# 136. *Nitrogenous Chelate Complexes of Transition Metals. Part I. The Constitution and Properties of the* 1 : 10-*Phenanthroline Complexes of Tervalent Gold.*

By C. M. Harris.

The structure of the 1 : 10-phenanthroline (phen) complexes of gold(III) halides has been investigated in nitrobenzene and acetone solutions by means of conductometric and spectrophotometric measurements. The low molecular conductivities of the compounds $AuX_3$,phen (X = Cl, Br) in these solvents are due to the rapid rearrangement of $2[Au(phen)X_2]^+ + 2X^- \rightleftharpoons [Au(phen)X_2]^+ + [AuX_4]^- +$ phen resulting from the ready reaction of halide with the dihalogeno-(1 : 10-phenanthroline)gold(III) ion in non-aqueous solution. A possible explanation of this is given in terms of the ability of gold(III) to utilise two additional $6p6d$ bonds perpendicular to its normal $5d6s6p^2$ planar arrangement.

The molecular conductivities (see Table 1) of the tervalent gold complexes $[Au(phen)X_2]X$ (X = Cl, Br; phen = 1 : 10-phenanthroline) were recently found to be of the order of 16—17 mho in nitrobenzene ($10^{-3}$M to $5 \times 10^{-4}$M) at 25°. These are much less than the values, 25—35 mho, usually associated with uni-univalent electrolytes in this solvent under comparable conditions. Since then, the perchlorates $[Au(phen)X_2]ClO_4$ (X = Cl, Br) have been shown to possess molecular conductivities (see Table 1) having twice the value of these simple halides. This suggests that the gold(III) halide complexes, $AuX_3$,phen, are not completely present as dihalogeno-(1 : 10-phenanthroline)gold(III) ions and halide ions when dissolved in nitrobenzene.

Table 1. *Molecular conductivities* (Λ) *in nitrobenzene at* 25°.

| Compound | Concn. (M) | Λ (mho) | Compound | Concn. (M) | Λ (mho) |
|---|---|---|---|---|---|
| $[Au(phen)Cl_2]Cl$ | $5·85 \times 10^{-4}$ | 15·7 | $[Au(phen)Cl_2][AuCl_4]$ | $5·7 \times 10^{-4}$ | 27·7 |
| $[Au(phen)Br_2]Br$ | $1·0 \times 10^{-3}$ | 16·9 | $[Au(phen)Br_2][AuBr_4]$ | $7·0 \times 10^{-4}$ | 27·1 |
| $[Au(phen)Cl_2]ClO_4$ | $2·5 \times 10^{-4}$ | 33·0 | $[PhenH][AuCl_4]$ | $1·23 \times 10^{-3}$ | 29·7 |
| $[Au(phen)Br_2]ClO_4$ | $1·0 \times 10^{-3}$ | 33·1 | $[PhenH][AuBr_4]$ | $1·0 \times 10^{-3}$ | 33·0 |

Table 2. *Molecular conductivities in acetone at* 25°.

| Compound | Concn. (M) | Λ (mho) | Compound | Concn. (M) | Λ (mho) |
|---|---|---|---|---|---|
| $[Au(phen)Cl_2]Cl$ | $2·3 \times 10^{-4}$ | 52·5 | $[Au(phen)Br_2][AuBr_4]$ | $1·0 \times 10^{-3}$ | 135 |
| $[Au(phen)Br_2]Br$ | $1·0 \times 10^{-3}$ | 55·4 | | $5·0 \times 10^{-4}$ | 192 |
| $[Au(phen)Br_2]ClO_4$ | $1·0 \times 10^{-3}$ | 153 | $[NEt_4][AuBr_4]$ | $5·0 \times 10^{-4}$ | 194 |
| $[Au(phen)Cl_2][AuCl_4]$ | $2·5 \times 10^{-4}$ | 193 | $Na[AuCl_4],2H_2O$ | $3·0 \times 10^{-4}$ | 166 |

