Five-co-ordinated Gold(III) Complexes. Part 1. Synthesis, Structure, and Properties of Bromodicyano(1,10-phenanthroline)gold(III)–Dimethylformamide (1/1)†

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The five-co-ordinated gold(III) complex bromodicyano(1,10-phenanthroline)gold(III)–dimethylformamide (1/1) has been synthesized by reaction between *trans*-$[Au(CN)_2Br_2]^-$ and 1,10-phenanthroline in water, followed by crystallization from dimethylformamide–diethyl ether at low temperature. The crystal structure has been determined by *X*-ray analysis from three-dimensional counter data, and refined by full-matrix least squares to R = 0.032 for 3 833 independent reflections. Crystals are triclinic, space group $P\bar{1}$, with a = 8.524(2), b = 9.708(4), c = 12.525(5) Å, α = 80.78(3), β = 106.79(3), γ = 110.86(3)°, and Z = 2. The co-ordination around the metal is distorted square pyramidal with the four basal atoms (one bromide atom, two carbon atoms from the cyano groups, and one nitrogen atom of the bidentate phenanthroline) nearly coplanar. The gold atom lies 0.058 Å above the base and the apical nitrogen atom is displaced from the vertical and at a relatively great distance from the metal. The dimethylformamide molecule of crystallization is connected in the structure by C–H · · · O hydrogen bonds. The crystallographic results are related to other physical measurements.

Although square-planar geometry is strongly preferred in gold(III) complexes, both solution data and *X*-ray structural determinations in the solid have shown that higher co-ordination numbers can occur. The anionic species $[Au(NCS)_5]^{2-}$, $[Au(NCS)_6]^{3-}$,[1] and $[AuBr_6]^{3-}$ [2] have been identified in solution, and the six-co-ordinate cationic complex $[Au(pdma)_2I_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine)], first postulated to exist in solution,[3] was later demonstrated to retain the same molecular structure in the solid state.[4] Stable five-co-ordinated complexes of the type $[Au(N\text{–}N)X_3]$ [N–N = 2,2′-biquinolyl (biquin),[5] 2,9-dimethyl-1,10-phenanthroline (dmphen),[6] or 2-(2′-pyridyl)quinoline (pyquin);[7] X = Cl or Br] have been reported, and, in some cases at least, characterized by single-crystal *X*-ray diffraction. Attempts to prepare the analogous five-co-ordinated species from $[AuX_4]^-$ and 1,10-phenanthroline (phen) failed and only the four-co-ordinated $[Au(phen)X_2]^+$ could be isolated.[8] However, if $[AuX_4]^-$ is replaced by the less substitutionally labile *trans*-$[Au(CN)_2X_2]^-$ (X = Cl or Br) the neutral five-co-ordinated species can also be formed with 1,10-phenanthroline. We report here on the synthesis, crystal structure, and some properties of the five-co-ordinated gold(III) complex $[Au(phen)(CN)_2Br]\cdot$dmf (dmf = dimethylformamide).

Results and Discussion

The yellow compound readily obtained by reacting equimolar amounts of *trans*-$[Au(CN)_2Br_2]^-$ and 1,10-phenanthroline in water–methanol is quite insoluble in water but soluble in solvents like dmf and dimethyl sulphoxide (dmso), where, freshly dissolved, it is essentially a non-conductor. It was this last fact which first suggested that a five-co-ordinated species would be likely. The increasing conductivity with time, paralleled by a significant change in the electronic spectrum, is consistent with a slow dissociation of the product to give possibly a more favoured four-co-ordinated species. The five-co-ordinated complex can thus be regarded as a metastable species, the rate of dissociation of which, to the four-co-ordinate product, is slow enough, probably due to the presence of the tightly bound cyanide groups, for it to be isolable. This leads to the conclusion that five-co-ordinated compounds of gold(III) can be obtained not only by sterically crowding the N–N bidentate ligand with ring substituents,[5–7] but also hindering the formation of the square-planar products with poor leaving groups in the substrate. Furthermore, the existence of five-co-ordinated species is strong evidence in support of the associative mechanism proposed, and now generally accepted, for ligand substitution processes at d^8 square-planar complexes.[9]

