

## The Structure of Bis(1,10-phenanthroline)palladium(II) Diperchlorate

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(Received 23 July 1980; accepted 25 August 1980)

**Abstract.**  $[\text{Pd}(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{ClO}_4)_2$ ,  $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Pd}^{2+} \cdot 2\text{ClO}_4^-$ , monoclinic,  $I2/c$ ,  $a = 14.557(6)$ ,  $b = 10.982(5)$ ,  $c = 14.880(6)$  Å,  $\beta = 95.51(4)^\circ$ ,  $Z = 4$ ,  $U = 2368$  Å<sup>3</sup>,  $D_c = 1.87$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.06$  mm<sup>-1</sup>.  $R = 0.045$  for 2289 reflexions [ $I > 2\sigma(I)$ ] and 209 parameters. The cation has twofold symmetry. Overcrowding of the ligands is relieved by a tetrahedral distortion of  $\text{PdN}_4$  [the angle between the planes through  $\text{PdN}_2$  is  $18.7(2)^\circ$ ] and by small distortions of the ligands. Pd–N distances are 2.059(4) and 2.043(4) Å.

**Introduction.** The dimensions of 1,10-phenanthroline (phen) are such that a planar arrangement of two of these groups about a metal atom, with normal  $M$ – $N$  distances, would give an impossibly close approach of H atoms of opposite ligands (McKenzie, 1971, and references therein). The strain can be relieved by bowing the ligands away from each other (Rund, 1968) in a manner similar to that observed in bis(2,2'-dipyridyliminato)palladium(II) (Freeman & Snow, 1965) or by a tetrahedral distortion of  $\text{PdN}_4$ .

Compounds do exist with a *trans* arrangement of planar phenanthrolines, e.g.  $[\text{Srphen}_2(\text{OH})_4](\text{ClO}_4)_2 \cdot 2\text{phen}$  and  $[\text{Baphen}_2(\text{OH})_4](\text{ClO}_4)_2 \cdot 2\text{phen}$  (Smith, O'Reilly, Kennard & White, 1977), but these have very long  $M$ – $N$  bonds, Sr–N = 2.793(7) and Ba–N = 2.956(7) Å. Rund (1968) suggested that for H–H distances of 2.4 Å the  $M$ – $N$  bond should be at least 2.8 Å.

$[\text{Pd}(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{ClO}_4)_2$  was obtained by the method of Livingstone (1951) and recrystallized from water. A crystal [described approximately by the following Miller indices and distances,  $d$ , in mm from an arbitrary origin:  $\bar{1}00$  (0.0052);  $100$  (0.0112);  $\bar{1}\bar{1}0$  (0.0083);  $110$  (0.0079);  $1\bar{1}0$  (0.0105);  $10\bar{1}$  (0.0145);  $237$  (0.0171)] was mounted on a Picker FACS-1 computer-controlled four-circle diffractometer. Cell parameters were determined by least squares from the setting angles of 12

reflexions. 6070 reflexions were measured with graphite-monochromated Mo  $K\alpha$  radiation giving 2289 independent reflexions with  $I > 2\sigma(I)$ .

Since there are four cations in the cell the Pd must be on a special position. The possibilities are (a) 0,0,0; (b)  $0, \frac{1}{2}, 0$ ; (c)  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ; (d)  $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$ ; and (e)  $0, y, \frac{1}{4}$ . Reflexions  $hkl$  with  $l$  odd are systematically weak, so (c) and (d) can be rejected; furthermore (b) is equivalent to (a). If the cation is on (a) it must have a symmetry centre, if on (e) a twofold axis.

A Patterson function showed Pd–Pd and Cl–Cl vectors compatible with Pd on (a) or on (e) with  $y \approx 0$ ; Cl also has  $y \approx 0$ . The Pd–C vectors indicated two slightly different orientations of the phenanthrolines which could only be explained if Pd was on the twofold axis. A Fourier synthesis based on signs calculated from  $[\text{Pdphen}_2]^{2+}$  and Cl gave the positions of the O atoms.

