Crystal Structures and Properties of $[Au(phen)\{(CN)_{0.92}Br_{0.08}\}_2]Br$ and $[Au(phen)(CN)\{(CN)_{0.82}Br_{0.18}\}]\cdot0.5$*trans*-$[Au(CN)_2Br_2]\cdot0.5Br\cdot phen$ (phen = 1,10-phenanthroline)† obtained by Disproportionation of Five-co-ordinate Bromodicyano(1,10-phenanthroline)gold(III). Two Examples of Secondary Co-ordination and CN/Br Disorder in Square-planar Gold(III) Complexes

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The disproportionation of neutral five-co-ordinate $[Au(phen)(CN)_2Br]$ (phen = 1,10-phenanthroline) in dimethylformamide (dmf) gives a conducting solution from which two charged species, $[Au(phen)\{(CN)_{0.92}Br_{0.08}\}_2]Br$ (**1**) and $[Au(phen)(CN)\{(CN)_{0.82}Br_{0.18}\}]\cdot0.5$*trans*-$[Au(CN)_2Br_2]\cdot0.5Br\cdot phen$ (**2**), have been separated and characterized by single-crystal *X*-ray analysis. Crystals of (**1**) are orthorhombic, space group *Fmm*2, $Z = 4$ with $a = 6.515(1)$, $b = 11.76(2)$, $c = 18.666(2)$ Å. Crystals of (**2**) are triclinic, space group $P\bar{1}$, $Z = 2$ with $a = 9.149(3)$, $b = 9.263(3)$, $c = 15.485(5)$, $\alpha = 93.58(2)$, $\beta = 105.10(2)$, $\gamma = 95.49(2)°$. The structures have been solved from three-dimensional counter data by Patterson and Fourier methods and refined by full-matrix least squares to *R* 0.031 and 0.044 for 729 and 2 701 observed reflections respectively. The co-ordination of the cation in both compounds is square planar with two positions occupied by the two N atoms of the phenanthroline ligand. In compound (**1**) the other two *cis* positions are occupied by equivalent CN groups substituted in 8% of cases by Br. In compound (**2**) one position is occupied by a CN group and the other by a CN group in 82% and Br in 18% of cases. Secondary co-ordination is shown by both the complex cations with Br^- at distances intermediate between bond and contact lengths, which gives rise to tetragonal bipyramidal and nearly square-pyramidal structures for (**1**) and (**2**) respectively.

Recently we re-examined the possibility of obtaining five-co-ordinate complexes of gold(III) containing N–N chelating ligands that were stable in the solid state and concluded that steric hindrance was not necessary if formation of the square-planar chelate products could be prevented by having poor leaving groups in the substrate. On replacing $[AuBr_4]^-$ with the less substitutionally labile *trans*-$[Au(CN)_2Br_2]^-$ we succeeded in obtaining the five-co-ordinate species bromodicyano(1,10-phenanthroline)gold(III), whose *X*-ray crystal structure showed it to be square pyramidal with the chelate spanning axial and equatorial sites and the two cyanides *trans* in the basal plane.[1] This compound dissolves in dimethylformamide (dmf) to give a solution whose conductance is that of a non-electrolyte but which increases with time and two different crystalline species, (**1**) and (**2**), have been isolated under suitable conditions from the solutions. This paper reports their crystal structures and properties, together with a comparative study suggesting that secondary bonding is quite common in this class of square-planar compounds.

Experimental

Preparation of Complexes.—The complex $[Au(phen)(CN)_2Br]\cdot dmf$ (phen = 1,10-phenanthroline) was prepared as previously reported and its purity checked by its elemental analysis and i.r. spectrum.[1]

Compound $[Au(phen)\{(CN)_{0.92}Br_{0.08}\}_2]Br$ (**1**). This was obtained on heating $[Au(phen)(CN)_2Br]\cdot dmf$ (0.582 g, 1 mmol) in dmf (10 cm^3) at 50 °C until constant conductance (1 h) and then treating the resulting solution at room temperature according to one of the following procedures. (*i*) Water was added dropwise until the solution became cloudy. It was then left to crystallize overnight at 0 °C. Fine red crystals were obtained which were filtered off and dried under reduced pressure and used for *X*-ray structure determination. (*ii*) An equal volume of water was added to the solution and the yellow-orange microcrystalline precipitate immediately formed was separated, washed with water, methanol, and diethyl ether, and dried under reduced pressure. (*iii*) The solution was put aside to evaporate at room temperature whereupon red microcrystals slowly formed over a period of 10 d. They were collected and worked up as in (*i*).

The compounds from all the preparations show very similar i.r. spectra with regard to both the number and frequency of bands, with only minor differences in the relative peak height of the vibration at 260 cm^{-1}, assignable to the Au–Br stretching. Other characteristic bands fall at 2 180 [ν(CN)], 464—475 [ν(Au–C)], and at 430 cm^{-1} [δ(Au–C–N)]. A series of elemental analyses carried out on crystals obtained from several preparations following method (*i*) gave analytical figures which indicate a variable composition due to isomorphous replacement of CN by Br, in the range 7—18%, as referred to a stoicheiometric species $[Au(phen)(CN)_2]Br$, $C_{14}H_8AuBrN_4$ [Found: (*a*) C, 32.8; H, 1.55; Br, 16.7; N, 10.8. (*b*) C, 31.6; H, 1.50; Br, 18.0; N, 10.2. $C_{14}H_8AuBrN_4$ requires C, 33.0; H, 1.55; Br,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

15.7; N, 11.0%]. The single crystal for the *X*-ray structure determination of (**1**) was chosen from the product analyzed as in (*b*).

