Bis[tris(pyrazol-1-yl)methane-$\kappa^2 N,N'$]-platinum(II) bis(hexafluorophosphate) nitromethane solvate

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Key indicators

Single-crystal X-ray study

$T = 150$ K

Mean σ(C–C) = 0.006 Å

R factor = 0.025

wR factor = 0.057

Data-to-parameter ratio = 17.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, [Pt($C_{10}H_{10}N_6$)$_2$](PF$_6$)$_2$·2CH$_3$NO$_2$, crystallizes with the Pt atom located on a crystallographic center of symmetry. The asymmetric unit comprises the anion, one-half cation and a nitromethane molecule. The anions and solvent pack to form a zigzag ribbon motif, alternating with layers of cations. The extended packing consists of a network of C—H···O, C—H···N and C—H···F intermolecular interactions.

Comment

Recently, Albrecht *et al.* (2000, 2001) have reported the synthesis of square-planar platinum(II) complexes with two potentially *mer*-coordinating ligands. In these complexes, one ligand is tridentate, whereas the second is monodentate with ligating groups above and below the coordination plane. We have recently demonstrated that certain complexes with this ligand architecture can act as outer-sphere two-electron reagents (Jude *et al.*, 2003). Reasoning that a similar architecture could be obtained with facially coordinating ligands such as tris(pyrazol-1-yl)methane (tpm), we undertook the synthesis and structural characterization of [Pt(tpm)$_2$]$^{2+}$ as the nitromethane-solvated PF$_6^-$ salt, (I) (Fig. 1). This crystallizes with the Pt atom located on a crystallographic center of symmetry.

(I)
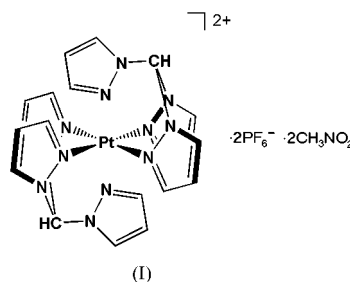
The asymmetric unit comprises the anion, one-half cation and a nitromethane molecule. The cation has a square-planar geometry about the Pt atom with distances of 1.996 (3) and 2.000 (3) Å for Pt—N1 and Pt—N3, respectively. The N1—Pt—N3 angle is 88.05 (1)°. The tpm ligand coordinates to the Pt atom in a bidentate fashion, forming a boat conformation for the resulting six-membered ring. The dihedral angle between the PtN$_4$ plane (Pt—N1—N2—N3—N4) and the coordinated rings are 30.1 (1) and 26.8 (1)° for rings N1/N2/C1/C2/C3 and N3/N4/C4/C5/C6, respectively. The uncoordinated ring, N5/N6/C8/C9/C10, folds over the PtN$_4$ plane, the dihedral angle being 65.0 (2)° and the Pt···N6 distance 3.509 (4) Å. The related Pd complex, [Pd(tpm)$_2$](BF$_4$)$_2$, reported by Canty *et al.* (1986), has Pd—N distances in the
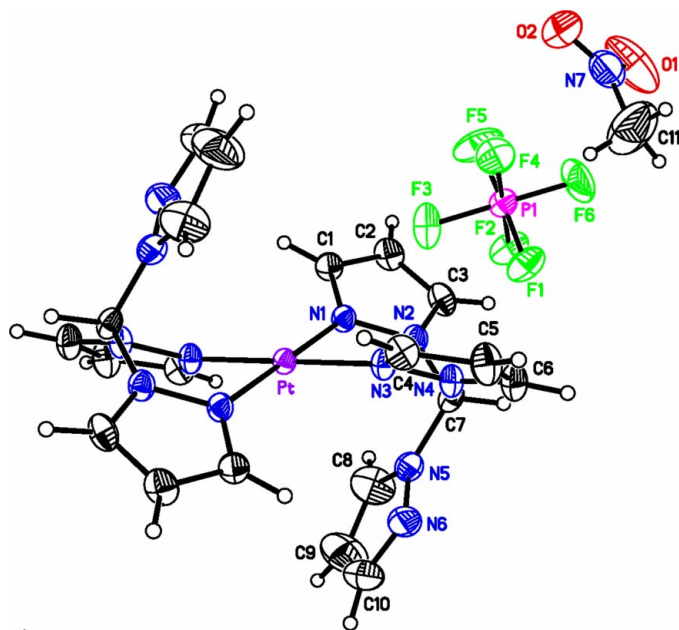
Figure 1
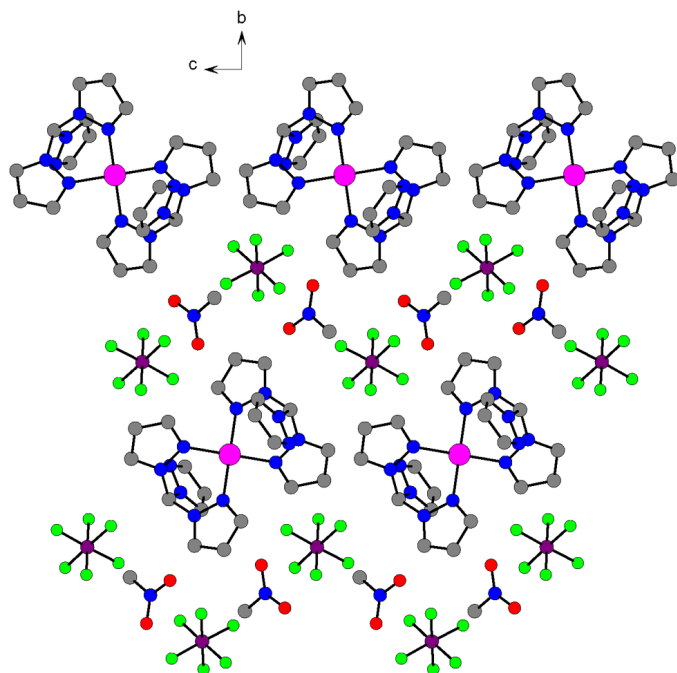The structure of (I) at 150 K, showing the atomic labeling and 50% probability ellipsoids.

