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## Key indicators

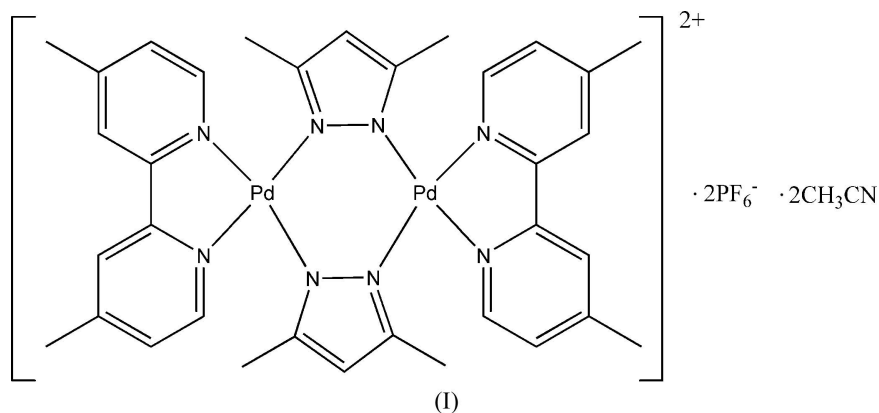
Single-crystal X-ray study  
*T* = 293 K  
Mean  $\sigma(\text{C}-\text{C})$  = 0.009 Å  
Disorder in solvent or counterion  
*R* factor = 0.063  
*wR* factor = 0.169  
Data-to-parameter ratio = 15.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**Bis( $\mu$ -3,5-dimethylpyrazolato- $\kappa^2N:N'$ )bis-  
[(4,4'-dimethyl-2,2'-bipyridine- $\kappa^2N,N'$ )-  
palladium(II)] bis(hexafluorophosphate)  
acetonitrile disolvate**

In the title complex,  $[\text{Pd}_2(\text{C}_5\text{H}_7\text{N}_2)_2(\text{C}_{12}\text{H}_{12}\text{N}_2)_2](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{CN}$ , two  $\text{Pd}(\text{dmbpy})$  units (dmbpy is 4,4'-dimethyl-2,2'-bipyridine) are bridged by two pyrazolate ligands in an exodentate fashion. The six-membered ring consisting of the two Pd atoms and the four pyrazole N atoms has a boat-shaped conformation. One acetonitrile solvent molecule is located in the clip-like cavity between the two  $\text{Pd}(\text{dmbpy})$  entities.

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## Comment

In a previous article, we reported two pyrazolate-bridged dinuclear  $\text{Pd}^{\text{II}}$  diimine complexes that bind inorganic anions (Huang *et al.*, 2005). In the present paper, we report a dinuclear palladium(II) complex, (I), based on 4,4'-dimethyl-2,2'-bipyridine (dmbpy) and 3,5-dimethylpyrazolate ligands (Fig. 1). The  $\text{Pd}^{\text{II}}$  center has a *cis*-square-planar geometry defined by an *N,N'*-bidentate 3,5-dimethylpyrazolate anionic ligand and a chelating 4,4'-dimethyl-2,2'-bipyridine ligand. The dihedral angle between the two coordination planes around the Pd atoms is  $69.6(2)^\circ$ . The  $\text{Pd1}(\text{dmbpy})$  and  $\text{Pd2}(\text{dmbpy})$  planes form a cleft with a cavity of approximate volume  $210 \text{ \AA}^3$ ; the planes are inclined at  $62.4(1)^\circ$ . An interesting feature of the structure is the presence of an acetonitrile solvent molecule in the clip-like cavity formed by the  $\text{Pd1}(\text{dmbpy})$  and  $\text{Pd2}(\text{dmbpy})$  planes, at a distance of  $3.209(5) \text{ \AA}$  ( $\text{N9} \cdots \text{C6}$ ). The other acetonitrile solvent molecule is 50% disordered over two sites.



## Experimental

A mixture of (4,4'-dimethyl-2,2'-bipyridine)dinitratopalladium(II) (41.5 mg, 0.10 mmol) and 3,5-dimethylpyrazole (9.6 mg, 0.10 mmol) was dissolved in water (5 ml). To the mixture was added a tenfold excess of potassium hexafluorophosphate, which resulted in the immediate deposition of the product as yellow microcrystals. The

crystals were filtered off, washed with a minimum amount of cold water and dried under vacuum (quantative yield 103.5 mg). Crystals were obtained by the vapor diffusion of diethyl ether into a 1.0 mM solution of (I) in acetonitrile. <sup>1</sup>H NMR (400 MHz, [D<sub>3</sub>] in acetonitrile): δ 2.44 (12H, s, dmbpy-CH<sub>3</sub>), 2.46 (12H, s, dmPz-CH<sub>3</sub>), 7.65 (4H, d, J = 5.8 Hz, dmbpy-H<sub>5,5'</sub>), 8.08 (4H, d, J = 5.8 Hz, dmbpy-H<sub>6,6'</sub>), 8.47 (4H, s, dmbpy-H<sub>3,3'</sub>).