Compound $[Au(phen)(CN)\{(CN)_{0.82}Br_{0.18}\}]\cdot0.5$*trans*-$[Au(CN)_2Br_2]\cdot0.5Br\cdot phen$ (**2**). To a solution of $[Au(phen)(CN)_2Br]\cdot dmf$ (0.582 g, 1 mmol) in dmf (10 cm^3) brought to constant conductance (50 °C, 1 h), diethyl ether was added at room temperature until incipient clouding occurred, and the resulting solution was left overnight at −10 °C. The crystalline product formed was filtered off and dried under reduced pressure. A microscopic observation revealed that it was a mixture of two well separated types of crystals of different colour and shape. The red ones were shown to be compound (**1**) by their i.r. spectrum and analysis, while the orange fraction, present in a small quantity, did not allow proper physicochemical determinations. A well formed crystal was then chosen and its *X*-ray structure solved.

Infrared spectra (4 000—600 cm^{-1}, KBr discs and Nujol mulls; 600—200 cm^{-1}, polyethylene dispersions) were recorded with a Perkin-Elmer 683 spectrophotometer. Conductance measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and CDC 334 immersion electrode.

Crystal Structure Determination of Compound (**1**).—Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation and ω—2θ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range $10 \leqslant \theta \leqslant 14°$. Crystal data are reported in Table 1. Intensities were corrected for Lorentz polarization and absorption (minimum transmission factor, 64.7%). Scattering factors and anomalous dispersion parameters were taken from ref. 2.

Table 1. Crystal data[a]

Compound	(1)	(2)
M	517.74	864.28
Crystal size (mm)	0.07 × 0.12 × 0.40	0.14 × 0.31 × 0.36
Space group	*Fmm*2	$P\bar{1}$
Unit-cell parameters	a = 6.515(1), b = 11.76(2), c = 18.666(2) Å $\alpha = \beta = \gamma = 90°$	a = 9.149(3), b = 9.263(3), c = 15.485(5) Å α = 93.58(2), β = 105.10(2), γ = 95.49(2)°
U/Å^3	1 424.8(4)	1 256.0(7)
F(000)	950.08	803.92
Z	4	2
D_c/g cm^{-3}	2.41	2.28
D_m/g cm^{-3}	2.38	2.32
μ(Mo-K_α)/cm^{-1}	130.8	74.3
$\theta_{min.}$—$\theta_{max.}$/°	2—35	2-27
Independent reflections	894	5 478
Reflections with $I > 3\sigma(I)$	729	2 701
Variables (last cycle)	68	346
Final R, R'[b]	0.031, 0.038	0.044, 0.048
Final shift/error max.	0.44	0.32
Largest peak (e Å^{-3}) in the final difference map (outside Au co-ordination sphere)	0.72	0.87
Weighting scheme (1/w)	$1/[\sigma^2(I) + 0.05(I)]$	$1/[\sigma^2(I) + 0.06(I)]$
S = Error in an observation of unit weight	1.11	1.08

[a] Data common to both determinations: graphite-monochromated Mo-K_α radiation λ = 0.710 69 Å, T = 22 °C; three standard reflections. [b] $R = \Sigma|\Delta F_o|/\Sigma|F_o|$; $R' = (\Sigma w|\Delta F_o|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

The structure was solved by Patterson and Fourier methods. Anomalies in the Fourier difference map and in the Au–C and C–N distances were indicative of some disorder in the CN region. Accurate refinement by trial and error showed the presence of 8% of Br substituting the CN groups. Hydrogen atoms were given calculated positions with C–H 0.95 Å and fixed isotropic thermal parameters of 5.0 Å^2. After a few cycles of isotropic refinement the structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms. Weights for the last cycle were applied according to the scheme given in Table 1. The Br:CN occupancy ratio for disordered positions was determined to be 0.087 by carrying out several refinements and choosing that giving the lowest R and the best set of distances. As the space group was chiral, two independent refinements were carried out on the enantiomeric structures. The data presented refer to the structure with the lowest R value (for reference, R_1 and R_2 for the opposite choice of axes were 0.034 and 0.042 respectively). All calculations were performed by the SDP system of programs.[3] Final positional parameters[4] are given in Table 2.

Crystal Structure Determination of Compound (**2**).—Intensity data and cell parameters (22 reflections in the range $10 \leqslant \theta \leqslant 14°$) were obtained by the procedure given for compound (**1**). Intensities were corrected for Lorentz polarization and absorption (minimum transmission factor, 48.6%). Crystal data are reported in Table 1.

The positions of the gold atoms and Br(2) were located from Patterson syntheses. All other non-hydrogen atoms were found in the subsequent Fourier maps. Anomalies in the Fourier difference map and in the Au(2)–C(3) and C(3)–N(3) distances were indicative of some disorder in the C(3)–N(3) region. Hydrogen atoms were given calculated positions with C–H 0.95 Å and fixed isotropic thermal parameters of 5.0 Å^2. After a few cycles of isotropic refinement the structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms. Weights for the last cycle were applied according to the scheme given in Table 1. The Br(3):C(3)–N(3) occupancy ratio in the disordered positions was determined to be 0.22 by the method reported for compound (**1**). Final positional parameters[4] are given in Table 3.

