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Structure of Bromodicyano(2,2':6',2''-terpyridine)gold(III)

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Abstract. $C_{17}H_{11}AuBrN_5$, $M_r = 562.19$, monoclinic, $P2_1/c$, $a = 13.229$ (2), $b = 11.069$ (2), $c = 12.849$ (1) Å, $\beta = 117.92$ (9)°, $V = 1661.3$ (4) Å^3, $Z = 4$, $D_x = 2.25$ g cm^{-3}, $\lambda(Mo~K\alpha) = 0.71069$ Å, $\mu = 112.3$ cm^{-1}, $F(000) = 1048$, $T = 298$ K, $R = 0.030$ for 2186 observed independent reflections. The coordination is distorted square-pyramidal and terpyridine acts as a bidentate ligand with one N atom in the basal square [Au—N = 2.078 (6) Å] and the other in the apical position at a distance of 2.839 (5) Å which is intermediate between the sum of the covalent and van der Waals radii. The geometry of the coordination polyhedron is discussed by comparing the present structure with other square-pyramidal or square-planar Au^{III} complexes of known molecular structure.

Introduction. The only Au complexes of 2,2':6',2''-terpyridine (terpy) reported and structurally characterized are [Au(terpy)Cl]Cl$_2$.3H$_2$O and the mixed-valence compound [Au(terpy)Cl]$_2$[AuCl$_2$]$_3$[AuCl$_4$] (Hollis & Lippard, 1983), in both of which terpy acts as a terdentate ligand and the [Au(terpy)Cl]$^{2+}$ cation displays a square-planar geometry. We report here the crystal structure of the neutral complex bromodicyano(terpy)gold(III) which, to our knowledge, is an uncommon example of a coordination compound where terpy acts as a bidentate ligand in a distorted square-pyramidal coordination environment.

Experimental. Bromodicyano(terpy)gold(III) was prepared by adding 2,2':6',2''-terpyridine (0.233 g, 1 mmol) dissolved in ethanol (2 cm^3) to a solution of *trans*-K[Au(CN)$_2$Br$_2$].3H$_2$O (0.502 g, 1 mmol) in water (20 cm^3) at 273 K with stirring. The pale yellow product that precipitated immediately was filtered off, washed with cold water, and dried under reduced pressure (0.534 g, 95%). It was crystallized from a concentrated solution of the crude product in dimethylformamide–diethyl ether (1:4, v:v) at 263 K (found: C, 36.2; H, 1.91; N, 12.3; Br 14.7%; $C_{17}H_{11}AuBrN_5$ requires C, 36.3; H, 1.97; N, 12.5; Br, 14.2%).

Single crystal of dimensions 0.19 × 0.21 × 0.31 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan ($2 \le \theta \le 27°$); cell parameters from 25 reflections in the range $8 \le \theta \le 14°$; 3614 independent

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors (Å²) with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Au	0.16501 (2)	−0.03721 (3)	−0.18574 (2)	2.583 (5)
Br	0.15107 (8)	−0.07724 (8)	−0.37492 (6)	5.04 (2)
N(1)	0.1668 (4)	−0.0118 (5)	−0.0245 (4)	2.6 (1)
N(2)	0.3168 (4)	0.1503 (5)	−0.0520 (4)	2.4 (1)
N(3)	0.4795 (5)	0.2779 (6)	−0.1840 (5)	4.7 (2)
N(4)	0.3005 (6)	−0.2781 (7)	−0.0946 (6)	5.6 (2)
N(5)	0.0206 (5)	0.1987 (7)	−0.2893 (6)	5.3 (2)
C(1)	0.1225 (5)	−0.1030 (7)	0.0125 (5)	2.8 (2)
C(2)	0.1117 (5)	−0.0930 (7)	0.1121 (5)	3.1 (2)
C(3)	0.1441 (5)	0.0131 (7)	0.1761 (5)	3.7 (2)
C(4)	0.1892 (5)	0.1030 (7)	0.1375 (5)	3.0 (2)
C(5)	0.2010 (5)	0.0913 (6)	0.0365 (5)	2.4 (1)
C(6)	0.2551 (5)	0.1876 (6)	0.0003 (5)	2.5 (2)
C(7)	0.2454 (6)	0.3076 (7)	0.0236 (5)	3.6 (2)
C(8)	0.3020 (6)	0.3940 (7)	−0.0077 (6)	4.1 (2)
C(9)	0.3673 (6)	0.3574 (7)	−0.0582 (6)	4.0 (2)
C(10)	0.3724 (5)	0.2351 (7)	−0.0806 (5)	2.9 (2)
C(11)	0.4408 (5)	0.1930 (7)	−0.1384 (5)	3.0 (2)
C(12)	0.4650 (5)	0.0733 (7)	−0.1426 (6)	3.6 (2)
C(13)	0.5330 (6)	0.0411 (8)	−0.1935 (6)	4.2 (2)
C(14)	0.5749 (5)	0.1281 (8)	−0.2380 (6)	4.5 (2)
C(15)	0.5443 (6)	0.2413 (9)	−0.2320 (7)	5.6 (2)
C(16)	0.2561 (5)	−0.1896 (7)	−0.1256 (5)	3.3 (2)
C(17)	0.0687 (6)	0.1121 (7)	−0.2546 (6)	3.5 (2)