The structure of the compound, crystallized from dmf–diethyl ether, is shown in the Figure, where the asymmetric unit cell, *i.e.* the gold(III) complex and the dmf molecule of crystallization, is shown. Bond distances and angles are given in Table 1. The co-ordination around the gold atom is distorted square pyramidal. The four basal (bas) Br, N(1), C(13), and C(14) atoms are nearly coplanar $[\Sigma(\Delta/\sigma)^2 = 24.7]$ and the Au atom is displaced towards the polyhedron centre by 0.058 Å. The straight line connecting Au with the apical (ap) N(2) atom makes an angle of 21.3(1)° with the perpendicular to the mean plane. A comparison of the present compound with other five-co-ordinated Au^{III} complexes with bidentate nitrogen ligands is shown in Table 2. The data are substantially similar, showing one N atom co-ordinated in a square-planar fashion at a distance from gold of 1.99—2.11 Å and the other N atom occupying the apical position at a longer distance of 2.58—2.68 Å.

† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

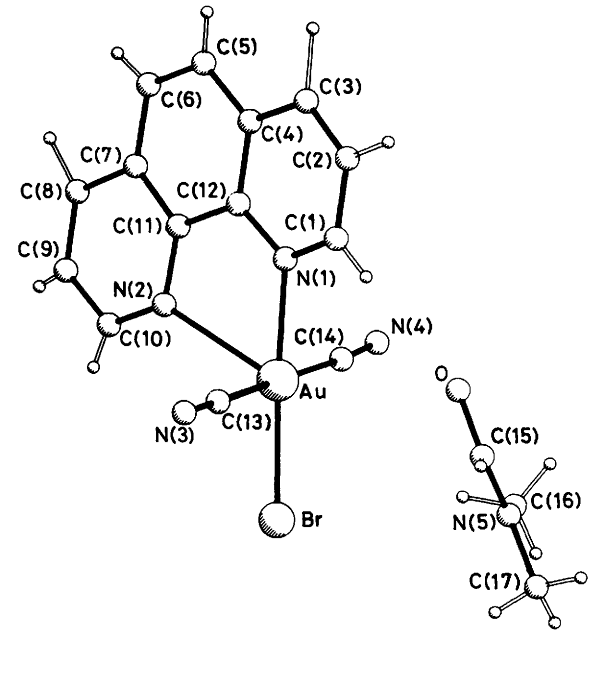

Figure. Structure of [Au(phen)(CN)$_2$Br]·dmf showing the atom-labelling scheme

Table 1. Bond distances (Å) and interatomic angles (°) with e.s.d.s in parentheses

