Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(6,7-Dimethyl-2,3-di-2-pyridylquinoxaline)bis(3-methylpyridine)platinum(II) bis(hexafluorophosphate) acetone solvate 0.5-hydrate

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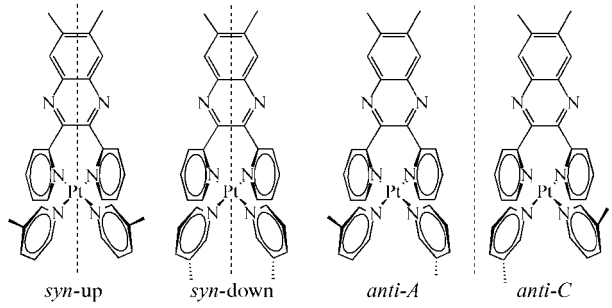
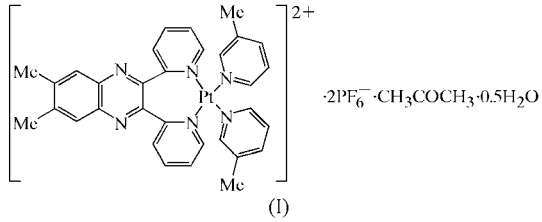
Received 3 November 2005
Accepted 2 December 2005
Online 24 December 2005

The crystal structure of the title compound, $[Pt(C_6H_7N)_2(C_{20}H_{16}N_4)](PF_6)_2\cdot C_3H_6O\cdot 0.5H_2O$, is composed of a bivalent square-planar platinum(II) complex, two PF_6^- counter-ions and solvent molecules. The di-2-pyridylquinoxaline ligands are known to confer an 'L shape' on square-planar platinum(II) complexes, which also display intercalating properties. The structural characterization reported here is a contribution to a wide-ranging study focused on structural and dynamical analyses of these substrates, which may provide better insight into their biological mechanisms and activities. The expected 'L-shaped' skeleton of the metallic complex combined with the antiparallel orientation of substituted pyridines (*anti* conformation) generates chiral objects, found in the solid state as a racemic mixture.

Comment

Many platinum complexes show biological properties related to their reactivity toward duplex DNA (Sundquist & Lippard, 1990). Beyond cisDDP (cisplatinum) activity (Harder & Rosenberg, 1970) due to the formation of covalent DNA complexes, some aromatic species were found to react with DNA through intercalation (Lerman, 1961). The intercalation was demonstrated to occur also for Pt coordination complexes bearing wide flat aromatic groups (Barton & Lippard, 1979). The great interest in these substrates led to careful characterization of metal complexes with extended flat moieties both by NMR and by X-ray crystallography; beyond the solid-state structure, the solution dynamic behavior is, of course, also related to activity (Rotondo *et al.*, 2003). Among the wide variety of complexes obtained using substituted pyridyls as ligands, those containing 6,7-dimethyl-2,3-di-2-pyridylquinoxaline (DMeDPQ) were found to coordinate Pt^{II} as a symmetrical seven-membered dipyridyl–metal chelate ring (Escuer *et al.*, 1989). The resulting 'L-shaped' complexes possess intercalating properties (Cusumano *et al.*, 2004). Moreover, the 'L-shaped' skeleton is prochiral, so that the combination with non-symmetrical ancillary ligands gives optically active complexes. For the $[Pt(DMeDPQ)(3\text{-Mepy})_2]^{2+}$ cation, the 3-methylpyridyl (3-Mepy) ligands are roughly perpendicular to the coordination plane. When the methyl groups of the 3-Mepy ligands are on the same side of the coordination plane, two C_s symmetric conformations will be generated (*syn*-up and *syn*-down); alternatively, the methyl groups can be placed on opposite sides, resulting in the loss of the mirror plane and the consequent development of two chiral C_1 enantiomeric conformers, *anti-C* and *anti-A* (see scheme below).