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Au—Br	2.390 (1)	C(2)—C(3)	1.382 (10)
Au—N(1)	2.078 (6)	C(3)—C(4)	1.367 (11)
Au—N(2)	2.839 (5)	C(4)—C(5)	1.383 (10)
Au—C(16)	2.006 (7)	C(5)—C(6)	1.475 (10)
Au—C(17)	2.020 (7)	C(6)—C(7)	1.381 (10)
N(1)—C(1)	1.360 (10)	C(7)—C(8)	1.385 (12)
N(1)—C(5)	1.337 (8)	C(8)—C(9)	1.362 (13)
N(2)—C(6)	1.342 (10)	C(9)—C(10)	1.392 (11)
N(2)—C(10)	1.345 (10)	C(10)—C(11)	1.488 (11)
N(3)—C(11)	1.330 (11)	C(11)—C(12)	1.371 (11)
N(3)—C(15)	1.332 (13)	C(12)—C(13)	1.380 (13)
N(4)—C(16)	1.115 (10)	C(13)—C(14)	1.363 (13)
N(5)—C(17)	1.121 (10)	C(14)—C(15)	1.330 (13)
C(1)—C(2)	1.356 (10)		

Br—Au—N(1)	175.6 (2)	N(1)—C(5)—C(4)	118.2 (6)
Br—Au—N(2)	116.5 (1)	C(4)—C(5)—C(6)	120.8 (6)
Br—Au—C(16)	89.0 (2)	N(1)—C(5)—C(6)	120.9 (5)
Br—Au—C(17)	88.5 (2)	N(2)—C(6)—C(5)	115.7 (6)
N(1)—Au—N(2)	67.9 (2)	C(5)—C(6)—C(7)	121.3 (6)
N(1)—Au—C(16)	90.3 (2)	N(2)—C(6)—C(7)	123.0 (6)
N(1)—Au—C(17)	92.1 (3)	C(6)—C(7)—C(8)	119.0 (7)
N(2)—Au—C(16)	104.8 (2)	C(7)—C(8)—C(9)	118.8 (7)
N(2)—Au—C(17)	77.8 (2)	C(8)—C(9)—C(10)	119.4 (8)
C(16)—Au—C(17)	177.0 (3)	N(2)—C(10)—C(9)	122.4 (7)
Au—N(1)—C(1)	116.2 (4)	C(9)—C(10)—C(11)	120.5 (7)
Au—N(1)—C(5)	122.8 (4)	N(2)—C(10)—C(11)	117.1 (6)
C(1)—N(1)—C(5)	120.8 (5)	N(3)—C(11)—C(10)	116.6 (7)
Au—N(2)—C(6)	96.0 (4)	C(10)—C(11)—C(12)	122.2 (6)
Au—N(2)—C(10)	131.9 (4)	N(3)—C(11)—C(12)	121.2 (7)
C(6)—N(2)—C(10)	117.4 (6)	C(11)—C(12)—C(13)	119.1 (7)
C(11)—N(3)—C(15)	116.9 (7)	C(12)—C(13)—C(14)	119.8 (8)
N(1)—C(1)—C(2)	121.4 (7)	C(13)—C(14)—C(15)	116.5 (8)
C(1)—C(2)—C(3)	119.3 (6)	N(3)—C(15)—C(14)	126.4 (8)
C(2)—C(3)—C(4)	118.0 (6)	Au—C(16)—N(4)	175.7 (7)
C(3)—C(4)—C(5)	122.1 (7)	Au—C(17)—N(5)	176.1 (7)