Least-squares refinement with 2289 reflexions [ $I > 2\sigma(I)$ ] gave  $R = 0.045$  for 209 parameters. The H atoms were located from a difference synthesis. No extinction correction was required. Atomic coordinates are listed in Table 1.\*

Calculations were carried out with the following programs: data reduction *UCFACS* (Duesler & Raymond, 1971); Fourier syntheses *ZALKINS* (A. Zalkin, Lawrence Radiation Laboratory, University of California); least-squares refinement, *LINUS* (Coppens & Hamilton, 1970); distances and angles, *ORFFE* (Busing, Martin & Levy, 1964); drawings, *ORTEP* (Johnson, 1965). Scattering factors were those of Cromer & Mann (1968) for Pd, Cl, O, N, and C and Stewart, Davidson & Simpson (1965) for H.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35608 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.  
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Table 1. Fractional atomic coordinates ( $\times 10^5$  for Pd and Cl,  $\times 10^4$  for O, N, and C, and  $\times 10^3$  for H)

Isotropic thermal parameters ( $\text{\AA}^2 \times 10^{-3}$ ) are calculated from the  $U_{ij}^*$  for atoms other than H.  $\Delta$  is the deviation ( $\text{\AA} \times 10^{-3}$ ) from the plane through the cation. Where parameters are fixed by symmetry the e.s.d.'s are given as daggers.

	x	y	z	$U_{iso}$	$\Delta$
Pd	0 (†)	991 (4)	25000 (†)	32	0 (†)
Cl	32300 (10)	1295 (13)	31293 (9)	49	
N(1)	400 (3)	1282 (3)	3538 (3)	35	-181 (4)
N(2)	645 (3)	-1111 (3)	3392 (3)	34	250 (4)
C(1)	228 (4)	2461 (5)	3623 (4)	47	-471 (6)
C(2)	522 (5)	3116 (6)	4405 (5)	55	-618 (7)
C(3)	976 (4)	2539 (6)	5126 (4)	51	-508 (6)
C(4)	1124 (3)	1288 (5)	5084 (4)	42	-278 (5)
C(5)	1575 (4)	579 (7)	5821 (4)	48	-182 (7)
C(6)	1717 (4)	-621 (7)	5728 (4)	51	74 (7)
C(7)	1433 (3)	-1242 (5)	4913 (4)	41	256 (5)
C(8)	1580 (4)	-2492 (6)	4762 (4)	48	559 (6)
C(9)	1311 (4)	-2990 (5)	3947 (5)	49	762 (6)
C(10)	861 (4)	-2276 (5)	3266 (4)	42	628 (5)
C(11)	828 (3)	691 (4)	4280 (3)	34	-120 (5)
C(12)	963 (3)	-584 (4)	4192 (3)	34	123 (5)
O(1)	3619 (7)	172 (6)	3997 (5)	110	
O(2)	3758 (6)	470 (8)	2469 (6)	128	
O(3)	2535 (6)	1002 (8)	3121 (6)	153	
O(4)	2814 (4)	-1013 (5)	2914 (4)	77	
H(1)	-14 (4)	286 (5)	313 (4)	53 (16)	-629 (55)
H(2)	47 (5)	393 (7)	451 (5)	83 (22)	-758 (70)
H(3)	119 (5)	292 (6)	558 (5)	40 (22)	-530 (68)
H(5)	179 (4)	89 (6)	627 (4)	43 (19)	-210 (52)
H(6)	198 (4)	-107 (6)	617 (4)	76 (20)	121 (64)
H(8)	181 (5)	-301 (7)	527 (5)	78 (22)	510 (69)
H(9)	135 (4)	-381 (6)	381 (4)	71 (20)	914 (64)
H(10)	68 (4)	-264 (6)	274 (4)	50 (20)	745 (60)

\*  $U_{iso} = (U_1 \cdot U_2 \cdot U_3)^{2/3}$  where  $U_1$ ,  $U_2$ , and  $U_3$  are the r.m.s. amplitudes of vibration along the principal axes of the  $U_{ij}$ .

**Discussion.** The  $[\text{Pdphen}_2]^{2+}$  ion, Fig. 1, has twofold symmetry, the N atoms being at the corners of a flattened tetrahedron. H(1)–H(1') and H(10)–H(10') are both 2.0 (1) Å. Bond distances and angles are listed in Table 2. The mean Pd–N distance is 2.051 (3) Å and the N(1)–Pd–N(2) angle is 81.0 (2)°, *cf.* 2.034 (4) Å and 80.0 (2)° in the bipyridyl complex  $[\text{Pdbpy}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (Chieh, 1972). The phenanthroline group is almost planar. N(1) and N(2) are on opposite sides of the plane so that the angle between the planes through the ligands, 22.5°, is larger than the angle between Pd, N(1), N(2) and Pd, N(1'), N(2'), 18.7 (2)°. The corresponding values for  $[\text{Pdbpy}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  are 33.2 and 24.6 (4)°, *i.e.* the complex with the smallest torsion angle has the longest Pd–N distance. The angles in  $[\text{Ptphen}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (Hazell & Mukhopadhyay, 1980) are 27.1 and 20.9 (5)°.

