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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(C-C) = 0.009 \text{ \AA}$
R factor = 0.060
wR factor = 0.141
Data-to-parameter ratio = 16.5

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

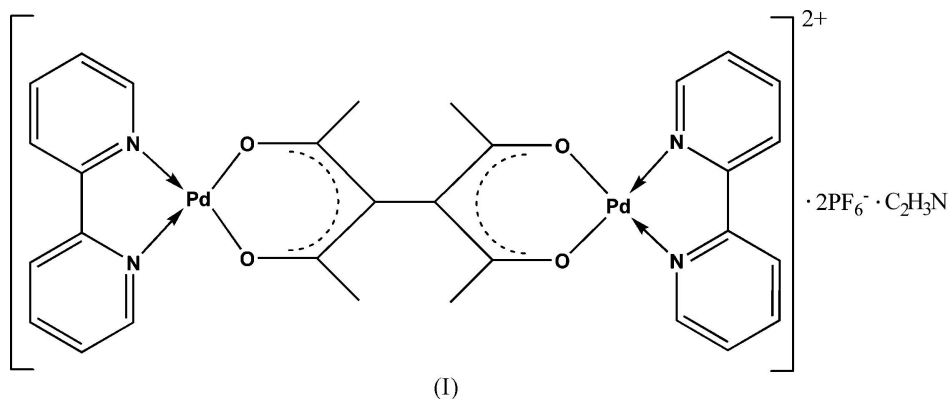
π -Stacking of μ -3,3'-bisacetylacetonato-bis[(2,2'-bipyridine)palladium(II)] hexafluorophosphate acetonitrile solvate

In the title complex, $[\text{Pd}_2(\text{C}_{10}\text{H}_{12}\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{PF}_6)_2 \cdot \text{CH}_3\text{CN}$, the Pd^{II} centers have a distorted *cis*-square-planar geometry defined by an *O,O'*-bidentate bisacetylacetonate dianion ligand and a chelating 2,2'-bipyridine ligand. The crystal structure is stabilized by electrostatic forces between the cations and anions, intermolecular π - π stacking interactions between pairs of 2,2'-bipyridine rings, and weak intermolecular hydrogen bonds involving hexafluorophosphate anions (C—H···F) and the solvent acetonitrile molecules (C—H···N).

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Comment

Palladium(II) or platinum(II) acetylacetonate compounds are receiving increasing attention owing to their importance as ideal precursors in preparing palladium or platinum films or coatings by chemical vapor deposition (CVD) (Nakamoto *et al.*, 1970). In spite of these investigations, there are few studies on (2,2'-bipyridine)palladium(II) acetylacetonate structures. In the present paper, we report the crystal structure of a new dinuclear palladium(II) complex, (I), bridged by a bisacetylacetonate dianion ligand (Fig. 1 and Table 1).



In the crystal structure, two of the anions lie on the glide plane. The occupancies of atoms P2, P3, F12 and F13 are 50%. Molecules of complex (I) pack by electrostatic forces between the cations and anions, π - π interactions between planar $[\text{Pd}(2,2'\text{-bipyridine})]$ units, and weak intermolecular hydrogen bonds involving anions and solvent molecules, as represented in Fig. 2. The centroid-centroid contact between two bipyridine molecules is 3.662 (4) Å, and the angle between the ring-centroid vector and the ring normal to one of the bipyridine planes is about 23°. The non-classical hydrogen bonds that connect cations and solvent acetonitrile molecules are detailed in Table 2.

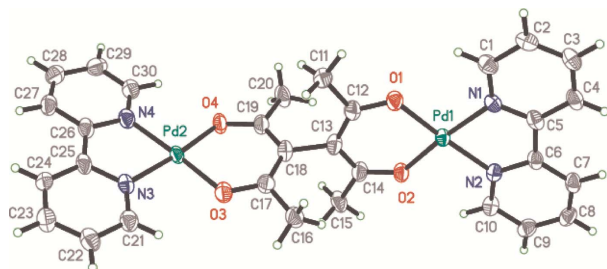


Figure 1
View of the cation of (I), showing 30% probability displacement ellipsoids and the atom numbering scheme.