reflections collected ($-16 \le h \le 16$, $0 \le k \le 14$, $0 \le l \le 16$), 2186 with $I_o \ge 3\sigma(I_o)$ used in the refinement; three standard reflections monitored every 2 h showed no significant variation during data collection; Lorentz, polarization and absorption correction (minimum transmission factor = 0.71). Solution by Patterson and Fourier methods; refinement by full-matrix least squares, anisotropic non-H and isotropic H atoms (all located in ΔF map), final $R = 0.030$, $wR = 0.026$, $w = 4F_o^2/[\sigma^2(F_o)^2 + (0.02F_o^2)^2]$; max. $\Delta/\sigma = 0.06$, $S = 1.09$; final difference-map peaks in the range -0.45 to 0.50 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol IV); all calculations performed with CAD-4 *SDP* system of programs (Frenz, 1978), and *PARST* (Nardelli, 1983).

Discussion. Final atomic and thermal parameters are given in Table 1. An *ORTEP* (Johnson, 1976) view of the molecule is shown in Fig. 1. Bond distances and angles are given in Table 2.*

The coordination around Au^{III} is distorted square-pyramidal (see Fig. 1). The Au atom is displaced from the least-squares plane defined by the Br, N(1), C(16), C(17) atoms [$\Sigma(\Delta/\sigma)^2 = 77.4$] towards the polyhedron centre by 0.072 Å, and the straight line

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* Lists of structure factors, H-atom positional and thermal parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54804 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0297]

connecting Au with the apical N(2) atom makes an angle of 28.7 (1)° with the perpendicular to the mean plane.

The Au—Br distance of 2.390 (1) Å is in agreement with the corresponding distances of 2.402 (1), 2.385 (3) and 2.398 (4) Å found in other Au^{III} complexes having similar coordination and where a Br atom is *trans* to the ring N atom (Marangoni, Pitteri, Bertolasi, Gilli & Ferretti, 1986; Robinson & Sinn, 1975; O'Connor & Sinn, 1978).

Although the terpyridine is commonly a terdentate ligand, in the present compound it acts as a bidentate one (see Fig. 1) with quite different Au—N(1) and Au—N(2) distances of 2.078 (6) and 2.839 (5) Å, respectively. Structural and electronic analysis of Au^{III} square-pyramidal complexes shows that the stereochemistry of the Au—N(apical) interaction is mainly determined on one side by the geometrical constraints inside the organic ligand and, on the other, by the necessity of minimizing the interaction of N with the d_{z^2} metal orbital in order to avoid the possibility of a high-spin Au^{III} ground state in d^8 square-pyramidal complexes, which is impossible because of the large ligand-field splitting in a third-transition series ion such as Au^{III} (Robinson & Sinn, 1975). The scatter plot of Fig. 2 shows that when the N(basal)—Au—N(apical) angle (α) increases, the

Au—N(apical) distance decreases as a consequence of a better overlap between the N lone pair and the d_{z^2} Au^{III} orbital. The interaction could reach a maximum when the angle α tends to 90°; however, as a consequence of the electronic constraints already discussed, the angles remain in the range 67–73° and Au—N distances in the range 2.58–2.839 Å; that is, intermediate between a true bond and a van der Waals interaction.