Results and Discussion

The five-co-ordinate square-pyramidal bromodicyano(1,10-phenanthroline)gold(III) complex dissolves readily in dmf giving a yellow solution whose initial conductance is that of a non-electrolyte, but it increases with time reaching a final value

Table 2. Positional parameters (×10^4), with estimated standard deviations (e.s.d.s) in parentheses, for compound (**1**)

Atom	x	y	z
Au	0	0	0
Br(1)	5 000	0	189.7(9)
Br(2)[a]	0	−1 450(29)	−882(8)
N(1)[b]	0	−1 860(18)	−1 130(11)
N(2)	0	−1 172(11)	878(8)
C(1)[b]	0	−1 129(12)	−748(5)
C(2)	0	−2 306(13)	851(7)
C(3)	0	−2 917(13)	1 487(9)
C(4)	0	−2 421(11)	2 151(6)
C(5)	0	−1 215(11)	2 162(4)
C(6)	0	−602(11)	1 520(4)
C(7)	0	−567(14)	2 825(5)

[a] Occupancy = 0.04. [b] Occupancy = 0.46.

Table 3. Positional parameters (× 10^4) with e.s.d.s in parentheses for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	0	0	0	C(9)	6 723(15)	441(17)	6 307(11)
Au(2)	1 653.9(6)	2 126.0(6)	6 732.1(4)	C(10)	5 739(15)	288(15)	6 906(10)
Br(1)	1 365(2)	2 400(2)	552(1)	C(11)	5 964(16)	−550(15)	7 634(12)
Br(2)	0	0	5 000	C(12)	4 935(16)	−573(16)	8 147(10)
Br(3)[a]	398(8)	1 539(10)	7 892(5)	C(13)	3 668(15)	173(17)	7 921(10)
N(1)	2 957(15)	−1 043(16)	−279(9)	C(14)	4 444(13)	1 022(14)	6 703(9)
N(2)	−866(13)	4 052(14)	5 950(9)	C(15)	4 176(13)	1 946(13)	5 996(8)
N(3)[b]	−144(14)	1 177(18)	8 035(10)	C(16)	8 165(16)	2 757(17)	3 561(11)
N(4)	2 917(11)	2 661(11)	5 879(7)	C(17)	9 221(18)	2 602(18)	3 069(12)
N(5)	3 444(12)	955(12)	7 207(8)	C(18)	9 018(16)	3 266(18)	2 311(11)
N(6)	6 963(12)	3 503(13)	3 318(8)	C(19)	7 795(16)	4 088(16)	2 017(10)
N(7)	4 381(13)	4 843(14)	2 740(8)	C(20)	7 596(20)	4 877(20)	1 241(11)
C(1)	1 926(16)	−716(17)	−176(10)	C(21)	6 398(19)	5 674(18)	1 002(10)
C(2)	11(13)	3 403(15)	6 231(9)	C(22)	5 270(18)	5 639(16)	1 496(10)
C(3)[b]	549(16)	1 535(19)	7 578(10)	C(23)	3 970(20)	6 372(17)	1 211(10)
C(4)	2 604(15)	3 488(14)	5 209(9)	C(24)	2 953(20)	6 335(19)	1 682(12)
C(5)	3 509(16)	3 653(15)	4 614(10)	C(25)	3 189(16)	5 565(18)	2 445(11)
C(6)	4 811(14)	2 972(16)	4 740(9)	C(26)	5 436(16)	4 909(15)	2 252(9)
C(7)	5 146(14)	2 078(15)	5 433(9)	C(27)	6 786(16)	4 138(15)	2 555(9)
C(8)	6 453(14)	1 269(16)	5 630(10)				

[a] Occupancy = 0.18. [b] Occupancy = 0.82.

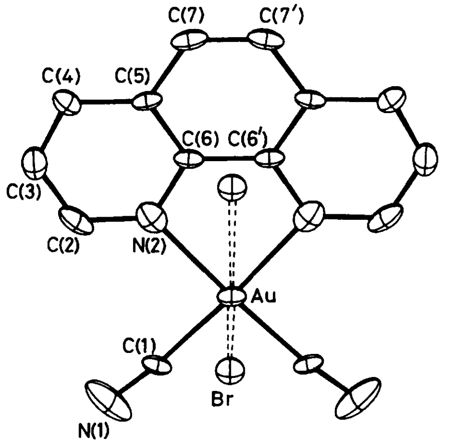

Figure 1. An ORTEP view of $[Au(phen)\{(CN)_{0.92}Br_{0.08}\}_2]Br$ (**1**) showing thermal ellipsoids at 40% probability

(33—38 ohm^{-1} cm^2 mol^{-1}) only about half of that expected for a 1:1 electrolyte (65—90 ohm^{-1} cm^2 mol^{-1}).[5] Consequently, a simple dissociation $[Au(phen)(CN)_2Br] \longrightarrow [Au(phen)(CN)_2]^+ + Br^-$ can be ruled out. It seems, therefore, more likely that the complex disproportionates in much the same way as the $[Au(N\text{-}N)X_3]$ analogues (N-N = phen or 2,2′-bipyridyl; X = Cl or Br).[6,7] Harris[6,7] showed quite convincingly that solutions of $[Au(N\text{-}N)X_3]$ in nitrobenzene, nitromethane, and acetone led immediately to disproportionation [equation (1)].

$$2[Au(N\text{-}N)X_3] \rightleftharpoons [Au(N\text{-}N)X_2]^+ + [AuX_4]^- + N\text{-}N \quad (1)$$

In this way the conductance results are readily explained and the final electronic spectrum could be reproduced exactly by adding equal contributions of $[Au(N\text{-}N)X_2]ClO_4$, $[NEt_4][AuX_4]$, and N-N.

