised from methyl alcohol and is almost insoluble in bromoform (cf. Gibson and Weller,

Part VIII) (Found : Au, 59.2. Calc. for  $C_{20}H_{56}O_8N_4S_2Au_4$  : Au, 59.2%). Alcoholic solutions are conducting.

2 : 2'-Dipyridyldiethylauric Nitrate (XXIII).—Solutions of diethylbromogold (0.71 g.) in ethanol (12 c.c.), 2 : 2'-dipyridyl (0.33 g.) in ethanol (5 c.c.), and silver nitrate (0.37 g.) in methyl alcohol (5 c.c.) were mixed and shaken for 30 minutes. The mixture was filtered from insoluble silver bromide, and the filtrate evaporated to dryness *in vacuo* at room temperature. The residue was dissolved in chloroform and ligroin (b. p. 40—60°) was added to induce crystallisation. White needles (0.79 g.) separated, melting at 191—192° (decomp.). Chloroform of crystallisation was driven off by heating the salt to constant weight at 80°, and the resulting product was shown by analysis to be 2 : 2'-dipyridyldiethylauric nitrate [Found : C, 35.6; H, 3.84; Au, 41.4;  $NO_3^-$  (by precipitation as nitron nitrate), 13.5.  $C_{14}H_{18}O_3N_2Au$  requires C, 35.8; H, 3.80; Au, 41.6;  $NO_3^-$ , 13.1%]. The chloroform-free substance melted at 191—192° (decomp.) and was readily soluble in water, alcohol, or chloroform, but only sparingly soluble in ligroin, acetone, or benzene.



(a)  $[Et_2Au en] [(CN)_2AuEt_2]$ , formula wt., 623.  
 (b)  $[Et_2Au en] [Br_2AuEt_2]$ , formula wt., 730.

The conductivity of aqueous solutions was measured at 25° with the results shown below :

Concentration in moles ( <i>c</i> )	0.00500	0.00250	0.00109	0.00100
Equivalent conductivity ( $\Lambda$ ), mhos	91.8	94.2	96.6	97.0
( $\sqrt{c}$ )	0.0706	0.0500	0.0330	0.0316

By plotting  $\Lambda$  against  $\sqrt{c}$  and extrapolating to infinite dilution,  $\Lambda_\infty$  is found to be 101 mhos. Since  $\Lambda_{NO_3^-}$  is 71 mhos, the mobility of the 2 : 2'-dipyridyldiethylauric cation must be 30 mhos.

An aqueous solution of 2 : 2'-dipyridyldiethylauric nitrate was treated with saturated aqueous picric acid solution. 2 : 2'-Dipyridyldiethylauric picrate (XIX; Y = picrate) was precipitated; recrystallised from ethanol it had m. p. 190—191° (decomp.) (Found : C, 38.0; H, 3.46; N, 11.1; Au, 30.8.  $C_{20}H_{20}O_7N_2Au$  requires C, 37.6; H, 3.12; N, 11.0; Au, 30.8%). The molecular weight of this picrate was determined in nitrobenzene, and the values in four different concentrations were as follows :

$c = 6.17$ ,  $\Delta t = 0.129^\circ$ ,  $M = 329$ ;  $c = 14.89$ ,  $\Delta t = 0.270^\circ$ ,  $M = 380$ ;  $c = 20.50$ ,  $\Delta t = 0.353^\circ$ ,  $M = 400$ ;  
 $c = 25.95$ ,  $\Delta t = 0.430^\circ$ ,  $M = 416$ .  $C_{20}H_{20}N_2O_7Au$  requires  $M$ , 639.

2 : 2'-Dipyridyldiethylauric Dibromodiethylaurate\* (XXIV).—This was known previously as 2 : 2'-dipyridyltetraethylbromodigold (Brain and Gibson, Part VII, *loc. cit.*). Diethylbromogold (1.56 g.) was mixed with 2 : 2'-dipyridyl (0.73 g., 2 moles) in benzene (15 c.c.). A yellow oil separated, but after careful evaporation of the benzene *in vacuo* at room temperature this oil gave place to a white crystalline solid, which was collected and washed with benzene. This product (1.7 g.) was soluble in acetone, chloroform, or nitrobenzene, but insoluble in water or benzene. It was recrystallised by slow evaporation, *in vacuo* at room temperature, of a solution in chloroform to which a little ligroin (b. p. 40—60°) had been added. The pure compound (1.55 g.) melted with decomposition at 121° (cf. Brain and Gibson, Part VII) (Found : C, 26.1; H, 3.5; Au, 47.3. Calc. for  $C_{18}H_{28}N_2Br_2Au_2$  : C, 26.1; H, 3.4; Au, 47.7%).

