

Structure of Bis(1,10-phenanthroline)platinum(II) Dichloride Trihydrate

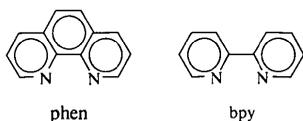
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Abstract. [Pt(C₁₂H₈N₂)₂]Cl₂·3H₂O, orthorhombic, *Fddd*, *a* = 30·116 (5), *b* = 9·648 (2), *c* = 32·699 (6) Å, *Z* = 16, *U* = 9501 Å³, *D_c* = 1·91 Mg m⁻³, $\mu(\text{Cu } K\alpha) = 13\cdot58 \text{ mm}^{-1}$. *R* = 0·030 for 1141 reflexions [*I* > 3 σ (*I*)] and 168 parameters. The cation has twofold symmetry. Overcrowding of the ligands is relieved by a tetrahedral distortion of PtN₄ [the angle between the planes through PtN₂ is 20·9 (5)°] and by distortion of the ligands. The structure is compared with other complexes with *trans* phenanthroline or bipyridyl groups. The [Ptphen₂]²⁺ groups are arranged in pairs with a Pt–Pt distance of 3·710 (1) Å. The packing is compared with that in a recent model for a high-temperature superconductor.

Introduction. The dimensions of 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) are such that a planar arrangement of two of these about a metal atom, with normal *M*–*N* distances, will result in an impossibly close approach of H atoms of opposing ligands (McKenzie, 1971, and references therein). The strain can be relieved by tetrahedral or rectangular deformation of the PtN₄ skeleton, by bending the ligands or by stretching the *M*–*N* bonds.



Bond stretching is not as likely as angle deformation. The rectangular distortion is governed largely by the bite of the ligands. Available information (Table 2) for complexes *ML*₂²⁺ (*L* = bpy or phen) shows that either *M* is on a symmetry centre so that *MN*₄ is exactly planar and the ligand is buckled, or the N atoms lie at the corners of a flattened tetrahedron and the ligands are approximately planar. In [Ptphen₂CN]⁺, which is formed from [Ptphen₂]²⁺ and CN⁻, there is a planar arrangement of three N atoms and the cyanide group, the remaining N being at the apex of a tetragonal pyramid (Wernberg & Hazell, 1980).

The crystals, which were provided by Ole Wernberg, were obtained from aqueous solution. A crystal

[described approximately by the following Miller indices and distances, *d*, in mm from an arbitrary origin: 19,0,13 (0·036); 19,0,13 (0·036); 0,5,21 (0·052); 0,8,17 (0·106); 0,0,1 (0·00)] was mounted on a Picker FACS-1 diffractometer. Cell dimensions were calculated from the setting angles of 15 reflexions. 1501 reflexions were measured with Ni-filtered Cu *K*α radiation and an ω -2 θ scan; of these, 1141 had $F_o^2 > 3\cdot0\sigma(F_o^2)$.

A Patterson synthesis showed Pt to be on a 16-fold position. A Fourier synthesis based on the signs calculated from Pt and Cl(1) (on a 32-fold position) showed the phenanthroline groups but also showed a peak, larger than that corresponding to Cl(1), on an eightfold position. Refinement with the extra atom as Cl(2) showed that Cl(1) had an unreasonably large thermal vibration. *U*_{iso} was 0·089 Å² for Cl(1) and 0·040 Å² for Cl(2). Assuming the structure to be disordered with Cl(1) having an occupation factor of 0·75 gave reasonable thermal parameters for both Cl(1) and Cl(2) and also the correct ratio of Cl:Pt. The Fourier synthesis also showed three peaks which were attributed to water molecules. A difference synthesis showed peaks at the positions where the H atoms of the phenanthrolines were expected. Full-matrix least-squares refinement of a scale factor, atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms, isotropic temperature factors for H atoms, and an isotropic extinction factor gave *R* = 0·030 for 1141 reflexions and 168 parameters. *g* was 1·1 (1) × 10⁻⁴ corresponding to a minimum value of *F_o*/*F_o*(corrected) of 0·89. The H atoms were kept at the positions calculated with C–H = 0·95 Å. Water molecules O(2) and O(3) have very large thermal motion; replacement of these by two half atoms gave an increase in *R*. However, there must still be some doubt as to the number of water molecules present.