Au–Br	2.402(1)	C(4)–C(5)	1.419(10)
Au–N(1)	2.091(5)	C(4)–C(12)	1.427(8)
Au–N(2)	2.608(7)	C(5)–C(6)	1.347(9)
Au–C(13)	2.004(6)	C(6)–C(7)	1.411(9)
Au–C(14)	1.986(6)	C(7)–C(8)	1.418(9)
N(1)–C(1)	1.309(8)	C(7)–C(11)	1.396(10)
N(1)–C(12)	1.359(9)	C(8)–C(9)	1.345(10)
N(2)–C(10)	1.337(9)	C(9)–C(10)	1.353(12)
N(2)–C(11)	1.350(8)	C(11)–C(12)	1.430(8)
N(3)–C(13)	1.126(8)	O–C(15)	1.241(12)
N(4)–C(14)	1.145(9)	N(5)–C(15)	1.316(14)
C(1)–C(2)	1.398(9)	N(5)–C(16)	1.425(13)
C(2)–C(3)	1.338(11)	N(5)–C(17)	1.436(14)
C(3)–C(4)	1.408(8)		
Br–Au–N(1)	176.6(2)	C(4)–C(5)–C(6)	121.5(6)
Br–Au–N(2)	111.2(1)	C(5)–C(6)–C(7)	120.7(6)
Br–Au–C(13)	89.9(2)	C(6)–C(7)–C(8)	122.7(6)
Br–Au–C(14)	90.3(2)	C(6)–C(7)–C(11)	120.6(6)
N(1)–Au–N(2)	72.1(2)	C(8)–C(7)–C(11)	116.6(6)
N(1)–Au–C(13)	90.3(2)	C(7)–C(8)–C(9)	119.2(7)
N(1)–Au–C(14)	89.4(2)	C(8)–C(9)–C(10)	120.7(7)
N(2)–Au–C(13)	98.6(2)	N(2)–C(10)–C(9)	123.0(7)
N(2)–Au–C(14)	83.4(2)	N(2)–C(11)–C(7)	122.8(6)
C(13)–Au–C(14)	177.8(3)	N(2)–C(11)–C(12)	118.0(5)
Au–N(1)–C(1)	117.4(4)	C(7)–C(11)–C(12)	119.1(5)
Au–N(1)–C(12)	120.6(4)	N(1)–C(12)–C(4)	118.2(5)
C(1)–N(1)–C(12)	122.0(5)	N(1)–C(12)–C(11)	122.5(5)
Au–N(2)–C(10)	135.4(5)	C(4)–C(12)–C(11)	119.3(5)
Au–N(2)–C(11)	105.8(4)	Au–C(13)–N(3)	179.4(6)
C(10)–N(2)–C(11)	117.6(6)	Au–C(14)–N(4)	176.2(6)
N(1)–C(1)–C(2)	121.5(6)		
C(1)–C(2)–C(3)	119.4(6)	C(15)–N(5)–C(16)	120.2(8)
C(2)–C(3)–C(4)	120.3(6)	C(15)–N(5)–C(17)	121.1(8)
C(3)–C(4)–C(5)	123.0(6)	C(16)–N(5)–C(17)	118.6(9)
C(3)–C(4)–C(12)	118.3(6)	O–C(15)–N(5)	126.1(8)
C(5)–C(4)–C(12)	118.7(6)		

Table 2. Geometrical parameters [distances (Å) and angles (°)] for some square-pyramidal gold(III) complexes, with e.s.d.s in parentheses

Compound	Au–N$_{bas}$	Au–N$_{ap}$	N$_{bas}$–Au–N$_{ap}$	Ref.
[Au(phen)(CN)$_2$Br]	2.091(5)	2.608(7)	72.1(2)	This work
[Au(dmphen)Cl$_3$]	2.09(1)	2.58(1)	73.2(5)	6
[Au(dmphen)Br$_3$]	2.08(2)	2.61(2)	71.9(9)	6
[Au(pyquin)Cl$_3$]	2.11(2)	2.68(2)	68.0(4)	7
[Au(pyquin)Br$_3$]	1.99(2)	2.64(2)	70.2(9)	7

Owing to the geometrical constraints of the organic ligand the N$_{bas}$–Au–N$_{ap}$ angle is confined to the range 68—73°, small systematic distance and angle differences being due to the differences between the phen, dmphen, and pyquin ligands. The apical Au–N bond is intermediate between the sums of covalent and van der Waals radii (2.04 and 3.7 Å respectively, according to Pauling[10]). The much shorter basal than apical Au–N bond distance is in agreement with the low-spin configuration of gold(III) complexes.

Both mutually *trans*-CN groups are essentially linear with Au–C distances of 2.004(6) and 1.986(6) Å. In accordance, the i.r. spectrum shows only one stretching vibration, ν(CN) at 2 175 cm^{-1}, at higher frequency with respect to that of free CN (*ca.* 2 080 cm^{-1}). The two vibrations at 457 and 423 cm^{-1} can be assigned to ν(Au–C) and δ(Au–CN) respectively, in agreement with previous assignments made for the far-i.r. spectra of complexes of the type *trans*-[Au(CN)$_2$X$_2$]$^-$ [11] and *trans*-[Au(CN)$_2$(py)X][12] (X = Cl, Br; py = pyridine). The Au–Br distance of 2.402(1) Å can be compared with the corresponding distances in [Au(dmphen)Br$_3$][6] and [Au(pyquin)Br$_3$][7] which are, on average, 2.418 Å when Br is *trans* to Br and 2.391 Å when *trans* to N, once more indicating a definite *trans* influence of the halogen. The ν(Au–Br) stretching falls at 256 cm^{-1}, showing very little influence, as previously pointed out,[12] from the Au–CN group vibrations which take place at right angles.