The apparent molecular weight in nitrobenzene varies with concentration as follows ( $C_{18}H_{28}N_2Br_2Au_2$  requires  $M$ , 826) :

<i>c</i>	7.4	14.3	16.8	19.9	26.2	28.3	36.9	39.5	42.4	54.1
$\Delta t$	0.110°	0.203°	0.231°	0.277°	0.356°	0.369°	0.475°	0.504°	0.545°	0.666°
$M$	462	484	500	494	508	529	537	540	537	559

From a graph of  $\Delta t$  plotted against *c*, values of  $\Delta t_{obs.}$  were read off for concentrations of 5, 10, 15, 20, 30, 40, and 50 g. of solute per kg. of nitrobenzene, and corresponding values of  $\Delta t_{calc.}$  were calculated for a molecular weight of 826. The ratio  $\Delta t_{obs.}/\Delta t_{calc.}$  (*i*) was then evaluated, for each of these concentrations,

and is seen from the table below to approach 2 with increasing dilution ( $V$ ). When the law of mass action is applied,  $K = \alpha^2/(1 - \alpha)V$ , where  $\alpha =$  degree of dissociation  $= i - 1$ ,  $V =$  dilution in l., and  $K =$  dissociation constant, the values of  $K$  obtained are remarkably constant.

$c$ .....	5.0	10.0	15.0	20.0	30.0	40.0	50.0
$V$ .....	137.6	68.8	45.9	34.4	22.9	17.2	13.8
$\Delta t_{\text{obs.}}$ .....	0.077°	0.145°	0.212°	0.276°	0.396°	0.513°	0.625°
$\Delta t_{\text{calc.}}$ .....	0.042°	0.083°	0.125°	0.167°	0.250°	0.334°	0.417°
$i$ .....	1.833	1.747	1.696	1.653	1.584	1.536	1.499
$K$ .....	0.0310	0.0321	0.0347	0.0357	0.0358	0.0360	0.0360

The conductivity in nitrobenzene at  $25^\circ \pm 0.1^\circ$ , measured in the usual manner, gave the following results:

Concentration ( $\times 10^4$ ), m. ....	2.04	4.67	8.30	11.65	18.2	28.3
$\Lambda$ (mhos) .....	26.7	26.6	26.3	26.0	25.4	24.6

Unlike the ethylenediamine complexes (Gibson and Colles, Part II, *loc. cit.*), dipyriddylic complexes are particularly stable to acid, and prolonged shaking with a large excess of hydrobromic acid was necessary to liberate the parent diethylbromogold, *e.g.*:

The complex (XXIV) (0.72 g.), suspended in water (2 c.c.), was shaken for 48 hours in 5*N*-hydrobromic acid (20 c.c.) in the presence of ligroin (b. p. 40–60°; 20 c.c.). The mixture was then filtered, and the ligroin layer was separated. The aqueous layer was re-extracted with more ligroin, and the combined extracts, after being washed in water, and dried ( $\text{Na}_2\text{SO}_4$ ), were evaporated *in vacuo* at room temperature. The product (0.47 g.; 80%) melted at 58° and was identical with an authentic specimen of diethylbromogold.

When 2 : 2'-dipyriddyldiethylauric dibromodiethylaurate is treated with bromine in chloroform, there is immediately formed 2 : 2'-dipyriddyldiethylauric bromoaurate (XXVII) (*q.v.*). When kept for a long time with an excess of bromine in chloroform, the latter is converted into 2 : 2'-dipyriddyldiethylaurate (XXIX) (*q.v.*).

*Thermal Decomposition of 2 : 2'-Dipyriddyldiethylauric Dibromodiethylaurate.*—(i) *In the solid state.* When (XXIV) was heated in a melting-point tube, decomposition usually occurred at 121°. In some instances, however, no visible changes occurred at this temperature, and decomposition was observed at 169°, the temperature at which 2 : 2'-dipyriddyldiethylauric bromoaurate (XXV) decomposes. The effect of heat on the solid was studied in more detail in a modified Victor Meyer's apparatus, the decomposition tube of which was immersed in a thermostatted oil-bath. The compound was stable when the bath-temperature was below 113°. The rates of gas evolution at 117° and 120° were similar to those obtained in the case of diethylthiocyanatogold (see Fig. 1, Part XI). From 0.205 g. of compound, the volume of gas evolved at each temperature, after correction to N.T.P. was 11.5 ml. If decomposition of 1 molecule of (XXIV) is assumed to yield 2 molecules of butane, the volume of gas to be expected is 11.1 ml. The residue in the decomposition tube consisted of free dipyriddylic, aurous bromide, and a trace of gold.