In the case of $[Au(phen)(CN)_2Br]$ the main difference lies in the slowness of the disproportionation, and the nature of the solid products (**1**) and (**2**) isolated from the solution is less obvious. ORTEP[8] views for compounds (**1**) and (**2**) are shown in Figures 1 and 2 respectively. Bond distances and angles are reported in Tables 4 and 5 for (**1**) and (**2**) respectively.

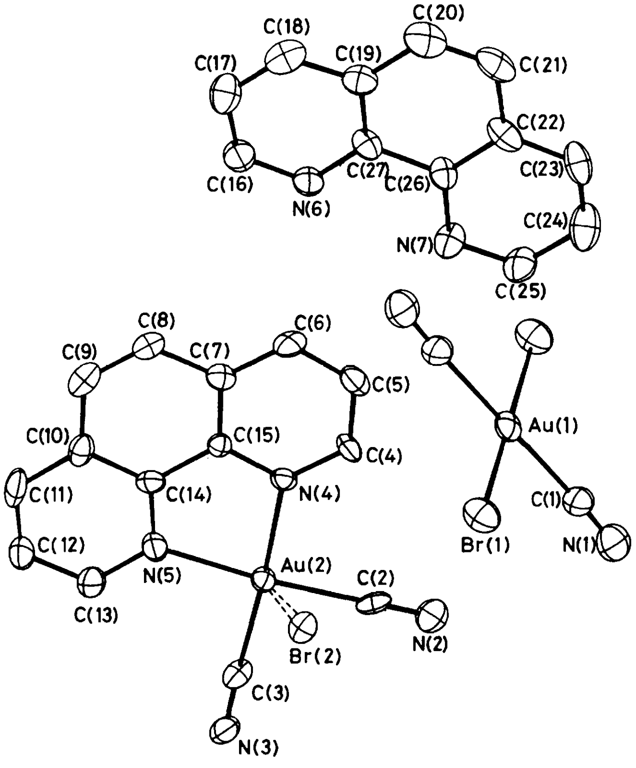

Figure 2. An ORTEP view of $[Au(phen)(CN)\{(CN)_{0.82}Br_{0.18}\}]\cdot0.5$*trans*-$[Au(CN)_2Br_2]\cdot0.5Br\cdot phen$ (**2**) showing thermal ellipsoids at 40% probability

Crystal (**1**) consists of $[Au(phen)\{(CN)_{0.92}Br_{0.08}\}_2]^+$ cations in *mm* crystallographic symmetry positions with the Au atom at 0,0,*z* (one *m* containing all the cation) and Br^- anions on *mm* crossing at $\frac{1}{2}$,0,*z*. The gold co-ordination is square planar for symmetry. The phenanthroline ligand is cut by the other symmetry plane, and the two symmetry-equivalent CN groups are substituted in 8% of cases by Br. The Au–CN and Au–N distances are 1.92(1) and 2.14(1) Å respectively. Two Br^- anions are octahedrally co-ordinated at a distance of 3.277(1) Å, which is intermediate between bond and contact lengths. The Au–Br line makes an angle of 6.20(3)° with the normal to the basal plane and is slightly bent towards the phenanthroline side. Each Br^- is shared by two gold(III) cations leading to a chain structure of octahedra.

Crystal (**2**) is built up of $[Au(phen)(CN)\{(CN)_{0.82}Br_{0.18}\}]^+$ cations in general positions, *trans*-$[Au(CN)_2Br_2]^-$ anions lying on symmetry centres at 0,0,0, Br^- ions on symmetry centres at 0,0,½, and free phenanthroline molecules in general positions. The cation displays a square-planar co-ordination with two *cis* positions occupied by the two N atoms of the phenanthroline ligand at a distance of 2.05(1) and 2.02(1) Å. Another position is occupied by a CN group and the last one by a CN group in 82% and Br in 18% of cases. The phenanthroline ligand is substantially planar, the angles between adjacent six-membered rings being 0.7(4) and 1.9(4)°. Bond distances and angles in the ligand are similar to those of the free molecule and match perfectly the data of previous structures.[1,9] The first co-ordination atoms define a plane ($\chi^2 = 10.8$) from which the Au atom is displaced by 0.022 Å² toward a fifth Br^- ligand, expanding the co-ordination to square pyramidal; each Br^- links two cations forming a dimer of two pyramids sharing the apical vertex. However, the Br^- is at a distance of 3.165(1) Å from Au^{III} which is intermediate between the Au–Br bond (2.43 Å) and van der Waals contact distance (4.09 Å). The Au–Br line makes an angle of 14.7(2)° with the normal to the basal plane. The Au–CN distance for the non-disordered ligand is 2.03(1) Å, similar to those of 2.004(6) and 1.986(6) Å previously determined.[1] The anion is perfectly planar for symmetry and Au–Br and Au–CN distances are 2.431(2) and 2.02(2) Å respectively.