Co-ordination of phen to the metal ion results in a shift to higher frequency (1 512 cm^{-1}) and splitting of its most intense ring vibration (1 505 cm^{-1} in the free ligand), as previously observed for a large series of phen transition-metal complexes.[13]

The phen ligand is not planar; it displays a significant curvature, the angles between the three six-membered rings [1 = N(1),C(1)–C(4),C(12); 2 = C(4)–C(7),C(11),C(12); 3 = C(7)–C(10),N(2),C(11)] being 1–2 = 2.7(2), 2–3 = 2.8(2), and 1–3 = 5.4(2)°.

As regards the crystal packing the most interesting feature concerns the solvation of the complex by dmf [ν(C=O) at 1 670 cm^{-1}]. The two molecules are in a 1:1 ratio; the C=O group of the asymmetric unit is connected by two weak C=O ··· H–C interactions, which could be considered as C–H ··· O hydrogen bonds, according to Taylor and Kennard,[14] with C(1)–H(1) of the same unit [C(1)–H(1) = 0.92(6), H(1) ··· O = 2.58(6), C(1) ··· O = 3.26(1) Å, C(1)–H(1) ··· O = 131(4)°] and C(3)–H(3) at $(1-x, 1-y, 1-z)$ [C(3)–H(3) = 1.2(1), H(3) ··· O = 2.46(8), C(3) ··· O = 3.302(8) Å, C(3)–H(3) ··· O = 124(7)°]. At the same time the C=O at $(1-x, 1-y, 1-z)$ is connected in the same way to C(1)–H(1) of the same unit and C(3)–H(3) of the asymmetric unit. The result is the building up of pairs of Au five-co-ordinated moieties interconnected by two dmf oxygen bridges.

Experimental

trans-K[Au(CN)$_2$Br$_2$]·3H$_2$O was prepared by oxidizing an aqueous solution of K[Au(CN)$_2$] with an excess of bromine.[15] The purity of the product, recrystallized from water, was

Table 3. Crystal data for $[Au(phen)(CN)_2Br]\cdot dmf$

Formula	$C_{17}H_{15}AuBrN_5O$
M	582.2
Crystal size/mm	0.28 × 0.47 × 0.33
Space group	$P\bar{1}$
Unit-cell parameters	a = 8.524(2), b = 9.708(4), c = 12.525(5) Å, α = 80.78(3), β = 106.79(3), γ = 110.86(3)°
U/Å^3	925.3(6)
Z	2
D_c/g cm^{-3}	2.09
F(000)	548
μ(Mo-K_α)/cm^{-1}	100.7
Radiation	Mo-K_α
Monochromator	Graphite
$\theta_{min.}$—$\theta_{max.}$/°	2—27
Standard reflections	3
T/°C	22
Independent reflections	3 833
Reflections with $I > 3\sigma(I)$	3 120
Variables (last cycle)	259
Final $R(=\Sigma\|\Delta F_o\|/\Sigma\|F_o\|)$	0.032
Final $R'[=(\Sigma w\|\Delta F_o\|/\Sigma w\|F_o\|^2)^{\frac{1}{2}}]$	0.040
Final max. shift/error	0.36
Largest peak in final difference map(outside Au co-ordination sphere)/e Å^{-3}	2.2 (0.83)
Weighting	$1/w^2 = 1/[\sigma^2(I) + 0.05(I)]$
Error in an observation of unit weight	1.19

Table 4. Positional parameters (× 10^4 for non-H atoms; × 10^3 for H atoms) with e.s.d.s in parentheses