The  $[\text{Mphen}_2]^{2+}$  ion does not retain 222 ( $D_2$ ) symmetry in the crystal. In the three  $[\text{Mphen}_2]^{2+}$  complexes which have been determined {the third is  $[\text{Hgphen}_2](\text{NO}_3)_2$  (Grdenić, Kamenar & Hergold-Brundić, 1978)} the symmetry is reduced to 2 ( $C_2$ ), although it is a different twofold axis which is retained

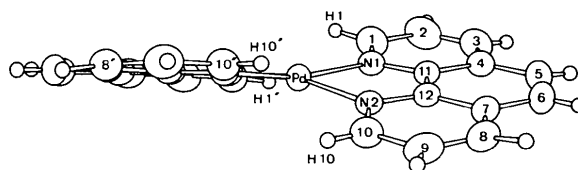


Fig. 1. The  $[\text{Pdphen}_2]^{2+}$  ion viewed along the line joining N(1') to N(2'). The chemical symbols for the C atoms have been omitted. H atoms have the same number as the C to which they are bonded.

Table 2. Bond lengths (Å), selected intramolecular distances (Å), and bond angles (°)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$ .			
Pd–N(1)	2.059 (4)	C(11)–C(12)	1.421 (7)
Pd–N(2)	2.043 (4)	N(1)–N(2)	2.664 (5)
N(1)–C(1)	1.328 (6)	C(1)–H(1)	0.97 (5)
N(2)–C(10)	1.335 (6)	C(2)–H(2)	0.91 (7)
N(1)–C(11)	1.377 (6)	C(3)–H(3)	0.83 (7)
N(2)–C(12)	1.363 (6)	C(5)–H(5)	0.79 (6)
C(1)–C(2)	1.401 (8)	C(6)–H(6)	0.87 (6)
C(9)–C(10)	1.395 (7)	C(8)–H(8)	0.98 (7)
C(2)–C(3)	1.361 (9)	C(9)–H(9)	0.93 (6)
C(8)–C(9)	1.352 (9)	C(10)–H(10)	0.90 (6)
C(3)–C(4)	1.394 (8)	H(1)–H(1')	1.96 (10)
C(7)–C(8)	1.411 (8)	H(10)–H(10')	2.04 (11)
C(4)–C(5)	1.449 (8)	Cl–O(1)	1.360 (6)
C(6)–C(7)	1.419 (8)	Cl–O(2)	1.356 (7)
C(4)–C(11)	1.396 (7)	Cl–O(3)	1.392 (7)
C(7)–C(12)	1.415 (7)	Cl–O(4)	1.417 (5)
C(5)–C(6)	1.342 (9)		
N(1)–Pd–N(2)	81.0 (2)	C(5)–C(4)–C(11)	118.4 (5)
N(1)–Pd–N(1')	101.8 (2)	C(4)–C(11)–C(12)	120.5 (5)
N(2)–Pd–N(2')	98.8 (2)	C(7)–C(12)–C(11)	119.6 (5)
Pd–N(1)–C(1)	130.1 (4)	N(1)–C(1)–H(1)	118 (3)
Pd–N(2)–C(10)	129.1 (4)	C(2)–C(1)–H(1)	120 (3)
Pd–N(1)–C(11)	112.2 (3)	C(1)–C(2)–H(2)	128 (5)
Pd–N(2)–C(12)	112.8 (3)	C(3)–C(2)–H(2)	111 (5)
N(1)–C(1)–C(2)	122.3 (6)	C(2)–C(3)–H(3)	122 (5)
N(2)–C(10)–C(9)	122.4 (5)	C(4)–C(3)–H(3)	119 (5)
N(1)–C(11)–C(12)	116.5 (4)	C(4)–C(5)–H(5)	121 (5)
N(2)–C(12)–C(11)	117.4 (4)	C(6)–C(5)–H(5)	117 (5)
N(1)–C(11)–C(4)	123.0 (5)	C(5)–C(6)–H(6)	122 (4)
N(2)–C(12)–C(7)	122.9 (5)	C(7)–C(6)–H(6)	116 (4)
C(1)–N(1)–C(11)	117.3 (4)	C(7)–C(8)–H(8)	119 (4)
C(10)–N(2)–C(12)	117.8 (4)	C(9)–C(8)–H(8)	121 (4)
C(1)–C(2)–C(3)	120.2 (6)	C(8)–C(9)–H(9)	125 (4)
C(8)–C(9)–C(10)	120.0 (5)	C(10)–C(9)–H(9)	115 (4)
C(2)–C(3)–C(4)	119.3 (6)	C(9)–C(10)–H(10)	117 (4)
C(7)–C(8)–C(9)	120.1 (5)	N(2)–C(10)–H(10)	120 (4)
C(3)–C(4)–C(5)	123.9 (6)	O(1)–Cl–O(2)	117.7 (6)
C(6)–C(7)–C(8)	124.6 (5)	O(1)–Cl–O(3)	102.8 (6)
C(3)–C(4)–C(11)	117.7 (6)	O(1)–Cl–O(4)	112.1 (4)
C(8)–C(7)–C(12)	116.5 (6)	O(2)–Cl–O(3)	105.4 (6)
C(6)–C(7)–C(12)	118.9 (6)	O(2)–Cl–O(4)	109.9 (4)
C(4)–C(5)–C(6)	120.9 (6)	O(3)–Cl–O(4)	108.3 (5)
C(5)–C(6)–C(7)	121.6 (6)		