Crystal data

[Pd<sub>2</sub>(C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>)<sub>2</sub>(C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·2C<sub>2</sub>H<sub>3</sub>N  
*M<sub>r</sub>* = 1143.57  
 Orthorhombic, *Pbca*  
*a* = 15.7488 (7) Å  
*b* = 25.5058 (9) Å  
*c* = 25.5058 (9) Å  
*V* = 10245.3 (7) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.483 Mg m<sup>-3</sup>  
 Mo Kα radiation  
*μ* = 0.85 mm<sup>-1</sup>  
*T* = 293.2 K  
 Prism, yellow  
 0.38 × 0.24 × 0.22 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 φ and ω scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2001)  
*T<sub>min</sub>* = 0.78, *T<sub>max</sub>* = 0.83  
 72334 measured reflections  
 11087 independent reflections  
 9713 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.044  
*θ<sub>max</sub>* = 27.0°

Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.063  
*wR* (*F*<sup>2</sup>) = 0.169  
*S* = 1.03  
 11087 reflections  
 724 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0771P)^2 + 27.5536P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 (Δ/σ)<sub>max</sub> = 0.001  
 Δρ<sub>max</sub> = 0.76 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.47 e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Pd1—Pd2	3.1492 (6)	Pd2—N4	2.035 (5)
Pd1—N1	2.022 (4)	Pd2—N7	2.022 (5)
Pd1—N2	2.019 (4)	Pd2—N8	1.996 (4)
Pd1—N5	2.002 (4)	N5—N7	1.373 (6)
Pd1—N6	2.008 (4)	N6—N8	1.382 (6)
Pd2—N3	1.999 (4)		
N1—Pd1—N2	80.7 (2)	N7—N5—Pd1	116.0 (3)
N3—Pd2—N4	80.9 (2)	N8—N6—Pd1	116.9 (3)
N5—Pd1—N6	85.1 (2)	N5—N7—Pd2	116.3 (3)
N7—Pd2—N8	85.1 (2)	N6—N8—Pd2	115.5 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8—H8...F8	0.93	2.46	3.20 (1)	137
C27—H27...F7 <sup>i</sup>	0.93	2.41	3.24 (1)	147

Symmetry code: (i) *x* + 1, *y*, *z*.

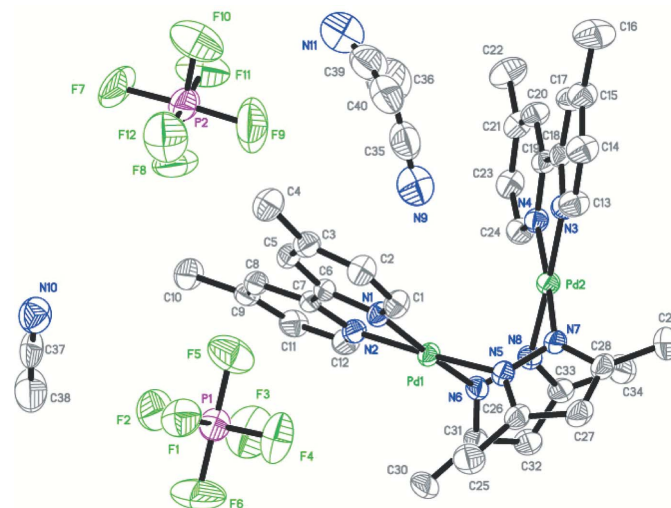


Figure 1

The asymmetric unit of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. For the PF<sub>6</sub><sup>-</sup> anions only one disorder component is shown. For the disordered acetonitrile molecule both disorder components are shown. H atoms have been omitted.

The aromatic H atoms were constrained to an ideal geometry, with C—H = 0.93 Å and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The methyl H atoms were constrained to an ideal geometry, with C—H = 0.96 Å and *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C). Both PF<sub>6</sub><sup>-</sup> anions have disordered F atoms and were refined over two sites with occupancies of 0.642 (8)/0.358 (8). The P—F distances were restrained to 1.58 (1) Å and F...F distances to 2.23 (1) Å.

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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References

Bruker (2001). SMART (Version 5.628), SAINT-Plus (Version 6.45) and SADABS (Version 2.10). Bruker AXS Inc., Madison, Wisconsin, USA.  
 Huang, H.-P., Li, S.-H. & Yu, S.-Y. (2005). *Inorg. Chem. Commun.* **8**, 656–660.  
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.  
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.