Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(μ-3,5-diphenylpyrazolato-κ^2N:N')-bis[(4,4′-dimethyl-2,2′-bipyridine-κ^2N,N')-palladium(II)] bis(hexafluorophosphate)

Hai-Ping Huang,* Qiong Wu, Li-Xia Liu and Qing-Fu Song

Laboratory for Self-Assembly Chemistry, Department of Chemistry, Renmin University of China, Beijing 100872, People's Republic of China

Correspondence e-mail: huanghaiping@ruc.edu.cn

Received 20 December 2006
Accepted 8 January 2007

Key indicators

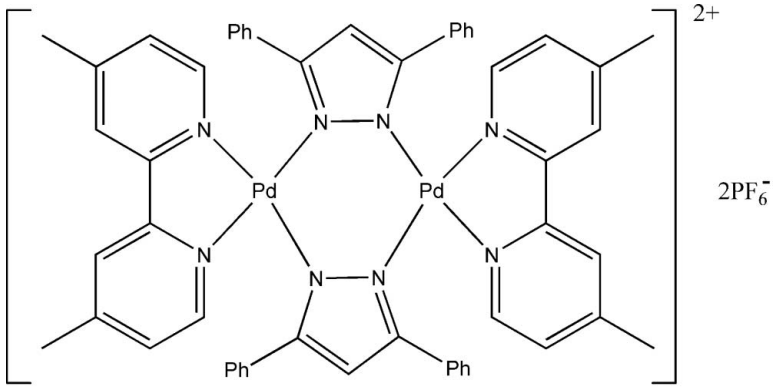
Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.012 Å
R factor = 0.069
wR factor = 0.197
Data-to-parameter ratio = 22.2

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

In the crystal structure of the title salt, $[Pd_2(C_{15}H_{11}N_2)_2(C_{12}H_{12}N_2)_2](PF_6)_2$, two (4,4′-dimethyl-2,2′-bipyridine)palladium(II) units are bridged by two pyrazolate ligands in an exodentate fashion. The six-membered ring consisting of the two Pd atoms and the four pyrazolyl N atoms has a boat-shaped conformation and the Pd atoms are four-coordinate in square-planar environments. The cation and both anions have crystallographically imposed mirror symmetry.

Comment

In previous publications, we have reported several pyrazolate-bridged dinuclear palladium(II) complexes having an inorganic anion as the charge-balancing species (Huang *et al.*, 2005), as well as a molecule that crystallizes as a solvate (Huang *et al.*, 2006). In the present paper, we report a dinuclear palladium(II) complex based on 4,4′-dimethyl-2,2′-bipyridine (dmbpy) and 3,5-diphenylpyrazolate ligands, *viz.* (I) (Fig. 1).



(I)

The Pd^{II} center has a *cis*-square-planar geometry defined by an N,N'-bidentate 3,5-diphenylpyrazolate anionic ligand and a chelating 4,4′-dimethyl-2,2′-bipyridine ligand. The dihedral angle between the two pyrazole planes is 72.8 (2)°. In the cation a crystallographic mirror plane passes through C13, C21 and the mid-points of the N—N bonds. In one anion, P1, F1, F3, F4 and F5 lie on a mirror plane; in the other anion, P2, F7 and F8 lie on a mirror plane. The cations and anions are held together only by electrostatic interactions.

Experimental

A mixture of (4,4′-dimethyl-2,2′-bipyridine)dinitratopalladium(II) (41.5 mg, 0.10 mmol) and 3,5-diphenylpyrazole (21.0 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 yellow microcrystals. The crystals were filtered off, washed with a minimum amount of cold water and dried under vacuum (quantative yield of 114.6 mg). Crystals were obtained by the vapor diffusion of diethyl ether into a 1 m*M* solution in acetonitrile. ^{1}H NMR (400 MHz, [D$_3$] acetonitrile): δ 2.45 (12H, *s*, dmbpy-CH$_3$), 7.17 (4H, *d*, *J* = 5.9 Hz, dmbpy-H$_{5,5'}$),7.20 (2H, *s*, Ph$_2$Pz—H$_4$), 7.42 (12H, *m*, Ph—H) 7.78 (4H, *d*, *J* = 5.8 Hz, dmbpy-H$_{6,6'}$), 8.05 (4H, *s*, dmbpy-H$_{3,3'}$), 8.26 (8*H*, *m*, Ph—H).