Figure 2
Extended packing motif of (I), viewed along the *a* axis. H atoms have been omitted for clarity.

range 1.987 (8)–2.006 (9) Å and N—Pd—N angles of 87.4 (3)–92.6 (3)°. The dihedral angles for the PdN$_4$ plane and the coordinated rings (rings *A* and *B*) are 36.8 and 39.9°, while that for the uncoordinated ring (ring *C*) is 51.0°. The [bis-(pyrazolyl)methane]palladium complex, [Pd(dpm)$_2$](BF$_4$)$_2$, reported by Minghetti *et al.* (1986), also has the Pd atom in a square-planar environment with comparable *M*—N and N—*M*—N distances and angles to those observed for (I) and [Pd(tpm)$_2$](BF$_4$)$_2$.

The anions and solvent molecules in (I) pack to form a zigzag ribbon motif (Fig. 2), alternating with layers of cations. The extended packing consists of a network of C—H···O, C—H···N and C—H···F intermolecular interactions (Table 1) involving atoms N6, O1 and F1–F5. Atoms O2 and F6 do not participate in interactions with H–acceptor distances less than 2.7 Å.

Experimental

K$_2$PtCl$_4$ and tris(pyrazol-1-yl)methane (2 equivalents) were combined in water and refluxed. The reaction could be easily monitored by observing two color changes. First, the deep orange color of K$_2$PtCl$_4$ was gradually replaced by a yellow color corresponding to the monosubstituted tpm complex. The yellow color faded gradually as the second tpm ligand attached to platinum, forming [Pt(tpm)$_2$]Cl$_2$. Metathesis of the chloride salt with NH$_4$PF$_6$ resulted in (I). Single crystals were obtained as colorless plates from CH$_3$NO$_2$–Et$_2$O solution. ^{1}H NMR (d_6-DMSO, δ): 9.53 (2H, s), 8.88 (4H, d), 8.05 (2H, d), 7.95 (4H, d), 7.75 (2H, d), 6.96 (4H, t), 6.53 (2H, t).

Crystal data

[Pt(C$_{10}$H$_{10}$N$_6$)$_2$](PF$_6$)$_2$·2CH$_3$NO$_2$	$D_x = 1.950$ Mg m^{-3}
$M_r = 1035.60$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7038
$a = 7.9329$ (4) Å	reflections
$b = 23.2431$ (10) Å	$\theta = 1.8$–28.3°
$c = 9.9054$ (4) Å	$\mu = 4.19$ mm^{-1}
$\beta = 105.044$ (1)°	$T = 150$ (2) K
$V = 1763.81$ (14) Å^3	Plate, colorless
$Z = 2$	$0.12 \times 0.10 \times 0.05$ mm

Data collection

Bruker SMART6000 CCD diffractometer	4387 independent reflections
ω scans	3090 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.047$
(*SADABS*; Sheldrick, 2001)	$\theta_{max} = 28.3$°
$T_{min} = 0.634$, $T_{max} = 0.818$	$h = -10 \rightarrow 10$
23878 measured reflections	$k = -30 \rightarrow 30$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.017P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$+ 3.1656P]$
$wR(F^2) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
4387 reflections	$\Delta\rho_{max} = 0.80$ e Å^{-3}
250 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···N6^i	0.95	2.51	3.136 (5)	123
C4—H4···O1^{ii}	0.95	2.58	3.481 (6)	159
C5—H5···F5^{ii}	0.95	2.59	3.259 (5)	128
C3—H3···F1	0.95	2.52	3.201 (4)	129
C2—H2···F3	0.95	2.42	3.174 (5)	137
C6—H6···F2^{iii}	0.95	2.38	3.190 (5)	144
C7—H7···F2^{iii}	1.00	2.56	3.450 (5)	149
C3—H3···F3^{iii}	0.95	2.55	3.321 (5)	139
C7—H7···F3^{iii}	1.00	2.53	3.444 (4)	152
C11—H11C···F4^{iii}	0.98	2.49	3.136 (7)	123
C1—H1···F2^{iv}	0.95	2.47	3.402 (5)	168

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

The H atoms were either located directly or calculated geometrically (aromatic, methyne and methyl: C—H = 0.95, 1.00 and 0.98 Å, respectively) and treated with a riding model in subsequent refinement cycles. The isotropic displacement parameters were set to aU_{eq} of the carrier atom (a = 1.5 for methyl H atoms and 1.2 for all others). The nitromethane solvent of crystallization and the PF_6 anion show some disorder, as indicated by the enlarged anisotropic displacement parameters compared with the cation. Since the structure is chemically reasonable, resolved disorder models were not attempted.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Crystal Impact, 1997); software used to prepare material for publication: *SHELXTL*.

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