(ii) *In solution.* When an ethyl-alcoholic solution of the compound was warmed on a water-bath, a vigorous gas evolution was noticed, accompanied by a separation of colourless needles, m. p. 169° (decomp.), of 2 : 2'-dipyriddyldiethylauric bromoaurate (*q.v.*) from the boiling solution.

2 : 2'-Dipyriddyldiethylauric Bromoaurate (XXV).—2 : 2'-Dipyriddyldiethylauric dibromodiethylaurate (0.61 g.) was warmed on a water-bath in absolute alcohol (15 c.c.). The compound dissolved completely in the boiling alcohol, but after a minute a vigorous gas evolution was observed, accompanied by a separation of colourless needles. These were collected, washed with hot alcohol, and dried (0.50 g.). The crude bromoaurate was purified by dissolving it in dry acetone and evaporating the solution carefully *in vacuo* at room temperature. Yield, 0.34 g.; m. p. 169° (decomp.) (Found: C, 22.4; H, 2.6; N, 4.1; Au, 51.3.  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{Br}_2\text{Au}_2$  requires C, 21.9; H, 2.3; N, 3.7; Au, 51.3%). The compound is sparingly soluble in water, ethanol, benzene, or chloroform, but dissolves readily in acetone or nitrobenzene, giving conducting solutions.

The molecular weight in nitrobenzene varies with concentration as follows ( $\text{C}_{14}\text{H}_{18}\text{N}_2\text{Br}_2\text{Au}_2$  requires  $M$ , 768):

$c$ .....	5.66	12.1	18.6	24.9	31.2	37.8	50.2
$\Delta t$ .....	0.091°	0.187°	0.274°	0.354°	0.436°	0.509°	0.669°
$M$ .....	428	440	466	496	493	511	517

These results were treated in the same manner as those from 2 : 2'-dipyriddyldiethylauric dibromodiethylaurate (*q.v.*), and values of the ratio  $\Delta t_{\text{obs.}}/\Delta t_{\text{calc.}}$  [(*i*)] and of  $K$  were evaluated for concentrations of 5, 10, 15, 20, 30, 40, and 50 g. of solute per kg. of nitrobenzene. Again, the value of  $i$  approaches 2 with increasing dilution ( $V$ ), and  $K$  is remarkably constant.

$c$ .....	5	10	15	20	30	40	50
$V$ .....	128	64	42.7	32	21.3	16	12.8
$\Delta t_{\text{obs.}}$ .....	0.083°	0.157°	0.227°	0.295°	0.420°	0.543°	0.667°
$\Delta t_{\text{calc.}}$ .....	0.045°	0.090°	0.135°	0.180°	0.269°	0.359°	0.449°
$i$ .....	1.845	1.744	1.682	1.639	1.561	1.512	1.486
$K$ .....	0.0360	0.0338	0.0343	0.0354	0.0337	0.0337	0.0359

*Thermal Decomposition of 2 : 2'-Dipyriddyldiethylauric Bromoaurate (XXV).*—(i) *In the solid state.* When heated in a melting-point tube, decomposition occurred at 169°. Decomposition was studied more carefully using the modified Victor Meyer's apparatus, with the bath-temperature at 165°. The volume of gas evolved from 0.344 g. of compound was 10.9 ml. (corrected to N.T.P.). The volume to be expected, on the assumption that each molecule of (XXV) yields one molecule of butane, is 10.0 ml.

(ii) *In solution.* When the compound was warmed in boiling toluene or xylene, there were obvious signs of decomposition, and highly coloured reddish-brown substances separated from solution. These solids were typical of bromoaurates, but the gold content varied from preparation to preparation, and because of their sparing solubility it was not possible to purify them or establish their identity.

2 : 2'-Dipyridyldiethylauric Bromoaurate (XXVII).—2 : 2'-Dipyridyldiethylauric dibromodiethylaurate (0.5 g.) in chloroform (5 c.c.) was treated with a solution of bromine (2 mols.) in chloroform, and there was an immediate separation of golden-brown needles. These were collected by centrifuging, and the compound (0.45 g.) was obtained pure by washing with 10 c.c. each of chloroform and carbon tetrachloride. When heated in a melting-point tube, it decomposes slowly above 195°, melting finally with decomposition at 223° (Found : C, 18.3; H, 1.95; Au, 42.5%; *M*, in nitrobenzene, 527, 583.  $C_{14}H_{18}N_2Br_4Au_2$  requires C, 18.1; H, 1.94; Au, 42.5%; *M*, 928). It is sparingly soluble in most of the common solvents, except acetone which it brominates.

