Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

(μ-3,5-Diphenylpyrazolato-κ^2N:N')bis(2,2′:6′,2″-terpyridyl-κ^3N)palladium(II) trinitrate

Hai-Ping Huang[a]* and Hong-Wei Ma[b]

[a]Laboratory for Self-Assembly Chemistry, Department of Chemistry, Renmin University of China, Beijing 100872, People's Republic of China, and [b]X-Ray Laboratory, Center for Physiochemical Analysis and Measurement, Institute of Chemistry, Chinese Academy of Sciences, #2, 1st Northern Street, Zhongguancun, Haidian Beijing 100080, People's Republic of China

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

Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.014 Å
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.157
Data-to-parameter ratio = 13.2

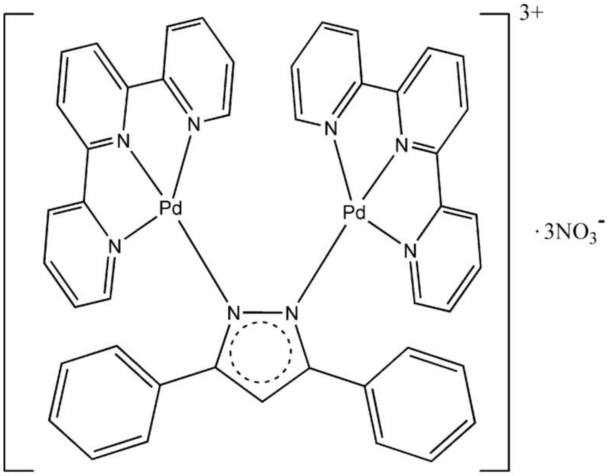
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 17 March 2007
Accepted 21 March 2007

In the title compound, $[Pd_2(C_{15}H_{22}N_2)(C_{15}H_{11}N_3)_2](NO_3)_3$, two planar Pd(terpy) units (terpy is 2,2′:6′,2″-terpyridyl) are bridged by a 3,5-diphenylpyrazolate ligand in an exodentate fashion, which results a clip-like cavity between the two Pd(terpy) planes. A nitrate anion is held in the cavity by an anion–π interaction. The cation has crystallographic twofold rotation symmetry.

Comment

The abiotic receptors for anionic species have potential application for anion sensing (Martínez-Máñez & Sancenón, 2003). In a previous article, we reported two pyrazolate-bridged dinuclear Pd^{II} diimine complexes that bind inorganic anions in their clip-like cavities (Huang *et al.*, 2005). In the present paper, we report a dinuclear palladium(II) complex, (I), based on 2,2′:6′,2″-terpyridyl (terpy) and 3,5-diphenyl pyrazolate ligands.



(I)

In the cation, a crystallographic twofold rotation axis passes through C16 and the mid-point of the N—N bond (Fig. 1). The two planar Pd(terpy) units are bridged by the 3,5-diphenyl-pyrazolate ligand in an exodentate fashion. This conformation creates an 'open book' disposition for the square-planar environment of the two Pd atoms. The dihedral angle between the two coordination planes around the Pd atoms is 64.0 (1)°. The two Pd(terpy) planes form a cleft with a cavity of approximately 280 Å^3. An interesting feature of the structure is the presence of a nitrate anion in the clip-like cavity formed by the Pd1(terpy) and Pd1^i(terpy) planes. The other two nitrate anions are located near the cation. The compound packs by electrostatic forces and C—H···O hydrogen bonds