Atomic coordinates are listed in Table 1.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35185 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^5$ for Pt, $\times 10^4$ for C, N, Cl, O and H)

Coordinates fixed by symmetry have their e.s.d.'s given as asterisks. Cl(1) has an occupation factor of 0.75. Isotropic thermal parameters, $U_{iso} \times 10^3$, are calculated from the U_{ij} for the non-hydrogen atoms. Δ is the deviation ($\text{\AA} \times 10^{-3}$) from the best plane through the phenanthroline ligand.

	x	y	z	$U_{iso} (\text{\AA}^2)$	Δ
Pt(1)	6341 (2)	12500 (*)	12500 (*)	32	3 (1)
N(1)	549 (3)	-349 (8)	850 (2)	32	79 (8)
N(2)	706 (2)	2278 (9)	714 (2)	34	-63 (8)
C(1)	417 (3)	-1656 (10)	932 (3)	36	-7 (10)
C(2)	338 (3)	-2617 (10)	622 (3)	34	-50 (10)
C(3)	390 (3)	-2243 (12)	222 (3)	40	-17 (11)
C(4)	511 (3)	-882 (11)	121 (3)	36	23 (10)
C(5)	559 (4)	-356 (12)	-285 (3)	45	11 (11)
C(6)	661 (4)	974 (12)	-358 (3)	45	4 (11)
C(7)	716 (3)	1940 (11)	-26 (3)	37	-23 (10)
C(8)	832 (4)	3341 (11)	-73 (3)	45	-2 (11)
C(9)	889 (3)	4148 (11)	264 (3)	45	13 (11)
C(10)	833 (3)	3589 (11)	656 (3)	34	9 (10)
C(11)	666 (3)	1438 (11)	373 (3)	35	-22 (9)
C(12)	577 (3)	15 (11)	446 (3)	34	44 (10)
Cl(1)	2835 (1)	3891 (5)	1669 (1)	63	
Cl(2)	1250 (*)	6250 (*)	1250 (*)	46	
O(1)	1250 (*)	6250 (*)	-400 (3)	72	
O(2)	738 (7)	8750 (*)	-1250 (*)	106	
O(3)	823 (7)	3750 (*)	-1250 (*)	140	
H(1)	372	-1923	1209	51 (22)	
H(2)	253	-3535	689	86 (39)	
H(3)	339	-2916	12	40 (23)	
H(5)	514	-968	-508	102 (50)	
H(6)	699	1277	-635	59 (31)	
H(8)	867	3720	-339	80 (41)	
H(9)	971	5096	235	45 (32)	
H(10)	889	4157	888	35 (20)	

Calculations were carried out on a Cyber 173 computer with the following programs: data reduction, including absorption correction, *DATAP* and *DSORTH* (State University of New York at Buffalo); Fourier syntheses, *ZALKINS* (A. Zalkin, Lawrence Radiation Laboratory); least-squares refinement, *LINUS* (Coppens & Hamilton, 1970); distances and angles, *ORFFE* (Busing, Martin & Levy, 1964); drawings, *ORTEP* (Johnson, 1965). Scattering factors were those of *International Tables for X-ray Crystallography* (1974) for Pt, Cromer & Mann (1968) for C, N, and O, and Stewart, Davidson & Simpson (1965) for H. Corrections were made for the anomalous dispersion of Pt (Cromer & Liberman, 1970).