(I)

Because free 3-Mepy rotation is observed in solution, the presence of all four conformers gives rise to an averaged NMR

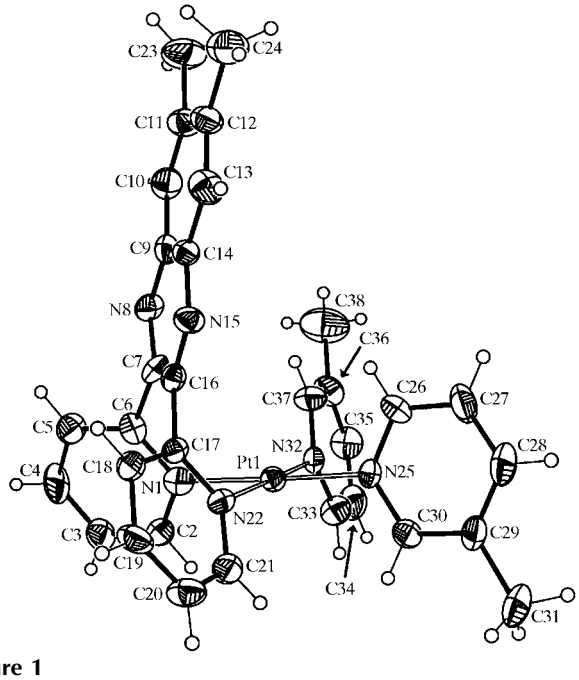


Figure 1
The cation of (I), showing the 'L-shaped' scaffold and the atom-labeling scheme. Displacements ellipsoids are drawn at the 30% probability level for all non-H atoms.

 DOI: 10.1107/S0108270105040163

signal (Rotondo *et al.*, 2004). In the solid state, only the chiral conformers (perhaps because they are thermodynamically favored) are detected, and since the space group is centrosymmetric, the crystal contains a racemic mixture. The asymmetric unit of the title compound, (I), comprises one Pt^{II} cation complex, two hexafluorophosphate ions, an acetone molecule and a water molecule with 50% occupancy. The metal is bound to four pyridyl N atoms (Table 1 and Fig. 1), which are positioned around platinum(II) in the typical square-planar geometry, the maximum deviation from the mean plane being 0.028 (5) Å (for atom N1). All the pyridyl rings are almost perfectly planar, as is the fused quinoxaline system. The angle between the metal coordination plane and the plane of the fused quinoxaline system is 75.8 (2)°, leading to the known 'L-shaped' arrangement (Fig. 1). Even though all four pyridyl rings tend to flip away from the coordination plane, the strained DMeDPQ pyridyl rings are less tilted than the free pyridyl ligands [the angles of the mean planes with respect to the coordination plane are 71.4 (3) and 70.2 (3)° *versus* 81.3 (3) and 83.1 (3)°, respectively]. This configuration confirms the previous hypothesis of Rotondo *et al.* (2004) regarding the stiffness of the DMeDPQ ligand often affecting partner ligands.

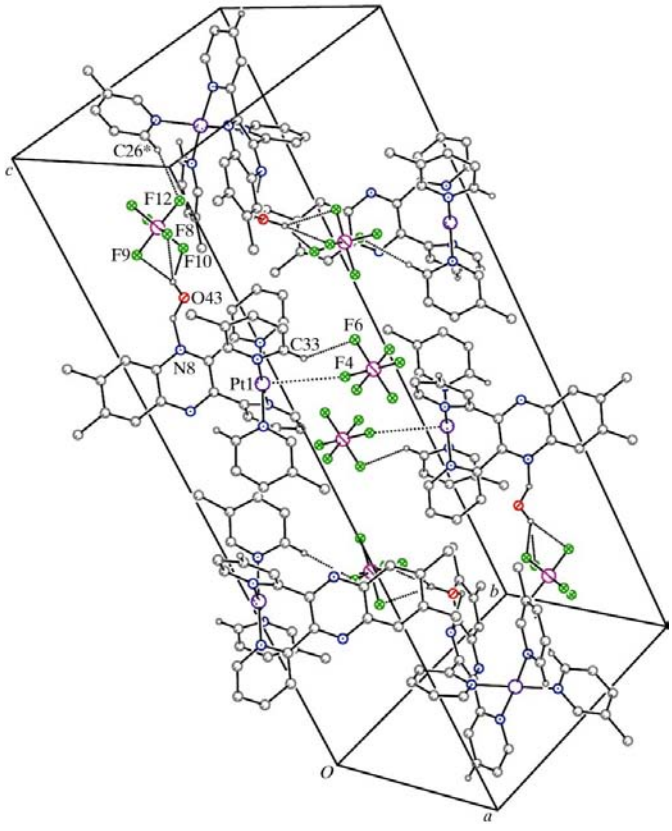


Figure 2
The crystal packing of (I), with intermolecular interactions shown as dotted lines; several atoms have been labeled for ease of correlation with Table 2. H atoms not involved in intermolecular interactions have been omitted for clarity. The atom marked with an asterisk (*) is at the symmetry position ($\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$).