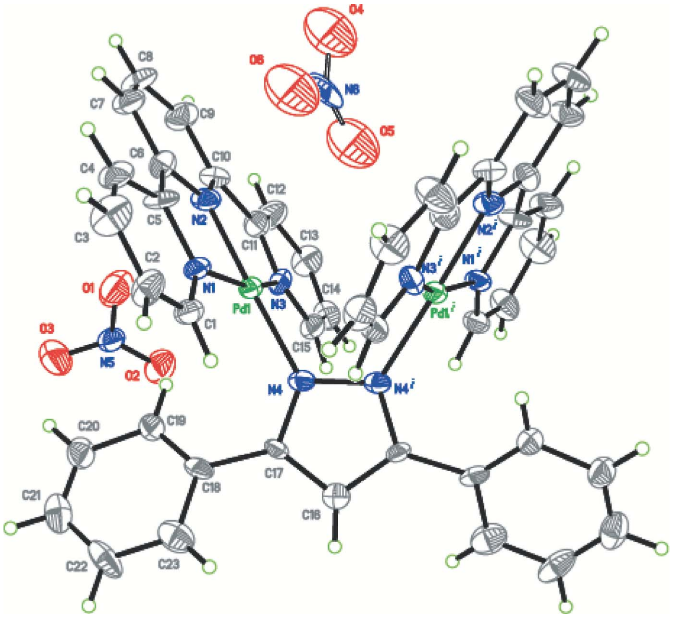


Figure 1
The molecular structure of the title compound (I), showing 30% probability displacement ellipsoids and the atom numbering scheme [Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$].

between the cations and anions. The non-classical hydrogen bonds that connect cations and anions are detailed in Table 2.

Experimental

A mixture of (2,2′:6′,2″-terpyridyl-κ^3N)dinitratopalladium(II) (46.4 mg, 0.10 mmol) and 3,5-diphenylpyrazole (10.5 mg, 0.05 mmol) was dissolved in water (5 ml). The mixture was stirred for six hours at room temperature to give a clear yellow solution. After evaporating this, the resulting yellow solid was recrystallized from methanol and diethyl ether (1:2). Yellow microcrystals were obtained in quantative yield (50.4 mg). Crystals were obtained by the vapor diffusion of diethyl ether into a 1 m*M* solution of (I) in acetonitrile. ^{1}H NMR (400 MHz, [D$_3$] acetonitrile): δ 7.32 (2H, *s*, Ph$_2$Pz—H$_4$), 7.40 (12H, *m*, Ph—H) 7.47 (4H, *d*, *J* = 5.8 Hz, dmbpy-H$_{6,6'}$),7.78 (4H, *d*, *J* = 5.8 Hz, dmbpy-H$_{6,6'}$), 8.14 (4H, *s*, dmbpy-H$_{3,3'}$), 8.34 (8H, *m*, Ph—H) p.p.m.

Crystal data

$[Pd_2(C_{15}H_{22}N_2)(C_{15}H_{11}N_3)_2](NO_3)_3$
$M_r = 1084.62$
Monoclinic, $C2/c$
$a = 25.917$ (5) Å
$b = 12.191$ (2) Å
$c = 16.116$ (3) Å
$\beta = 122.96$ (3)°
$V = 4272$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.91$ mm^{-1}
$T = 291$ (2) K
0.25 × 0.18 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.804$, $T_{\max} = 0.875$
7944 measured reflections
4070 independent reflections
3366 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.157$
$S = 1.07$
4070 reflections
309 parameters
19 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 1.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—N2	1.917 (7)	Pd1—N1	2.029 (7)
Pd1—N4	1.997 (5)	N4—N4^i	1.40 (1)
Pd1—N3	2.015 (7)		
N2—Pd1—N4	177.3 (3)	N4—Pd1—N1	100.9 (2)
N2—Pd1—N3	81.2 (3)	N3—Pd1—N1	162.4 (3)
N4—Pd1—N3	96.4 (2)	N4^i—N4—Pd1	119.8 (2)
N2—Pd1—N1	81.6 (3)		

Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O2^{ii}	0.93	2.52	3.35 (1)	149
C7—H7···O3^{iii}	0.93	2.42	2.99 (2)	119
C9—H9···O6^{iv}	0.93	2.54	3.42 (2)	158
C12—H12···O6^{iv}	0.93	2.38	3.28 (2)	164

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

The aromatic H atoms were constrained to an ideal geometry, with C—H distances of 0.93Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. One nitrate is disordered about the twofold axis. The O atoms were refined isotropically with half-occupancy. The N—O distances of this disordered nitrate were restained to 1.20 (1) Å and the O···O distances to 2.10 (1) Å. The largest peak in the final difference Fourier map is located 1.57 Å from atom O6.

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

This work was supported by Renmin University of China.

References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Huang, H.-P., Li, S.-H. & Yu, S.-Y. (2005). *Inorg. Chem. Commun.* **8**, 656–660.
Martínez-Máñez, R. & Sancenón, F. (2003). *Chem. Rev.* **103**, 4419–4476.
Rigaku (1999). *RAPID-AUTO*. Manual No. MJ13159A01. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2001). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.