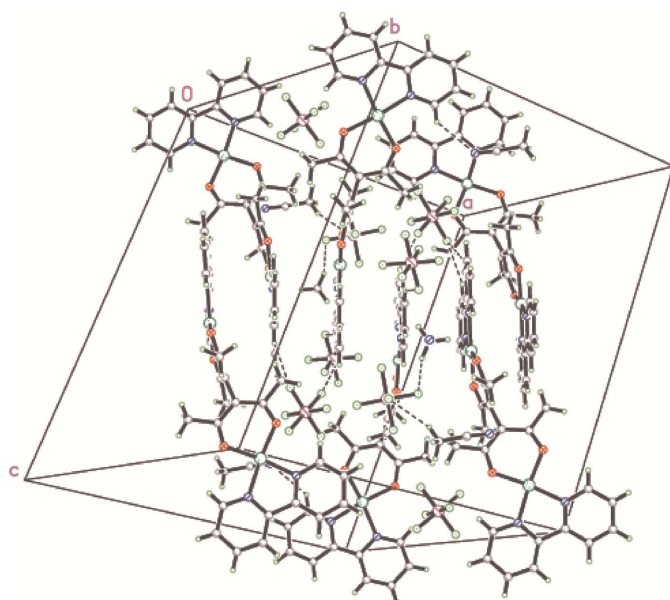


Figure 2
The packing of (I). Hydrogen bonds are shown as dashed lines.

Experimental

A mixture of (2,2'-bipyridine)dinitratopalladium(II) (77.3 mg, 0.2 mmol) and bisacetylacetonate (19.8 mg, 0.1 mmol) was dissolved in water (2 ml). The reaction mixture was stirred overnight at room temperature. A tenfold excess of potassium hexafluorophosphate was then added, resulting in the immediate deposition of the product (I) as yellow microcrystals. The crystals were filtered off, washed with a minimum amount of cold water and dried under vacuum (yield 98.4 mg, 93.5%). Crystals appropriate for data collection were obtained by the vapor diffusion of diethyl ether into a 1.0 mM solution of (I) in acetonitrile at room temperature. ^1H NMR (400 MHz, $[\text{D}_3]\text{acetonitrile}$): δ 2.21 (12H, s, CH_3), 7.82 (4H, t, $J = 8.5$ Hz, bpy- $\text{H}_{4,4'}$), 8.34 (8H, m, bpy- $\text{H}_{3,3'}$ and bpy- $\text{H}_{5,5'}$), 8.70 (4H, d, $J = 5.6$ Hz, bpy- $\text{H}_{6,6'}$) p.p.m.

Crystal data

$[\text{Pd}_2(\text{C}_{10}\text{H}_{12}\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2](\text{PF}_6)_2 \cdot 2\text{C}_2\text{H}_3\text{N}$

$M_r = 1052.36$

Monoclinic, $C2/c$

$a = 22.070$ (4) Å

$b = 16.104$ (3) Å

$c = 23.479$ (5) Å

$\beta = 109.70$ (3)°

$V = 7856$ (3) Å³

$Z = 8$

$D_x = 1.779$ Mg m⁻³

Mo $K\alpha$ radiation

$\mu = 1.10$ mm⁻¹

$T = 298$ (2) K

Block, yellow

0.30 × 0.30 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

$T_{\min} = 0.73$, $T_{\max} = 0.81$

16272 measured reflections

8574 independent reflections

6165 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.0^\circ$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.141$

$S = 1.09$

8574 reflections

521 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.62$ e Å⁻³

$\Delta\rho_{\min} = -1.06$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—Pd1	2.003 (4)	O1—Pd1	1.966 (4)
N2—Pd1	2.004 (4)	O2—Pd1	1.953 (4)
N3—Pd2	2.000 (4)	O3—Pd2	1.968 (4)
N4—Pd2	2.017 (5)	O4—Pd2	1.958 (4)
N1—Pd1—N2	81.12 (18)	N3—Pd2—O4	174.35 (18)
N1—Pd1—O1	93.32 (17)	N3—Pd2—N4	81.59 (19)
N1—Pd1—O2	173.83 (16)	N4—Pd2—O3	174.05 (19)
N2—Pd1—O1	173.59 (17)	N4—Pd2—O4	92.80 (18)
N2—Pd1—O2	92.78 (16)	O1—Pd1—O2	92.82 (15)
N3—Pd2—O3	92.97 (18)	O3—Pd2—O4	92.62 (17)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots F2 ⁱ	0.93	2.45	3.200 (8)	138
C7—H7 \cdots F11 ⁱⁱ	0.93	2.45	3.332 (7)	157
C21—H21 \cdots N5	0.93	2.57	3.310 (8)	137
C22—H22 \cdots F3 ⁱⁱⁱ	0.93	2.47	3.209 (8)	136
C24—H24 \cdots F10 ^{iv}	0.93	2.47	3.357 (6)	160
C27—H27 \cdots F10 ^{iv}	0.93	2.39	3.282 (8)	160

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

The aromatic H atoms were constrained to an ideal geometry, with C—H distances of 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The methyl H atoms of the bisacetylacetonate dianion were also constrained to an ideal geometry, with C—H distances of 0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The deepest hole in the final Fourier difference map was located 0.69 Å from atom F9.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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