A possible explanation of this conductivity difference between the halides $[Au(phen)X_2]X$

and the perchlorates [Au(phen)$X_2$]$ClO_4$ is the reaction in this solvent of halide ions with the complex gold cation thus:

$$[Au(phen)X_2]^+ + 2X^- \rightleftharpoons [AuX_4]^- + phen$$

This would satisfactorily account for the molecular conductivities of the simple halides being approximately half those of the perchlorates, since two moles of [Au(phen)$X_2$]X would form one mole of [Au(phen)$X_2$][Au$X_4$] and one mole of 1 : 10-phenanthroline. Foss and Gibson [2] postulated this type of equilibrium in aqueous solution for 2 : 2′-dipyridyldiethylgold(III) bromide because they could isolate only the dibromodiethylaurate(III) derivative [Au$Et_2$(dipy)][Au$Et_2Br_2$]. Block and Bailar [1] have also observed that the 2 : 2′-dipyridyl compound [Au(dipy)$Cl_2$]Cl could be prepared from alcohol solution only impure and is readily converted by water, or gentle heating, into the tetrachloroaurate(III) derivative, [Au(dipy)$Cl_2$][Au$Cl_4$]. The 1 : 10-phenanthroline compounds, [Au(phen)$X_2$]X

FIG. 1. FIG. 2.

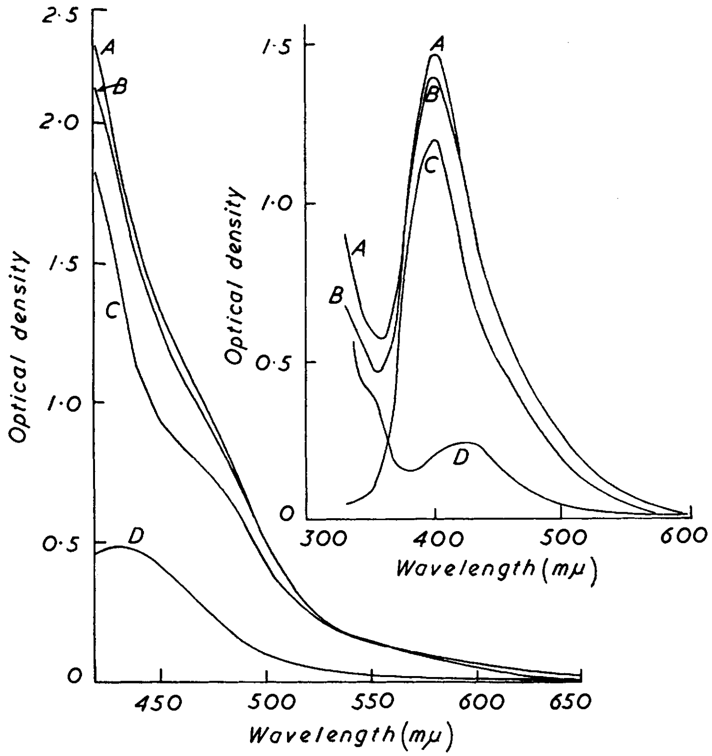

FIG. 1. *Absorption spectra of gold complexes in nitrobenzene* (1·33 *mm. cell*).
*A*. 3·33 × $10^{-3}$M-[Au(phen)$Br_2$][Au$Br_4$] and also composite curve, *C* + *D*.
*B*. 6·67 × $10^{-3}$M-Au(phen)$Br_3$.
*C*. 3·33 × $10^{-3}$M-[N$Et_4$][Au$Br_4$].
*D*. 3·33 × $10^{-3}$M-[Au(phen)$Br_2$]$ClO_4$.

FIG. 2. *Absorption spectra of gold complexes in acetone* (0·5 *cm. cell*).
*A*. $10^{-3}$M-Au(phen)$Br_3$.
*B*. Composite curve, *C* + *D*.
*C*. 5 × $10^{-4}$M-[N$Et_4$][Au$Br_4$].
*D*. 5 × $10^{-4}$M-[Au(phen)$Br_2$]$ClO_4$.

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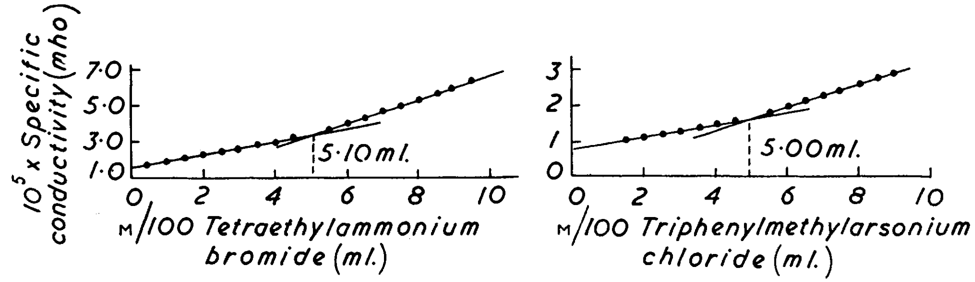
[1] Block and Bailar, *J. Amer. Chem. Soc.*, 1951, **73**, 4722.
[2] Foss and Gibson, *J.*, 1949, 3063.