The compound was also prepared by mixing monoethylgold (0.5 g.) (Part III, *J.*, 1934, 860) and 2 : 2'-dipyridyl (0.5 g.) in chloroform (45 c.c.). The reddish-brown precipitate (0.52 g.) was collected and washed with chloroform (Found : Au, 42.2%).

2 : 2'-Dipyridyl Dibromoaurate (XXIX).—2 : 2'-Dipyridyldiethylauric dibromodiethylaurate (0.35 g.) dissolved in chloroform (3 c.c.) was treated with a large excess (>4 mols.) of bromine in chloroform. 2 : 2'-Dipyridyldiethylauric dibromoaurate separated immediately, but, after the mixture had been stored overnight, this had given place to magenta needles. These were collected, washed with carbon tetrachloride, and dried (0.48 g.) (Found : C, 10.6; H, 0.86; Au, 32.9.  $C_{10}H_{10}N_2Br_2Au_2$  requires C, 10.1; H, 0.84; Au, 33.1%). The compound decomposes slowly above 285°, melting finally with decomposition at 305°. It is fairly soluble in water.

2 : 2'-Dipyridyldibromoauric Bromoaurate (XXVIII).—Tribromogold (0.82 g.) (Part II, *loc. cit.*) was dissolved in aqueous potassium bromide (0.4 g. in 20 c.c. of water). The resulting solution of potassium bromoaurate was filtered off, and then stirred while 2 : 2'-dipyridyl (0.2 g.) in methanol (5 c.c.) was added. The orange-red bromoaurate (0.63 g.) was collected, washed with water, and dried (Found : Au, 38.2.  $C_{10}H_8N_2Br_6Au_2$  requires Au, 38.2%). When heated in a melting-point tube it sintered above 200°, finally melting with decomposition at 270°. It was sparingly soluble in all the usual solvents except acetone, which it brominated.

By treatment with hydrobromic acid, (XXVIII) was converted into 2 : 2'-dipyridyl dibromoaurate (*q.v.*) (Found : Au, 33.0%).

*Reaction of Diethylgold with 2 : 2'-Dipyridyl in Aqueous Solution.*—Diethylgold (0.3 g.) and 2 : 2'-dipyridyl (0.14 g.) were shaken together in distilled water (15 c.c.) in a stoppered bottle. Both compounds quickly dissolved, in spite of their individual sparing solubility in water. When a portion of the filtered solution was treated with aqueous picric acid, there was immediate precipitation of a golden-yellow picrate, which was collected, recrystallised from ethyl alcohol, and shown to be 2 : 2'-dipyridyldiethylauric picrate (XIX; Y = picrate). The remaining solution was evaporated at reduced pressure and room temperature to a syrup (0.43 g.). When this syrup was stirred with benzene, crystals of 2 : 2'-dipyridyldiethylauric dibromodiethylaurate (0.22 g.), m. p. 121° (decomp.), separated, and the filtered benzene contained free dipyridyl.

A second aqueous solution, obtained likewise, was shaken with benzene and remained unchanged; when, however, its bromide ion concentration was increased by addition of solid potassium bromide and the resulting solution was shaken with a fresh portion of benzene, there separated, at the interface of the benzene and aqueous layers, a colourless precipitate of 2 : 2'-dipyridyldiethylauric dibromodiethylaurate.

2 : 2'-Dipyridyldiethylauric Tetraethyl-*μ*-disulphatodiaurate\* (XXXII).—Diethylgold (2.5 g.), dissolved in a mixture of ligroin (b. p. 40—60°; 15 c.c.) and absolute alcohol (5 c.c.), was shaken with finely powdered silver sulphate (3 g.) for 6 hours in a stoppered bottle. The contents were then filtered, the insoluble matter was washed well with acetone, and the filtrate and washings were evaporated to dryness, to give a residue of crude tetraethylsulphatodigold (XVI) (2.2 g.). This solid was dissolved in a minimum of ethanol and mixed with an ethanolic solution of 2 : 2'-dipyridyl (0.58 g.). The solution was evaporated *in vacuo* at room temperature, and the dipyridyl complex which separated was recrystallised from hot ethanol, containing a trace of acetone. The compound (0.86 g.), m. p. 161° (decomp.), exhibited the properties previously described by Gibson and Weller (Part VIII, *loc. cit.*). It gave 2 : 2'-dipyridyldiethylauric picrate (XIX; Y = picrate) when picric acid was added to its aqueous solution.