In general, Au^{III} complexes with pyridine derivatives present a large variety of Au—N bond distances: from 1.931 (7) Å, found in a distorted square-planar tridentate complex with terpyridine (Hollis & Lippard, 1983), to 2.839 (5) Å, found in the present compound and discussed above. According
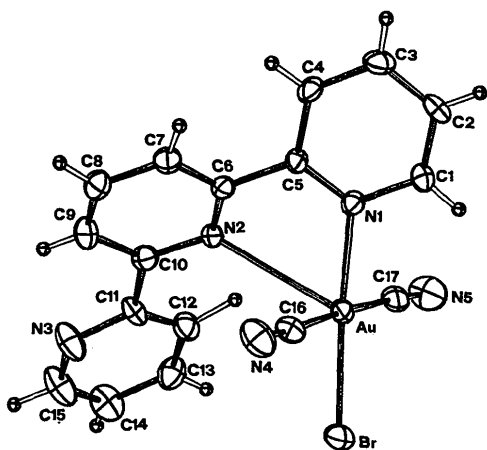

Fig. 1. An ORTEP (Johnson, 1976) view of the title compound showing the atom-labelling scheme. The thermal ellipsoids are at 40% probability.
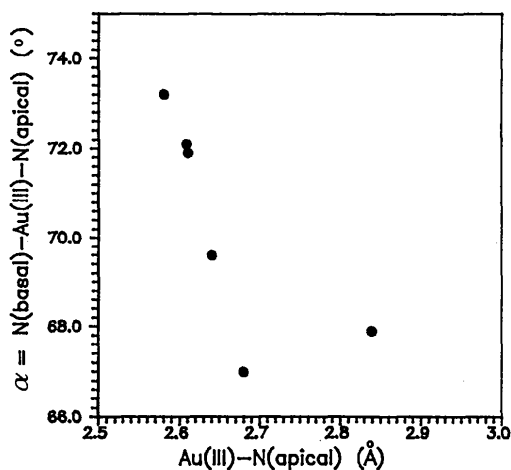

Fig. 2. Scatterplot of the angle N(basal)—Au^{III}—N(apical) (α) vs the bond distance Au^{III}—N(apical) for square-pyramidal derivatives [data taken from: Robinson & Sinn (1975); O'Connor & Sinn (1978); Marangoni et al. (1986); present work].

Table 3. Au—N bond distances (Å) and C—N—C internal angles (°) in the structures of Au^{III}—pyridine derivatives having σ(Au—N) < 0.01 Å and σ(C—N—C) < 1°

	Au—N	C—N—C	Reference
[Au(terpy) (CN)₂Br]	2.078 (6)	120.8 (5)	(a)
	2.839 (5)	117.4 (6)	
[Au(terpy)Cl]Cl₂	2.029 (6)	121.5 (7)	(b)
	2.018 (6)	121.1 (7)	
	1.931 (7)	123.4 (7)	
[Au(terpy)Cl]₂[AuCl₂]₃[AuCl₄]	2.030 (8)	120.1 (9)	(b)
	2.022 (9)	121.0 (9)	
	1.941 (8)	124.5 (9)	
[Au(phen)(CN)₂Br]	2.091 (5)	122.0 (5)	(c)
	2.608 (7)	117.6 (6)	
[Au(bpy)Cl₃]	2.025 (8)	120.5 (8)	(d)
	2.026 (8)	119.8 (9)	
	2.014 (9)	118.9 (9)	
	2.018 (9)	120.8 (8)	
[Au(bpy)(1-methyluracil)₂]ClO₄	2.028 (5)	120.9 (6)	(d)
	2.027 (5)	120.6 (6)	

terpy = 2,2':6',2''-terpyridine; phen = 1,10-phenanthroline; bpy = 2,2'-bipyridyl.

(a) Present work; (b) Hollis & Lippard (1983); (c) Marangoni, Pitteri, Bertolasi, Gilli & Ferretti (1986); (d) Micklitz, Lippert, Müller, Mikulcik & Riede (1989).

to the principles of the valence shell electron pair repulsion (VSEPR) theory (Gillespie, 1972) this spread of distances should be paralleled by variations of the internal C—N—C angles of the pyridine rings. When the Au^{III}—N distance is very short, the metal behaves like a strong electron-withdrawing substituent which increases the value of the C—N—C angle; on the other hand, when the distance is longer, the metal becomes less electronegative allowing such an angle to shrink. This interrelation between distances and angles is actually observed. Table 3 reports Au—N and C—N—C values derived from the most accurate crystal structure determinations of square-planar and square-pyramidal Au^{III}—pyridine derivatives. The C—N—C angle is on average 120.7 [8]° for the 'normal' Au—N distances (mean value 2.03 [2] Å) but becomes smaller (117.4 and 117.6°) for the longer distances of 2.839 and 2.608 Å, while it becomes larger (123.4 and 124.5°) for the shortest Au—N distances of 1.931 and 1.941 Å.