($X = Cl, Br$), are not converted by water into the tetrahalogenoaurate(III) derivatives, $[Au(phen)X_2][AuX_4]$, and Block and Bailar were able to isolate the nitrate, $[Au(phen)Cl_2]NO_3$, from an aqueous solution of the chloride. The perchlorates, $[Au(phen)X_2]ClO_4$ ($X = Cl, Br$), were similarly prepared by the author.

The bromide $[Au(phen)Br_2]Br$ was examined spectrophotometrically in $6{\cdot}67 \times 10^{-3}$M-nitrobenzene in the range 4200—6500 Å (see Fig. 1). The shape of this curve is somewhat similar to that of the $[AuBr_4]^-$ ion which was measured in the form of the tetraethylammonium salt, $[NEt_4][AuBr_4]$, in $3{\cdot}33 \times 10^{-3}$M-solution. The dibromo-(1 : 10-phenanthroline)gold(III) ion, measured as its perchlorate in $3{\cdot}33 \times 10^{-3}$M-solution, absorbed at 4320 Å. The composite curve, constructed from the separate curves of the $[Au(phen)Br_2]^+$ and $[AuBr_4]^-$ ions, is almost identical with the absorption curve of $3{\cdot}33 \times 10^{-3}$M-$[Au(phen)Br_2][AuBr_4]$. This clearly supports the postulated equilibrium and indicates that in nitrobenzene the reaction is largely complete. Similar results were also obtained for $10^{-3}$M-$[Au(phen)Br_2]Br$. These spectrophotometric measurements are further supported by the conductometric titration of $[Au(phen)Br_2]ClO_4$ with tetraethylammonium bromide in nitrobenzene. A sharp end-point (see Fig. 3), corresponding to the addition of 2 g.-ions of bromide to one of the complex gold(III) cation was obtained. That this equilibrium occurred with the chloride also, was demonstrated by a similar conductometric titration of the chloro-complex, $[Au(phen)Cl_2]ClO_4$, with triphenylmethylarsonium chloride (see Fig. 4). The chloro-compounds are not amenable to spectrophotometric measurements in nitrobenzene since solvent absorption prevents measurements below 4200 Å.

FIG. 3. FIG. 4.



FIGS. 3 and 4. *Conductometric titrations of gold complexes in nitrobenzene at* 25°.

Fig. 3: Titration of 50 ml. of M/2000-$[Au(phen)Br_2]ClO_4$ by bromide.

Fig. 4: Titration of 1000 ml. of M/4000-$[Au(phen)Cl_2]ClO_4$ by chloride.

The same type of equilibrium occurs with these compounds in acetone, as shown by their molecular conductivities (see Table 2). However, the solutions are not stable, and the compounds $[Au(phen)X_2]X$ appear to be slowly reduced since the solutions gradually fade. The bromide was examined spectrophotometrically in this solvent in the range 3300—6000 Å and, within the order of experimental error, a $10^{-3}$M-solution of $[Au(phen)Br_2]Br$ gave a curve almost identical with that of a $5 \times 10^{-4}$M-solution of $[Au(phen)Br_2][AuBr_4]$ as well as a composite curve constructed from those for $5 \times 10^{-4}$M-$[NEt_4][AuBr_4]$ and $5 \times 10^{-4}$M-$[Au(phen)Br_2]ClO_4$ (see Fig. 2).

The fact that the equilibrium reaction with these gold(III) halide complexes of 1 : 10-phenanthroline occurs in acetone and nitrobenzene, and does not apparently take place to any extent in water, can be attributed to the higher solvation energies of the reacting ions in water than in either acetone of nitrobenzene. This type of equilibrium explains the failure of Block and Bailar [1] to obtain compounds with two molecules of phenanthroline per gold atom. Such compounds could presumably only be obtained in the absence of halogens or other groups which show a similar tendency to co-ordinate to the gold(III) atom and replace the chelate.