Table 4. Bond distances (Å) and angles (°), with e.s.d.s in parentheses, for compound (**1**)

Au–Br(2)	2.37(3)	C(3)–C(4)	1.37(2)
Au–N(2)	2.14(1)	C(4)–C(5)	1.41(2)
Au–C(1)	1.92(1)	C(5)–C(6)	1.40(1)
N(1)–C(1)	1.11(2)	C(5)–C(7)	1.45(2)
N(2)–C(2)	1.33(2)	C(6)–C(6′)	1.41(2)
N(2)–C(6)	1.37(2)	C(7)–C(7′)	1.33(2)
C(2)–C(3)	1.39(2)		

Br(2)–Au–Br(2′)	91.8(7)	Au–C(1)–N(1)	173.2(12)
Br(2)–Au–N(2)	94.1(6)	N(2)–C(2)–C(3)	118.9(11)
Br(2)–Au–N(2′)	174.1(6)	C(2)–C(3)–C(4)	123.8(12)
Br(2)–Au–C(1′)	89.4(6)	C(3)–C(4)–C(5)	116.0(10)
N(2)–Au–N(2′)	79.9(4)	C(4)–C(5)–C(6)	120.1(8)
N(2)–Au–C(1)	96.6(4)	C(4)–C(5)–C(7)	122.4(8)
N(2)–Au–C(1′)	176.5(4)	C(6)–C(5)–C(7)	117.5(8)
C(1)–Au–C(1′)	86.9(4)	N(2)–C(6)–C(5)	119.9(9)
Au–N(2)–C(2)	127.8(9)	N(2)–C(6)–C(6′)	119.1(9)
Au–N(2)–C(6)	110.9(7)	C(5)–C(6)–C(6′)	120.9(8)
C(2)–N(2)–C(6)	121.3(10)	C(5)–C(7)–C(7′)	121.5(10)

The most striking feature of both (**1**) and (**2**) is their ability to form secondary bonds with Br^- anions outside the square-planar (s.q.) co-ordination although in different ways. In (**1**) the co-ordination is nearly octahedral, or better, tetragonal bipyramidal (t.b.p.), and in (**2**) nearly square pyramidal (s.p.). We have investigated the occurrence of such a feature in gold(III) square-planar complexes (the search was carried out on the Cambridge Crystallographic Data Base[10]). Of 102 entries nearly 15% were found to display secondary co-ordination and the compounds involved are listed in Table 6.

Two different situations can be identified. T.b.p. co-ordination is mostly achieved by intermolecular contacts with two single ions, typically Cl^-, ClO_4^-, I^-, Br^-, or neutral O atoms (R–OH or pyridine *N*-oxide) while six-co-ordination caused by intramolecular contacts is rare owing to the difficulty ligands have in matching the geometrical constraints. In two cases six-co-ordination is achieved by the use of Cl and S as equatorial ligands (entries 14 and 16 of Table 6).

On the contrary, s.p. five-co-ordination is usually observed with multidentate ligands having a position free for further

Table 5. Bond distances (Å) and angles (°), with e.s.d.s in parentheses, for compound (**2**)

Au(1)–Br(1)	2.431(2)	N(4)–C(15)	1.36(2)	C(7)–C(8)	1.45(2)	C(18)–C(19)	1.41(2)
Au(1)–C(1)	2.02(2)	N(5)–C(13)	1.34(2)	C(7)–C(15)	1.40(2)	C(19)–C(20)	1.42(2)
Au(2)–Br(3)	2.433(9)	N(5)–C(14)	1.35(2)	C(8)–C(9)	1.32(2)	C(19)–C(27)	1.40(2)
Au(2)–N(4)	2.02(1)	N(6)–C(16)	1.34(2)	C(9)–C(10)	1.46(2)	C(20)–C(21)	1.36(2)
Au(2)–N(5)	2.05(1)	N(6)–C(27)	1.33(2)	C(10)–C(11)	1.39(2)	C(21)–C(22)	1.44(2)
Au(2)–C(2)	2.03(1)	N(7)–C(25)	1.33(2)	C(10)–C(14)	1.40(2)	C(22)–C(23)	1.41(2)
Au(2)–C(3)	1.93(2)	N(7)–C(26)	1.37(2)	C(11)–C(12)	1.38(2)	C(22)–C(26)	1.37(2)
N(1)–C(1)	1.06(2)	C(4)–C(5)	1.40(2)	C(12)–C(13)	1.38(2)	C(23)–C(24)	1.32(3)
N(2)–C(2)	1.07(2)	C(5)–C(6)	1.38(2)	C(14)–C(15)	1.42(2)	C(24)–C(25)	1.40(2)
N(3)–C(3)	1.11(2)	C(6)–C(7)	1.38(2)	C(16)–C(17)	1.39(2)	C(26)–C(27)	1.47(2)
N(4)–C(4)	1.32(2)			C(17)–C(18)	1.34(2)		