Discussion. The $[\text{Ptphen}_2]^{2+}$ ion has twofold symmetry, the N atoms being at the corners of a flattened tetrahedron. Bond distances and angles are shown on Fig. 1. The phenanthroline group is almost planar, but the deviations from planarity are such that the angle between the two phenanthrolines, 27.1° , is larger than that between planes through Pt, N(1) and N(2) and through Pt, N(1') and N(2'), $20.9 (5)^\circ$. The mean Pt-N distance, $2.033 (6) \text{\AA}$, and the N(1)-Pt-N(2) angle, $80.1 (3)^\circ$, are similar to those in $[\text{Ptphen}_2\text{CN}]^+$, i.e. $2.041 (3) \text{\AA}$ and $81.7 (2)^\circ$. Thus bond stretching and rectangular distortion, other than that imposed by the bite of the phenanthroline, do not seem to play a part in relieving the strain caused by the close approach of H(1) and H(10'). H atom positions could not be refined. $\text{H}(1) \cdots \text{H}(10')$ is calculated to be 1.95\AA if it is assumed that $\text{C}-\text{H} = 1.05 \text{\AA}$ and that the C-H bond

Table 2. Geometries of trans complexes ML_2 ($L = \text{phen}$ or bpy)

φ_N is the angle between planes through MN_1N_2 and through MN_3N_4 ; φ_L is the angle between the two ligands. D is the mean deviation of non-hydrogen ligand atoms from the plane through that ligand; two values are given when the ligands are not related by symmetry.

	M-N	$\angle \text{NMN}$	φ_N	φ_L	D	Distortion*	Symmetry	Reference
$[\text{Ptphen}_2]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	$2.033 (6) \text{\AA}$	$80.1 (3)^\circ$	$20.9 (5)^\circ$	27.1°	0.026\AA	Twist	2	(a)
$[\text{Pt bpy}_2]\text{TCNQ}_2$	$2.02 (1)$	$78.3 (4)$	0.0	0.0	0.178	Bow	1	(b)
$[\text{Pt bpy}_2]\text{TCNQ}_3$	$2.02 (2)$	$77 (1)$	0.0	0.0	0.164	Bow	1	(c)
$[\text{Pd phen}_2](\text{ClO}_4)_2$	-	-	-	-	-	Bow	1	(d), † (e)
$[\text{Pd bpy}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	$2.034 (4)$	$80.0 (2)$	$24.6 (4)$	33.2	$0.027,$ 0.060	Twist		(f), (g) ‡
$[\text{Cu bpy}_2](\text{ClO}_4)_2$	$1.99 (1)$	$82.7 (5)$	$37.3 (7)$	46.7	$0.033,$ 0.098	Twist		(h)
$[\text{Cu bpy}_2]\text{S}_2\text{O}_6$	1.983	81.9	38.2	46.1	0.052	Twist	2	(i), † (j)
$[\text{Ag bpy}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	$2.160 (5)$	$77.4 (3)$	$27.9 (4)$	32.3	$0.054,$ 0.013	Twist		(k)
$[\text{Hg phen}_2](\text{NO}_3)_2$	$2.339 (5)$	$72.8 (2)$	$27.5 (4)$	25.9	$0.020,$ 0.013	Twist	2^\dagger	(l)

References: (a) This work; (b) Dong, Endres, Keller, Moroni & Nöthe (1977); (c) Endres, Keller, Moroni, Nöthe & Dong (1978); (d) Rund (1968); (e) Rund (1979); (f) Chieh (1972); (g) Hinamoto, Ooi & Kuraya (1972); (h) Nakai (1971); (i) Ferrari, Fava & Pelizzi (1977); (j) Fava (1979); (k) Atwood, Simms & Zatzko (1972); (l) Grdenić, Kamenar & Hergold-Brundić (1978).



† Twofold axis through the phenanthroline.

‡ Preliminary communications.

bisects the NCC angle. If the ion were planar, $H(1) \cdots H(10')$ would have been *ca* 1.3 Å.

The geometries of several *trans* complexes, ML_2 ($L = \text{bpy}$ or phen), are compared in Table 2. The strain resulting from the close proximity of the H atoms can be relieved by tetrahedral distortion of the MN_4 and by deformation of the ligand. For the $[\text{Pt}(\text{bpy})_2]\text{-TCNQ}$ compounds, crystallographic symmetry requires that MN_4 is planar and the ligands are bowed so that the ligands are on either side of the MN_4 plane, *cf.* bis(2,2'-dipyridyliminato)palladium(II) (Freeman & Snow, 1965). When there is tetrahedral distortion the ligands are usually twisted about the centre bond so that the angle between the ligands, ϕ_L , is greater than that between the MN_2 planes, ϕ_N . $\phi_L - \phi_N$ decreases as the $M-N$ distance increases, although, as might be expected, phenanthroline deforms less readily than bipyridyl.