The behaviour of these nitrogenous gold compounds can be compared with those of the isoelectronic platinum(II) and also with those of palladium(II). The ions $[Pd(chel)_2]^{2+}$ (chel = 1 : 10-phenanthroline or 2 : 2′-dipyridyl)[2a] and $[Pt(dipy)_2]^{2+}$ [2b] can be isolated as perchlorates or tetrachloroplatinates(II), whereas in the presence of chloride ions, they are readily converted into the non-electrolytes $[M(chel)X_2]$ (M = Pd, Pt).

## EXPERIMENTAL

1 : 10-*Phenanthrolinium Tetrachloroaurate*(III).—1 : 10-Phenanthroline monohydrate (0·20 g.) dissolved in water (10 ml.) and 5N-hydrochloric acid (1·0 ml.) was treated with a solution of $NaAuCl_4,2H_2O$ (0·34 g.) in water (10 ml.) containing 5N-hydrochloric acid (1·0 ml.). The yellow precipitate was washed with water, acidified with a few drops of hydrochloric acid, and then with small amounts of 95% ethanol. The yellow microcrystalline compound was dried ($P_2O_5$) under vacuum (Found: C, 28·0; H, 1·9; Au, 37·8. $C_{12}H_9N_2Cl_4Au$ requires C, 27·7; H, 1·7; Au, 37·9%). The *compound* was soluble in acetone and ethanol forming yellow solutions.

1 : 10-*Phenanthrolinium Tetrabromoaurate*(III).—This *compound* was prepared similarly to the above chloro-compound. The deep red microcrystals were insoluble in water, soluble in acetone and slightly soluble in cold 95% ethanol (Found: C, 20·7; H, 1·4; Au, 28·2. $C_{12}H_9N_2Br_4Au$ requires C, 20·6; H, 1·3; Au, 28·2%).

*Tetraethylammonium Tetrabromoaurate*(III).—This *compound* was obtained as insoluble red microcrystals by mixing aqueous solutions of tetraethylammonium bromide and sodium tetrachloroaurate(III) dihydrate containing excess of potassium bromide. The precipitate was washed with cold water and dried ($P_2O_5$) (Found: C, 15·0; H, 2·9; Au, 30·4. $C_8H_{20}NBr_4Au$ requires C, 14·85; H, 3·1; Au, 30·5%).

*Dichloro*-(1 : 10-*phenanthroline*)*gold*(III) *Chloride*.—To a boiling solution of 1 : 10-phenanthroline monohydrate (0·55 g.) in water (40 ml.) was added sodium tetrachloroaurate(III) dihydrate (0·90 g.) in water (20 ml.), with stirring. The pale yellow precipitate of $[Au(phen)Cl_2][AuCl_4]$ which was first deposited, dissolved when boiled for a few min. The addition of finely powdered ammonium chloride (15 g.) then gave an immediate orange precipitate. The solution was stirred until all the ammonium chloride had dissolved, and then cooled to room temperature. The orange compound was filtered off and washed with small amounts of ethanol followed by dry ether; yield of vacuum-dried material, 0·80 g. (Found: Cl, 22·4; Au, 40·4. Calc. for $C_{12}H_8N_2Cl_3Au$: Cl, 22·0; Au, 40·8%). This compound was soluble in cold water, yielding an acid solution which turned blue litmus red.

*Dichloro*-(1 : 10-*phenanthroline*)*gold*(III) *Perchlorate*.—To an aqueous solution (25 ml.) of sodium tetrachloroaurate(III) dihydrate (0·40 g.) was added 1 : 10-phenanthroline monohydrate (0·26 g.), and the resulting mixture boiled for some minutes. The boiling solution was treated dropwise with a solution (5·0 ml.) of sodium perchlorate (2·0 g.). The yellow crystals were filtered off, and washed with distilled water and then small amounts of cold acetone, followed by dry ether; yield of vacuum-dried material, 0·27 g. (Found: C, 26·7; H, 1·8; N, 4·8; Au, 35·9. $C_{12}H_8O_4N_2Cl_3Au$ requires C, 26·3; H, 1·5; N, 5·1; Au, 36·0%).