Br(1)–Au(1)–C(1)	90.4(4)	C(16)–N(6)–C(27)	117.1(13)	C(11)–C(10)–C(14)	118.4(13)	C(20)–C(19)–C(27)	120.7(14)
Br(3)–Au(2)–N(4)	173.6(4)	C(25)–N(7)–C(26)	115.6(13)	C(10)–C(11)–C(12)	118.7(14)	C(19)–C(20)–C(21)	120.4(15)
Br(3)–Au(2)–N(5)	94.6(4)	Au(1)–C(1)–N(1)	177.2(15)	C(11)–C(12)–C(13)	120.8(14)	C(20)–C(21)–C(22)	119.8(15)
Br(3)–Au(2)–C(2)	89.4(4)	Au(2)–C(2)–N(2)	178.3(13)	N(5)–C(13)–C(12)	120.0(14)	C(21)–C(22)–C(23)	120.1(14)
N(4)–Au(2)–N(5)	80.9(4)	Au(2)–C(3)–N(3)	176.9(14)	N(5)–C(14)–C(10)	121.4(12)	C(21)–C(22)–C(26)	121.0(15)
N(4)–Au(2)–C(2)	94.9(5)	N(4)–C(4)–C(5)	122.6(13)	N(5)–C(14)–C(15)	117.0(11)	C(23)–C(22)–C(26)	118.8(15)
N(4)–Au(2)–C(3)	176.3(6)	C(4)–C(5)–C(6)	119.6(13)	C(10)–C(14)–C(15)	121.5(12)	C(22)–C(23)–C(24)	119.0(15)
N(5)–Au(2)–C(2)	175.2(5)	C(5)–C(6)–C(7)	118.6(13)	N(4)–C(15)–C(7)	122.0(11)	C(23)–C(24)–C(25)	119.2(17)
N(5)–Au(2)–C(3)	95.4(6)	C(6)–C(7)–C(8)	124.6(12)	N(4)–C(15)–C(14)	116.9(11)	N(7)–C(25)–C(24)	124.4(15)
C(2)–Au(2)–C(3)	88.9(6)	C(6)–C(7)–C(15)	118.7(12)	C(7)–C(15)–C(14)	121.1(12)	N(7)–C(26)–C(22)	122.8(14)
Au(2)–N(4)–C(4)	128.5(9)	C(8)–C(7)–C(15)	116.6(12)	N(6)–C(16)–C(17)	124.3(15)	N(7)–C(26)–C(27)	117.8(12)
Au(2)–N(4)–C(15)	112.7(8)	C(7)–C(8)–C(9)	121.9(13)	C(16)–C(17)–C(18)	117.0(16)	C(22)–C(26)–C(27)	119.3(14)
C(4)–N(4)–C(15)	118.5(11)	C(8)–C(9)–C(10)	122.6(14)	C(17)–C(18)–C(19)	122.1(15)	N(6)–C(27)–C(19)	123.6(13)
Au(2)–N(5)–C(13)	127.2(10)	C(9)–C(10)–C(11)	125.5(14)	C(18)–C(19)–C(20)	123.4(15)	N(6)–C(27)–C(26)	118.2(12)
Au(2)–N(5)–C(14)	112.2(9)	C(9)–C(10)–C(14)	116.0(13)	C(18)–C(19)–C(27)	115.8(14)	C(19)–C(27)–C(26)	118.2(12)
C(13)–N(5)–C(14)	120.6(12)						

Table 6. Co-ordination types[a] and Au···X contacts (Å) in gold(III) square-planar complexes,[b] with e.s.d.s in parentheses

Five-co-ordination	X	Co-ordination type	Au···X	Equivalent Au···Br[a]	Δ(Au)[c]	Ref.
1 $[\mathrm{Au(pq)Br_3}]$	N intra.	s.p. 3	2.64(2)	3.03	0.075	*d*
2 $[\mathrm{Au(pq)Cl_3}]$	N intra.	s.p. 3	2.68(2)	3.07	0.042	*d*
3 $[\mathrm{Au(dmphen)Cl_3}]$	N intra.	s.p. 3	2.58(1)	2.97	0.095	*e*
4 $[\mathrm{Au(dmphen)Br_3}]$	N intra.	s.p. 3	2.61(2)	3.00	0.118	*e*
5 $[\mathrm{Au(phen)(CN)_2Br}]$	N intra.	s.p. 3	2.608(7)	3.00	0.058	1
6 $[\mathrm{Au(tpp)Cl}]$	$\mathrm{Cl^-}$	s.p. 1	3.01(1)	3.15	0.09	*f*
7 $[\mathrm{AuMe_2(tpzm)}]^+$	N intra.	s.p. 3	3.139(7)	3.53	0.040	*g*
8 $[\mathrm{AuMe_2(tpm)}]^+$	O ($\mathrm{NO_3^-}$)	s.p. 1	3.07(1)	3.47	0.024	*g*
9 $[\mathrm{Au(phen)(CN)(CN,Br)}]^+$	$\mathrm{Br^-}$	s.p. 2	3.165(1)	3.16	0.022	*h*
Six-co-ordination						
10 $[\mathrm{Au(S_2CNEt_2)_3}]$	S intra.	t.b.p. 4	3.097(4)	3.20	0.003	*i*
	S intra.		3.181(5)	3.28		
11 $[\mathrm{Au\{NH(CH_2CH_2NH_2)_2\}Cl}]^{2+}$	$\mathrm{Cl^-}$	t.b.p. 1	3.05(1)	3.19	0.063	*j*
	O ($\mathrm{ClO_4^-}$)		3.10(1)	3.50		
12 $[\mathrm{Au\{N(CH_2CH_2NH_2)_2\}Cl}]^+$	O ($\mathrm{ClO_4^-}$)	t.b.p. 3	3.09(1)	3.49	0.043	*j*
	O ($\mathrm{ClO_4^-}$)		3.09(1)	3.49		
13 $[\mathrm{Au(pdma)_2}]^{3+}$	$\mathrm{I^-}$	t.b.p. 1	3.35(2)	3.14	0.00	*k*
	$\mathrm{I^-}$		3.35(2)	3.14		
14 $[\mathrm{Au(tha)Cl_3}]$	S intra.	t.b.p. 5	3.675(8)	3.78	0.064	*l*
	S		3.82(2)	3.92		
15 $[\mathrm{AuCl_4}]^-$	O (pyo)	t.b.p. 2	3.105(7)	3.50	0.00	*m*
	O (pyo)		3.105(7)	3.50		
16 $[\mathrm{Au(dpk{\cdot}H_2O)Cl_2}]^+$	O (OH)	Other	2.77(1)	3.17	0.013	*n*
	$\mathrm{Cl^-}$		3.230(7)	3.37		
17 $[\mathrm{Au(phen)(CN,Br)_2}]^+$	$\mathrm{Br^-}$	t.b.p. 2	3.277(1)	3.28	0.0	*h*
	$\mathrm{Br^-}$		3.277(1)	3.28		