A quarter of the unit cell is shown in Fig. 2. The $[\text{Pt}(\text{phen})_2]^{2+}$ ions form pairs with a Pt-Pt distance of 3.710 (1) Å. The ions, when seen down **a**, are not superimposed but are rotated by $\tau = 20.2$ (3)°. Little &

Lorentz (1976) have proposed a model for a high-temperature superconductor in which cyanine-dye chromophores are attached to $[\text{Pt}(\text{phen})_2]^{2+}$ and the units should stack so that the Pt atoms interact to form a conducting spine. If the Pt-Pt distance were as long as in $[\text{Pt}(\text{phen})_2]\text{Cl}_2$ the Pt-Pt interactions would be very weak and, unlike the $[\text{Pt}(\text{CN})_4]^{2-}$ complexes (Williams, Keefer, Washecheck & Enright, 1976) where Pt-Pt = 3.65, 3.75 Å for $\tau = 0^\circ$ and 2.89 Å for $\tau = 45^\circ$, it would not be possible to decrease the Pt-Pt distance by rotating the ions since they are non-planar and such a rotation would increase the interactions between the phenanthroline ligands.

Note added in proof: The structure of $[\text{Pd}(\text{phen})_2](\text{ClO}_4)_2$ has been redetermined (Rund & Hazell, unpublished). The $\text{Pd}(\text{phen})_2$ cation has twofold symmetry. Pd-N = 2.051 (3) Å, $\angle \text{NPdN} = 81.0$ (2)°, $\phi_N = 18.7$ (2)°, $\phi_L = 22.5$ °, $D = 0.028$ Å.

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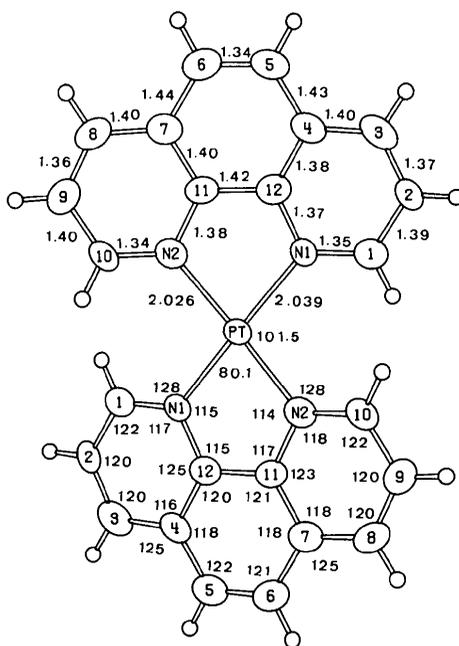


Fig. 1. Bond distances (Å) and angles (°). The e.s.d.'s are: Pt-N $\sigma = 0.008$; C-N $\sigma = 0.012$; C-C $\sigma = 0.014$ Å; $\angle \text{NPtN}$ $\sigma = 0.3$; $\angle \text{PtNC}$ $\sigma = 0.7$; $\angle \text{NCC}$, $\angle \text{CNC}$, and $\angle \text{CCC}$ $\sigma = 0.9^\circ$.

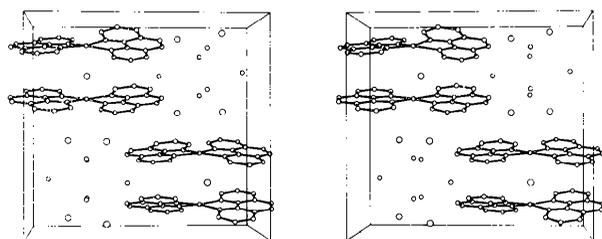


Fig. 2. Stereoview of a quarter of the unit-cell contents as seen along **b**. **a** (0 to $a/2$) is across the page, **c** (0 to $c/2$) is down the page, **b** runs from $-b/2$ to $b/2$. The large circles represent Cl^- .