*Dibromo*-(1 : 10-*phenanthroline*)*gold*(III) *Bromide*.—A solution of sodium tetrachloroaurate(III) dihydrate (4·0 g.) in water (100 ml.) was treated with 1 : 10-phenanthroline monohydrate (4·2 g.) in hot water (200 ml.). The clear solution was treated, while hot, with potassium bromide (5·0 g.) in the minimum amount of hot water. There was an immediate precipitate of dark reddish-brown crystals. On cooling, the compound was filtered off, washed with water, and dried at 100°; yield 5·7 g. (Found: Au, 31·7. Calc. for $C_{12}H_8N_2Br_3Au$: Au, 31·95%).

*Dibromo*-(1 : 10-*phenanthroline*)*gold*(III) *Perchlorate*.—A solution (600 ml.) of the preceding bromide (0·50 g.) in boiling water was treated with a hot solution (80 ml.) of ammonium perchlorate (12 g.). The dark yellow precipitate was filtered off from the cooled solution and washed well with cold water followed by small amounts of ethanol and dry ether; yield of

[2a] Livingstone, *J. Proc. Roy. Soc., N.S.W.*, 1951, **85**, 151; 1952, **86**, 32.
[2b] Morgan and Burstall, *J.*, 1934, 965.

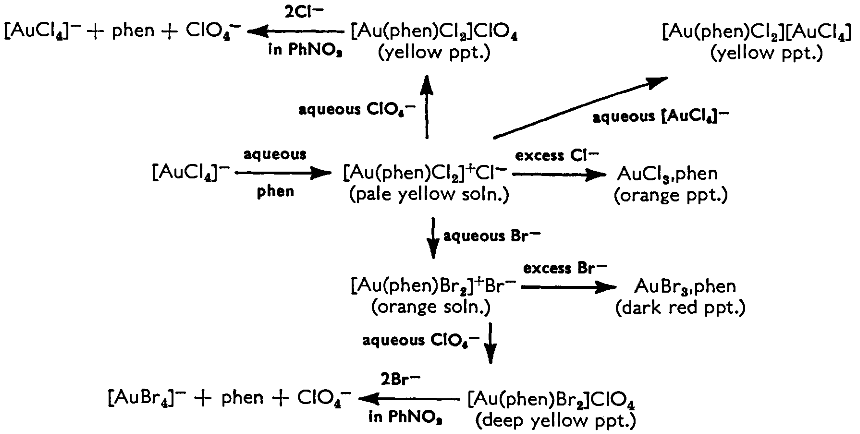
vacuum-dried material, 0·40 g. (Found: C, 23·1; H, 1·4; N, 4·5; Au, 31·5. $C_{12}H_8O_4N_2ClBr_2Au$ requires C, 22·6; H, 1·3; N, 4·4; Au, 31·0%).

*Dichloro-*(1 : 10*-phenanthroline*)*gold*(III) *Tetrachloroaurate*(III).—A boiling solution (50 ml.) of 1 : 10-phenanthroline monohydrate (0·20 g.) was treated dropwise with a hot solution (15 ml.) of sodium tetrachloroaurate(III) dihydrate (0·80 g.). After a few minutes' heating the yellow crystals were filtered off, and washed with cold water, absolute ethanol, and dry ether; yield of vacuum-dried material, 0·80 g. (Found: C, 18·5; H, 1·0; N, 3·7; Au, 49·9. Calc. for $C_{12}H_8N_2Cl_6Au_2$: C, 18·3; H, 1·0; N, 3·6; Au, 50·1%).

*Dibromo-*(1 : 10*-phenanthroline*)*gold*(III) *Tetrabromoaurate*(III).—A warm stirred solution of sodium tetrachloroaurate(III) dihydrate (1·0 g.) and sodium bromide (4·0 g.) in water (30 ml.) was treated slowly with a boiling solution (25 ml.) of 1 : 10-phenanthroline monohydrate (0·25 g.). The precipitate was filtered from the hot solution and washed with water followed by cold acetone. The acetone appeared to remove an orange compound and leave dark red micro-crystals of the required *compound* (Found: C, 13·9; H, 0·8; Au, 37·4. $C_{12}H_8N_2Br_6Au_2$ requires C, 13·7; H, 0·8; Au, 37·42%).