in each case. Here N(2)–Pd–N(2') = 98.8 (2) is smaller than N(1)–Pd–N(1') = 101.8 (2)°, which would make N(2)–N(2') smaller than N(1)–N(1'). As a result N(2), C(10) and C(9) and their associated H

atoms deviate more from the plane through [Pdphen<sub>2</sub>]<sup>2+</sup> than do N(1), C(1), and C(2) (Table 1).

Cl—O distances range from 1.356 to 1.417 Å. The O atoms are very anisotropic. Correction of bond lengths assuming riding motion (Busing & Levy, 1964) gives minimum values of 1.410, 1.413, 1.439 and 1.425 Å, giving a mean value of 1.422 (3) Å, cf. 1.433 (3) Å in KClO<sub>4</sub> (Johansson & Lindqvist, 1977).

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*Acta Cryst.* (1980). **B36**, 3105–3107

## Tris(triphenylphosphine)gold(I) Tetraphenylborate

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(Received 8 July 1980; accepted 18 August 1980)

**Abstract.** C<sub>54</sub>H<sub>45</sub>AuP<sub>3</sub><sup>+</sup>·C<sub>24</sub>H<sub>20</sub>B<sub>4</sub><sup>-</sup>, [Au(C<sub>18</sub>H<sub>15</sub>P)<sub>3</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>], *M<sub>r</sub>* = 1241.13, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 16.747 (6), *b* = 20.645 (8), *c* = 18.398 (7) Å, β = 95.06 (2)°, *U* = 6336 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.301 Mg m<sup>-3</sup>, μ(Mo *Kα*) = 2.4 mm<sup>-1</sup>. Final *R* = 0.054 for 8753 reflexions. The Au atom shows trigonal planar coordination with Au—P 2.365 (3), 2.384 (3), 2.403 (3) Å, and P—Au—P 115.2 (2), 119.3 (2), 125.4 (2)°.

**Introduction.** During attempts to recrystallize L<sub>4</sub>Au<sup>+</sup>·BPh<sub>4</sub><sup>-</sup> (*L* = PPh<sub>3</sub> throughout this paper), large colourless crystals were obtained from acetonitrile. The approximate cell volume, determined from preliminary photographs, indicated that one ligand had been lost. In view of the paucity of information on three-coordinate Au<sup>I</sup> complexes, a crystal structure determination was undertaken.

Data were collected on a Stoe four-circle diffractometer with a profile-fitting method (Clegg, 1981).

11 522 intensities were measured in the range 7 < 2θ < 55° (monochromated Mo *Kα* radiation). After *L<sub>p</sub>* and empirical absorption corrections (crystal size 0.75 × 0.35 × 0.2 mm), averaging equivalent reflexions gave 8753 unique data with *F* > 4σ(*F*).

The structure was solved by the heavy-atom method and refined to *R<sub>w</sub>* = ∑*w*<sup>1/2</sup>Δ/∑*w*<sup>1/2</sup>|*F<sub>o</sub>*| = 0.054 = *R*. The weighting scheme was *w*<sup>-1</sup> = σ<sup>2</sup>(*F*) + 0.0005*F*<sup>2</sup>. The Au and P atoms were anisotropic; the phenyl rings were treated as rigid groups with C—C 1.395, C—H 0.96 Å and all angles 120°, *U*(H) = 1.2*U*(C). Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.\* A final difference map showed no peaks > 1 e Å<sup>-3</sup>.

\* Lists of structure factors, H atom coordinates and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35589 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.