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meso-(1,1,4,7,10,10-Hexaphenyl-1,4,7,10-tetraphosphadecane-P,P',P'',P''') platinum(II) Bis(tetraphenylborate)

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Abstract. *meso*-[Pt($C_{42}H_{42}P_4$)][B($C_{24}H_{20}$)]$_2$.3CH$_2$Cl$_2$, $M_r = 1759.05$, monoclinic, $P2_1/c$, $a = 15.761$ (1), $b = 28.731$ (3), $c = 20.832$ (2) Å, $\beta = 114.967$ (6)°, $V = 8551.80$ Å^3, $Z = 4$, $D_m = 1.38$, $D_x = 1.366$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 5.921$ mm^{-1}, $F(000) = 3584$, $T = 283$ K, final $R = 0.080$ for 7308 observed reflections. The X-ray structure analysis shows a slightly distorted square-planar coordination of the Pt atom by the P atoms. All four P atoms are located within a plane (maximum deviation 0.016 Å). The Pt atom is 0.161 Å out of this plane. The Pt—PPh bonds [2.274 (4) Å] are significantly shorter than the Pt—PPh$_2$ bonds [2.327 (4) Å]. The PhP—Pt—PPh$_2$ angles and the PhP—Pt—PPh angle are constrained to about 85° (mean value 84.3, Δ_{max} 0.7°). The Ph$_2$P—Pt—PPh$_2$ angle is wide open [105.8 (2)°]. The thermodynamic destabilization of the square-planar arrangement of the title compound is compared with the destabilization of the corresponding chiral form and differences are discussed. Short intramolecular contact distances lead, in both cases, to the occurrence of related five-coordinate trigonal-bipyramidal and distorted tetrahedral compounds, thus releasing the strain of a planar P$_4$ configuration.

Introduction. The X-ray structure analysis of chiral [Pt(P_4)](BPh$_4$)$_2$ (2), where P_4 is 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, has been performed only recently (Brüggeller & Hübner, 1990). It has been shown that the square-planar arrangement of P_4 is destabilized in (2). This destabilization is a necessary requirement for the addition of a fifth ligand and the formation of non-planar structures in

several Pt^{II} complexes (De Felice, Ganis, Vitagliano & Valle, 1988). Similar phenomena have been observed for (2) and *meso*-[Pt(P_4)](BPh$_4$)$_2$ (1) (Brüggeller, 1990). The distortions of square-planar P_4 configurations as well as the possibility of the addition of a fifth ligand which may result in a deviation from a planar P_4 arrangement are of interest in homogeneous catalysis. Preparative results indicate that with respect to a square planar to tetrahedral movement of P_4 upon addition of a fifth ligand, (2) is more destabilized than (1). This is in agreement with molecular modelling studies of chiral and *meso* P_4, which indicate that there is no smooth transition from planar to non-planar structures in the case of chiral P_4 (Brown & Canning, 1984). In order to establish the kind of destabilization in (1) and to make a comparison with (2) possible, an X-ray structure analysis of (1) was performed.

(1)   (BPh$_4$)$_2$
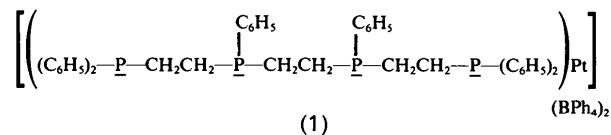
Experimental. Single crystals of (1) have been obtained by the slow production of (1) in a CH$_2$Cl$_2$/EtOH mixture ($v/v = 3/1$) *via* the following stoichiometric reaction:

2 *meso*-[Pt(CN)(P_4)](BPh$_4$) → *meso*-[Pt(P_4)](BPh$_4$)$_2$

+ *meso*-[Pt(P_4)](CN)$_2$.
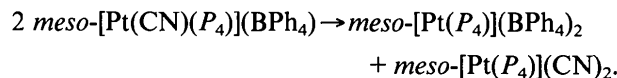
Attempts to prepare suitable crystals from solutions of (1), and from *meso*-[PtCl(P_4)](BPh$_4$) (Brüggeller, 1989) in the presence of Na(BPh$_4$) by loss of the

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