Atom	x	y	z
Au	881.9(3)	2 552.6(2)	2 493.9(2)
Br	−126(1)	1 169.3(8)	860.3(6)
N(1)	1 872(6)	3 697(5)	3 952(4)
N(2)	−519(7)	4 618(6)	2 209(4)
N(3)	−1 778(8)	67(7)	3 615(5)
N(4)	3 668(9)	5 040(8)	1 472(6)
C(1)	2 839(7)	3 166(7)	4 810(5)
C(2)	3 595(8)	3 874(7)	5 811(5)
C(3)	3 363(8)	5 144(7)	5 887(5)
C(4)	2 302(7)	5 726(6)	4 985(5)
C(5)	1 986(8)	7 056(7)	5 020(6)
C(6)	917(8)	7 557(7)	4 157(6)
C(7)	88(7)	6 777(6)	3 178(5)
C(8)	−1 077(9)	7 243(7)	2 258(6)
C(9)	−1 877(9)	6 403(8)	1 376(6)
C(10)	−1 591(9)	5 122(8)	1 365(6)
C(11)	335(7)	5 456(6)	3 094(5)
C(12)	1 496(7)	4 931(6)	3 997(5)
C(13)	−823(8)	956(6)	3 207(5)
C(14)	2 639(8)	4 100(7)	1 816(5)
O	4 167(7)	1 496(6)	3 362(6)
N(5)	4 278(8)	144(7)	2 072(7)
C(15)	4 055(10)	317(9)	3 033(8)
C(16)	4 750(15)	1 388(13)	1 313(10)
C(17)	4 145(13)	−1 278(11)	1 791(10)
H(1)	304(6)	230(5)	478(4)
H(2)	436(6)	340(6)	654(4)
H(3)	400(20)	590(10)	670(10)
H(5)	235(7)	735(6)	577(5)
H(6)	66(9)	841(7)	407(6)
H(8)	−110(9)	833(8)	242(6)
H(9)	−241(7)	667(6)	83(5)
H(10)	−220(10)	470(10)	85(8)

checked by elemental analysis and comparing its i.r. spectrum with that reported in the literature.[11]

$[Au(phen)(CN)_2Br]\cdot dmf$ was prepared by adding 1,10-phenanthroline (0.180 g, 1 mmol) dissolved in methanol (1 cm^3) to a solution of *trans*-$K[Au(CN)_2Br_2]\cdot 3H_2O$ (0.502 g, 1 mmol) in water (20 cm^3) at 0 °C and under stirring. The yellow product that precipitated immediately was filtered off, washed with cooled water, and dried under reduced pressure (0.46 g, 90%). It was then crystallized from a concentrated solution of the crude product in dmf–diethyl ether at −10 °C, m.p. 178 °C (colour changes continuously between 105 and 178 °C) (Found: C, 35.1; H, 2.60; Br, 13.8; N, 12.05. $C_{17}H_{15}AuBrN_5O$ requires C, 35.0; H, 2.60; Br, 13.7; N, 12.0%); u.v. absorptions (freshly prepared solution in MeOH, 240—400 nm): 263, 309, and 323 nm. The spectrum both in methanol and other solvents changes with time; conductometric measurements show that freshly prepared 10^{-3} mol dm^{-3} solutions in dmf or dmso are non-conducting, but their conductivity increases with time.

Physical Measurements.—I.r. spectra (4 000—600 cm^{-1}, KBr discs; 600—200 cm^{-1}, polyethylene dispersions) were recorded on a Perkin-Elmer 683 spectrophotometer; u.v. spectra were measured on a Varian-Cary 219 spectrophotometer with 1-cm quartz cells at 25 °C; conductometric measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and CDC 334 immersion electrode at 25 °C.

Crystal Structure Determination.—The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation and $\omega/2\theta$ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 24 centred reflections in the range $11.3 < \theta < 13.9°$. The intensities of three standard reflections, monitored every 2 h, showed a loss in intensity of 21% in 4 d; all data were corrected for Lorentz, polarization, anisotropic decay, and absorption (minimum transmission factor: 50.4%). Scattering factors and anomalous dispersion parameters were taken from International Tables.[16] The position of the gold atom was obtained from a Patterson synthesis; all other non-H atoms were located in the subsequent Fourier map and the 1,10-phenanthroline H atoms were found from difference Fourier maps. After three cycles of isotropic refinement, the structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-H atoms. H atoms of the dmf molecule were assigned calculated positions (C–H 0.95 Å) and fixed isotropic thermal parameters (5 Å^2). Weights for the last cycle were applied according to the scheme given in Table 3. All calculations used the SDP system of programs.[17] Final positional parameters[18] are given in Table 4.

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