The molecular weight, measured in nitrobenzene, varied with concentration as shown below :

<i>c</i> .....	6.27	12.09	18.07	23.60	29.42
$\Delta t$ .....	0.067°	0.109°	0.144°	0.164°	0.181°
<i>M</i> .....	646	764	865	999	1120

When *M* is plotted against *c*, a straight line results, and, by extrapolation, the apparent molecular weight at infinite dilution (*c* = 0) is found to be 515, or approximately one-third of the formula weight ( $C_{36}H_{56}O_8N_4S_2Au_4$  requires *M*, 1524).

*o*-Phenanthrolinodiethylauric Bromide (XXXVI).—Diethylgold (1.01 g.) was dissolved in light petroleum (b. p. 40—60°; 15 c.c.), and to this solution was added *o*-phenanthroline hydrate (0.58 g., 2 mols.) in ethyl alcohol (5 c.c.). The white precipitate which separated was collected and washed thoroughly with ligroin to remove unchanged reactants. The crude product was purified by dissolving it in cold methyl alcohol, filtering, and evaporating the alcoholic solution *in vacuo* at room temperature. The pure bromide (0.98 g.) separated as colourless needles, m. p. 173° (decomp.) (Found : C, 36.9; H, 3.58; Au, 38.3.  $C_{14}H_{18}N_2BrAu$  requires C, 37.3; H, 3.48; Au, 38.3%). *o*-Phenanthrolinodiethylauric bromide was sparingly soluble in cold or hot water, soluble in cold methyl or ethyl alcohol, very slightly soluble in ligroin, chloroform, dioxan, or nitrobenzene. It was stable on storage and showed no tendency to darken when exposed to light. It was recovered unchanged after being boiled under

reflux for 30 minutes in methanol. The addition of aqueous picric acid to an alcoholic solution of the compound (0.25 g.) precipitated an insoluble picrate (0.37 g.), m. p. 209—210° (decomp.), shown by analysis to be *o*-phenanthroline diethylauric picrate (XXXVII) (Found: Au, 29.9.  $C_{22}H_{20}O_7N_3Au$  requires Au, 29.7%).

*o*-Phenanthroline diethylauric dibromodiethylaurate (XXXVIII).—Diethylbromogold (0.5 g.) was dissolved in light petroleum (b. p. 40—60°; 5 c.c.) and stirred continuously during the addition of a solution of *o*-phenanthroline hydrate (0.15 g., 1 mol.) in ethanol (10 c.c.). The white precipitate which separated was collected, washed with ligroin, and dried. The compound (0.6 g.) prepared in this way was pure and melted with decomposition at 153°. It can be recrystallised by dissolving it in cold chloroform and then carefully evaporating off the solvent *in vacuo* at room temperature (Found: C, 28.0; H, 2.9; Au, 46.4.  $C_{20}H_{28}N_2Br_2Au_2$  requires C, 28.2; H, 3.3; Au, 46.3%). In cold solvents, except chloroform, the compound is very sparingly soluble. When warmed in solution it undergoes decomposition to give (XXXIX) (see below).

*o*-Phenanthroline diethylauric bromoaurite (XXXIX).—The preceding compound (0.25 g.) was heated carefully under reflux in chloroform (25 c.c.) for 10 minutes. After 5 minutes, a colourless crystalline compound separated from the refluxing solution. The product (0.1 g.), colourless plates, m. p. 182° (decomp.), was collected, washed with a little cold chloroform, and dried (Found: Au, 49.8.  $C_{16}H_{18}N_2Br_2Au_2$  requires Au, 49.8%).

*The Solubility of Diethylbromogold in Hydrobromic Acid.*—Diethylbromogold (0.5 g.) was shaken for 3 hours with *n*-hydrobromic acid (100 c.c.) at room temperature. Undissolved compound was then separated, and the acid filtrate neutralised with sodium hydroxide. No precipitation occurred. The solution was made strongly alkaline, a little solid sodium dithionite was added, and the mixture was boiled to coagulate the precipitated gold. The gold, when collected and dried, weighed 0.06 g., equivalent to 0.104 g. of diethylbromogold. From a similar experiment with 2*N*-acid, 0.102 g. of gold was collected, equivalent to 0.174 g. of diethylbromogold. In a blank determination with distilled water (100 c.c.) only 0.012 g. of diethylbromogold dissolved.

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