## DISCUSSION

The reactions studied in this investigation are summarised below and provide an interesting example of the change in relative reactivity of complex ions on passing from aqueous to non-aqueous media. For example, the dihalogeno-(1 : 10-phenanthroline)-gold(III) ion can be readily obtained in aqueous solution by treating the tetrahalogeno-aurate(III) ion with 1 : 10-phenanthroline, whereas in solvents of lower dielectric constant and smaller solvating ability, such as nitrobenzene and acetone, the $[Au(phen)X_2]^+$ ions (X = Cl, Br) readily pass to the $[AuX_4]^-$ ions (X = Cl, Br) in the presence of halide ions. The instantaneous nature of this reaction in non-aqueous solution, and the much deeper colour of the halides $AuX_3$,phen (X = Cl, Br) than of the corresponding perchlorates $[Au(phen)X_2]ClO_4$ (X = Cl, Br) in the solid state, call for comment.



Tervalent gold is usually square-co-ordinated in its compounds,[3,4,5] and this square-planar configuration together with the diamagnetism of gold(III) compounds is consistent with the use by gold of $5d6s6p^2$ bonds. Harris and Nyholm[6] have recently prepared sexicovalent gold(III) complexes of the type $[Au(diarsine)_2X_2]ClO_4$ (X = Br and I; and diarsine = *o*-phenylenebisdimethylarsine), and the formation of these complexes has been

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[3] Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1st Edn., 1947, p. 508; 2nd Edn., 1950, p. 625.

[4] Sidgwick, " The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, Vol. 1, pp. 177—192.

[5] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 2nd Edn., 1948, pp. 100—102.

[6] Harris and Nyholm, *J.*, 1957, 63—70.

interpreted in terms of collinear $6p6d$ bonds from gold binding the two halogens at right angles to the $5d6s6p^2$ bond hybrids which hold the four arsenic atoms in a square plane. It is expected that this type of sexicovalent arrangement should be distorted with elongated gold-halogen bonds, owing to the repulsion effect of the filled $5d_{z^2}$ gold orbital normal to the plane of the square. This type of structure has been shown to occur with the diarsine complexes of Ni(II), Pd(II), and Pt(II) of general formula $[M(diarsine)_2X_2]$.[7] A distorted octahedral arrangement for gold(III) can also be seen in the structures of the intensely coloured complexes $Cs_2[AgCl_2][AuCl_4]$ and $Cs_2[AuCl_2][AuCl_4]$ studied by Elliot and Pauling.[8] Owing to packing in the crystal two additional Au(III)–Cl bonds are observed at 3·1 Å. These are perpendicular to the $[AuCl_4]^-$ plane which contains Au(III)–Cl bonds at 2·42 Å in length.

The reactions and colours of the 1 : 10-phenanthroline complexes studied in these investigations can be interpreted in terms of the formation of additional $6p_z6d_{z^2}$ collinear bonds at the gold(III) atom. For example, we believe that in view of the above discussion, the markedly deeper colour of the halides $AuX_3$,phen (X = Cl,Br) than of the corresponding perchlorates $[Au(phen)X_2]ClO_4$ (X = Cl,Br) is probably due to the presence in the crystal of two additional elongated gold · · · halogen bonds perpendicular to a planar dihalogeno-(1 : 10-phenanthroline)gold(III) ion, thus:

$$Au(phen)X_2 \cdots\cdots X \cdots\cdots Au(phen)X_2 \cdots\cdots X \cdots\cdots Au(phen)X_2 \cdots\cdots$$

This type of structure also gives a reasonable mechanism for the very rapid rearrangement of $AuX_3$,phen molecules in nitrobenzene and in acetone and for the conductometric titrations of the $[Au(phen)X_2]^+$ ions with halide ions in these solvents. The ready ionisation of these molecules in water to $[Au(phen)X_2]^+$ and $X^-$ ions can be ascribed to the much greater solvation energy associated with water than with the non-aqueous solvents, nitrobenzene and acetone. Support for these ideas is provided by a recent spectrophotometric investigation of the reaction of the $[AuBr_4]^-$ ion with bromide ions in nitrobenzene;[9] this provides evidence that gold(III) can form a higher sexicovalent complex similar to those of palladium.[10]

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[7] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127; Harris and Nyholm, *J.*, 1956, 4375—4383.

[8] Elliot and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846.

[9] Harris and Reece, *Nature*, in the press.

[10] Harris, Livingstone, and Reece, *Austral. J. Chem.*, 1957, **10**, No. 3, 282—286.