Crystal data

$[Pd_2(C_{15}H_{11}N_2)_2(C_{12}H_{12}N_2)_2](PF_6)_2$
M_r = 1309.73
Trigonal, *R*3*m*
a = 38.2597 (8) Å
c = 12.3356 (6) Å
V = 15637.7 (8) Å^3
Z = 9
D_x = 1.252 Mg m^{-3}
Mo *K*α radiation
μ = 0.63 mm^{-1}
T = 294 (1) K
Prism, yellow
0.35 × 0.14 × 0.14 mm

Data collection

Rigaku Saturn70 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.89, T_{max} = 0.92
40292 measured reflections
8178 independent reflections
7667 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.4°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.197
S = 1.08
8178 reflections
369 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.154P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.09 e Å^{-3}
$\Delta\rho_{min}$ = −1.44 e Å^{-3}
Absolute structure: Flack (1983), with 4023 Friedel pairs
Flack parameter: 0.02 (4)

Table 1
Selected geometric parameters (Å, °).

Pd1—N1	2.025 (5)	Pd1—N4	2.042 (5)
Pd1—N2	2.016 (5)	Pd1—Pd1^{i}	3.0410 (8)
Pd1—N3	2.040 (5)		
N1—Pd1—N2	81.03 (19)	N2—Pd1—N3	175.8 (2)
N1—Pd1—N3	96.7 (2)	N2—Pd1—N4	95.0 (2)
N1—Pd1—N4	175.3 (2)	N3—Pd1—N4	87.0 (2)

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

Aromatic H atoms were constrained to an ideal geometry, with C—H distances of 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(C). Methyl H atoms were rotated to fit the electron density, with C—H distances of 0.96 Å and with U_{iso}(H) = 1.5U_{eq}(C). The two hexafluorophosphate anions are disordered. The F—P distances were restrained to 1.58 (1) Å and F···F distances to 2.23 (1) Å. The largest peak and deepest hole in the final difference Fourier map are located 4.31 and 0.12 Å from atoms H10*C* and P2, respectively.

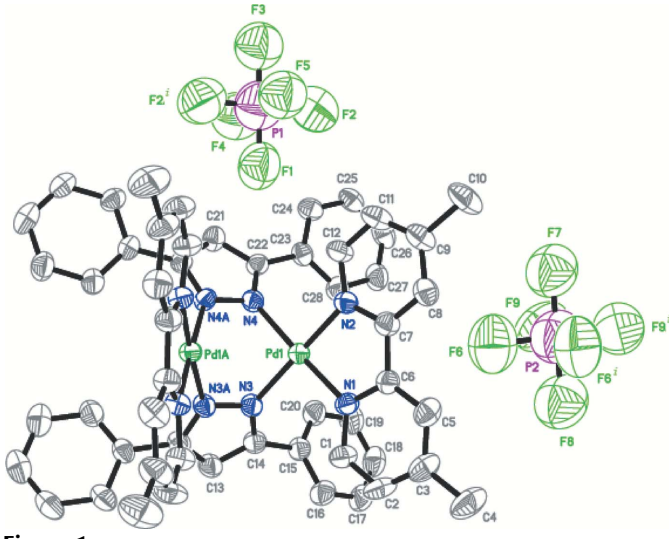


Figure 1
The structure of the constituent ions of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. In the cation, symmetry code: (A) *x*, *x* − *y*, *z*. In the P1-containing anion, symmetry code: (i) *x*, *x* − *y*, *z*. In the P2-containing anion, symmetry code: (i) 1 − *x* + *y*, *y*, *z*.

Data collection: *CrystalClear* (Rigaku/MSC, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

This work was supported by Renmin University of China.

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Huang, H.-P., Li, S.-H. & Yu, S.-Y. (2005). *Inorg. Chem. Commun.* **8**, 656–660.
Huang, H.-P., Wu, Q. & Mei, G.-Q. (2006). *Acta Cryst.* E**62**, m3465–m3466.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–354.
Rigaku/MSC (2004). *CrystalClear* Version 1.3.6, Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.