The crystal packing of (I) is mainly stabilized by an O—H···N hydrogen bond augmented by a number of weak O—H···F hydrogen bonds, all involving the half-occupancy water molecule; several short C—H···F contacts also occur (Table 2 and Fig. 2). The close proximity between an F atom and the metal center should be noted [Pt1···F4 = 3.503 (1) Å, and the angle between the Pt1···F4 vector and the normal to the coordination plane is 8.1 (2)°]. This interaction characterizes many Pt complexes devoid of steric hindrance in the apical position; atom F4 is indeed located on the side opposite the cumbersome quinoxaline system. As is the case with most cationic complexes, the cations of (I) are held together mainly through interactions with anions and solvent groups (Fig. 2).

Experimental

The title complex was prepared as described by Rotondo *et al.* (2004); colorless crystals suitable for X-ray analysis were obtained by slow evaporation from acetone.

Crystal data

$[Pt(C_{20}H_{16}N_4)(C_6H_7N)_2](PF_6)_2\cdot C_3H_6O\cdot 0.5H_2O$
$M_r = 1050.73$
Monoclinic, $P2_1/n$
$a = 9.815$ (3) Å
$b = 13.105$ (3) Å
$c = 32.039$ (7) Å
$\beta = 96.620$ (15)°
$V = 4093.6$ (18) Å^3
$Z = 4$
$D_x = 1.705$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 3.9$–12.5°
$\mu = 3.60$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.22 × 0.18 × 0.08 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: empirical (using intensity measurements) (North *et al.*, 1968)
$T_{min} = 0.506$, $T_{max} = 0.757$
9390 measured reflections
7214 independent reflections
3904 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 25°$
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 15$
$l = -38 \rightarrow 38$
3 standard reflections
every 196 reflections
intensity decay: 6.8%

Table 1
Selected geometric parameters (Å, °).

Pt1—N32	2.005 (10)	Pt1—N22	2.019 (9)
Pt1—N1	2.017 (10)	Pt1—N25	2.022 (9)
N32—Pt1—N1	89.4 (4)	N32—Pt1—N25	92.5 (4)
N1—Pt1—N22	86.3 (4)	N22—Pt1—N25	91.7 (4)

Table 2
Geometry of hydrogen bonds and short intermolecular contacts (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O43—H43*A*···F8	0.99	2.03	2.79 (3)	132
O43—H43*A*···F9	0.99	2.32	3.29 (3)	166
O43—H43*A*···F10	0.99	2.40	3.23 (3)	140
O43—H43*B*···N8	0.99	2.35	3.00 (3)	122
C3—H3···F9^{i}	0.93	2.50	3.30 (2)	144
C35—H35···F9^{ii}	0.93	2.55	3.241 (19)	132
C26—H26···F12^{iii}	0.93	2.51	3.41 (2)	161
C33—H33···F6	0.93	2.51	3.275 (19)	140

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+1, y, z$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 10.6011P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.067$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.122$	$\Delta\rho_{max} = 0.83$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.71$ e Å^{-3}
7214 reflections	
532 parameters	
H-atom parameters constrained	

The space group of (I) was assumed to be centrosymmetric during the data-reduction procedure, and this hypothesis was confirmed by subsequent evaluation (Orpen *et al.*, 1992). All H atoms were treated as riding, with methyl C—H distances of 0.96 Å and aromatic C—H distances of 0.93 Å. The U_{iso}(H) values were fixed by the riding-model technique, being $1.2U_{eq}$(C) for aromatic and $1.5U_{eq}$(C) for methyl H atoms. The water molecule was located in a Fourier difference analysis and refined as a rigid group, while its occupancy factor was calculated by linking it to a free variable; the value found after ten least-squares cycles was fixed in order to reduce the number of parameters.

Data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XPREPW* (Bruker, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XPW* (Bruker, 1997); software used to prepare material for publication: *PARST97* (Nardelli, 1995) and *WinGX-PC* (Version 1.6.4.05; Farrugia, 1999).

The author is grateful to Professor Renzo Cini and his group for providing the instrument for data collection at the University of Siena, Italy.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: RB1020). Services for accessing these data are described at the back of the journal.

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