[a] The global co-ordination is distorted square pyramidal (one contact) or octahedral (two contacts). Equivalent Au···Br distances are calculated assuming covalent radii of 0.75, 0.74, 1.04, 1.00, 1.14, and 1.35 Å for N, O, S, Cl, Br, and I respectively.[11] Bond and van der Waals Au–Br distances are approximately 2.43 and 4.09 Å respectively. [b] pq = 2-(2′-Pyridyl)quinoline; dmphen = 2,9-dimethyl-1,10-phenanthroline; tpp = 5,10,15,20-tetraphenylporphyrinate; tpzm = tris(1-pyrazolyl)methane; tpm = tris(2-pyridyl)methane; pdma = *o*-phenylenebis(dimethylarsine); tha = thianthrene; pyo = pyridine *N*-oxide; dpk = di-2-pyridyl ketone. [c] Absolute value (Å) of the displacement of the Au atom from the mean plane of the basal co-ordinated atoms. [d] C. J. O'Connor and E. Sinn, *Inorg. Chem.*, 1978, **17**, 2067. [e] W. T. Robinson and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1975, 726. [f] R. Timkovich and A. Tulinsky, *Inorg. Chem.*, 1977, **16**, 962. [g] A. J. Canty, N. J. Minchin, P. C. Healy, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 1795. [h] This work. [i] J. H. Noordik, *Cryst. Struct. Commun.*, 1973, **2**, 81. [j] G. Nardin, L. Randaccio, G. Annibale, G. Natile, and B. Pitteri, *J. Chem. Soc., Dalton Trans.*, 1980, 220. [k] W. F. Duckworth and N. C. Stephenson, *Inorg. Chem.*, 1969, **8**, 1661. [l] N. W. Alcock, K. P. Ang, K. F. Mok, and S. F. Tan, *Acta Crystallogr., Sect. B*, 1978, **34**, 3364. [m] M. S. Hussain and E. O. Schlemper, *J. Chem. Soc., Dalton Trans.*, 1982, 751. [n] G. Annibale, L. Canovese, L. Cattalini, G. Natile, M. Biagini-Cingi, A. M. Manotti-Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1981, 2280.

apical pyramidal co-ordination, in which case the pyramid is remarkably distorted owing to the small ligand bite.

The majority of both s.p. and t.b.p. complexes are observed as $\mathrm{AuL_4}$···X or X···$\mathrm{AuL_4}$···X monomeric molecular units inside the crystals. Exceptions are pyramidal dimers $\mathrm{AuL_4}$···Br···$\mathrm{AuL_4}$, entry 2 of Table 6, and bipyramidal infinite chains of the type ···X···$\mathrm{AuL_4}$···X···$\mathrm{AuL_4}$··· with X = $\mathrm{ClO_4^-}$ (entry 12) or $\mathrm{Br^-}$ (entry 17). Sometimes these chains are obtained by interlinking intramolecular pyramids by the use of an equatorial shared ligand (entries 14 and 16). In one case (entry 15), finally, bipyramids are linked in chains by OH···O hydrogen bonds. In Figure 3 are shown sketches of the observed secondary co-ordination schemes of these gold(III) complexes. The scarce occurrence of infinite chains seems to indicate that secondary co-ordination is not necessarily related to the increase in Madelung energy of the one-dimensional (− + − +) lattice, but mostly to a simple single anion–gold(III) interaction.

Table 6 reports the observed Au···X distances for secondary co-ordination. As the figures refer to different situations we thought it worthwhile to reduce all distances to the equivalent Au···Br ones assuming covalent radii of 0.75 for N, 0.74 for O, 1.04 for S, 1.00 for Cl, 1.14 for Br, and 1.35 Å for I.[11] Such equivalent distances are shown in the fourth column of Table 6 and plotted in Figure 4(*a*) and (*b*).

Figure 4(*a*) shows that the added apical ligand is bound at a distance which is intermediate between bond and van der Waals lengths; shortest distances in the range 2.97—3.16 Å corresponding to intramolecular contacts (entries 1, 3—5), the two $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ contacts (entries 6 and 9) being slightly longer (3.15 and 3.16 Å). The two inter- and intra-molecular distances at 3.47 and 3.53 Å correspond to situations of much weaker interaction. Comparison of Au–X bond distances in the square-planar moiety shows that the entering apical ligand is able to displace the Au atom from the basal plane (towards the ligand) by up to 0.118 Å but not significantly to lengthen the basal Au–$\mathrm{X_{eq}}$ bonds. The two Au–$\mathrm{X_{eq}}$ bond length distributions (one with and the other without the apical bond) are practically coincident, the main scattering factor being connected with the usual *trans* influence in this class of compounds.

Figure 4(*b*) shows a scatterplot of the two equivalent Au···Br secondary *trans*-co-ordination distances for t.b.p. compounds. It shows that the two distances increase together, indicating that the entering of a sixth apical substituent cannot be considered a nucleophilic addition *trans* to the other apical group. In such a case, lengthening of the apical ligand bond with progressive approaching of the *trans* ligand would have been observed. Conversely, the present plot is more consistent with rehybridization of the central atom from s.p. dsp^3 to t.b.p., nearly $d^2\,sp^3$. As for Au–X bond distances in the square-planar

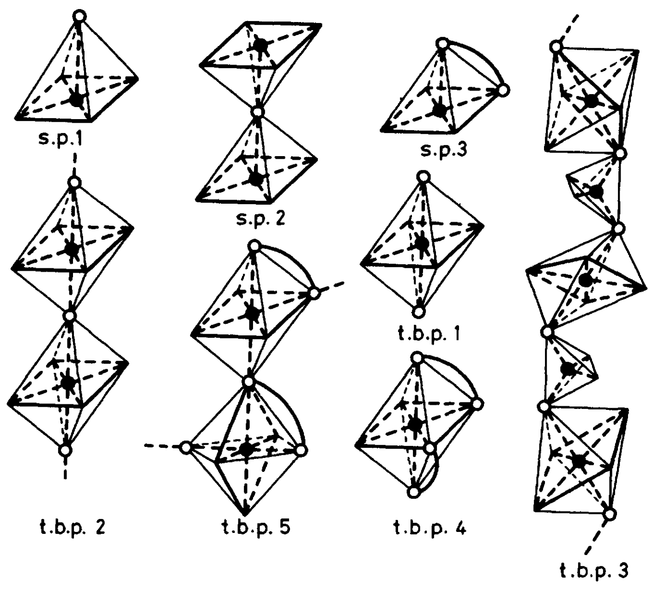

Figure 3. Sketches of the observed secondary co-ordination schemes of square-planar gold(III) complexes; s.p. 1—s.p. 3 and t.b.p. 1—t.b.p. 5 as in the third column of Table 6

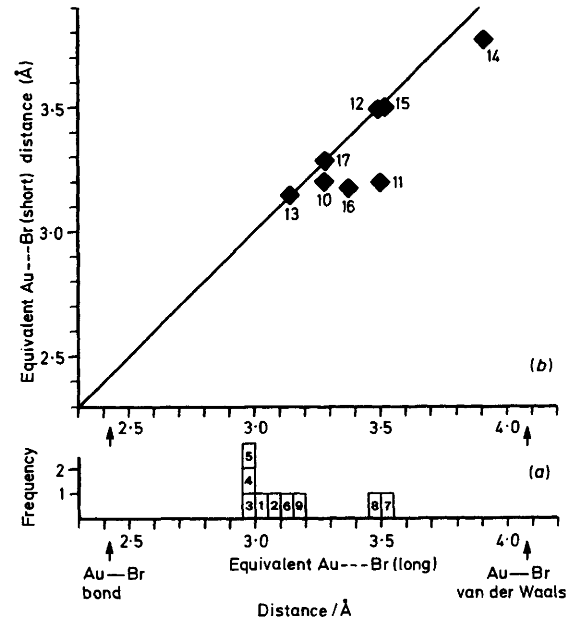

Figure 4. (*a*) Histogram of equivalent Au ··· Br secondary co-ordination distances for the square-pyramidal compounds of Table 6. (*b*) Scatterplot of the two equivalent Au ··· Br secondary *trans* co-ordination distances for octahedral compounds of Table 6. In both cases the bond and contact Au ··· Br distances are assumed to be 2.43 and 4.09 Å respectively. Numbers refer to the compounds in Table 6

basal plane, considerations similar to those for pyramidal co-ordination hold. On the other hand, it is reasonable that no lengthening of the short (strong) equatorial bonds is observed, since the mathematical form of the relationship between bond lengths of the entering (axial) and leaving (equatorial) group is logarithmic[12] allowing the relevant approach of the new ligand without any significant lengthening of the old bond.

All the phenomena of secondary co-ordination can be interpreted by saying that 10 *Dq* is relevant for d^8 gold(III) complexes owing to both its high oxidation number and its position in the third transition series, so that high-spin octahedral complexes cannot be achieved, while low spin s.p. and t.b.p. geometries are easily obtained by perturbation of low-spin square-planar complexes.

The general situation is that of three different geometries which can in some way be permutated according to the most favourable packing conditions. Such reasoning can, however, be extended to take into account complex equilibria in solution among the different species, though with different populations. These agree with the suggestion that high-co-ordination species have been found in solution on the grounds of kinetic studies[13] and can be taken as a warning that both the thermodynamic and kinetic behaviour of gold(III) complexes may be much more complicated than is usually believed.

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