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Di-μ-hydroxo-bis[(2,2′-bipyridine)palladium(II)] trifluoromethanesulfonate

Rafael A. Adrian,[a] Ronald E. Benson,[b] Lee M. Daniels,[b] Edward R. T. Tiekink[a]* and Judith A. Walmsley[a]*

[a]Department of Chemistry, The University of Texas at San Antonio, 6900 North Loop 1604 West, San Antonio, Texas 78249-0698, USA, and [b]Rigaku Americas Corporation, 9009 New Trails Drive, The Woodlands, Texas 77381, USA

Correspondence e-mail:
edward.tiekink@utsa.edu,
judith.walmsley@utsa.edu

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The cation in the title complex, $[Pd_2(OH)_2(C_{10}H_8N_2)_2](CF_3SO_3)_2$, is essentially planar and features square-planar Pd centers that are linked *via* a pair of symmetric hydroxo bridges. In the crystal structure, extensive O—H⋯O hydrogen bonding and π–π interactions lead to the formation of cationic columns.

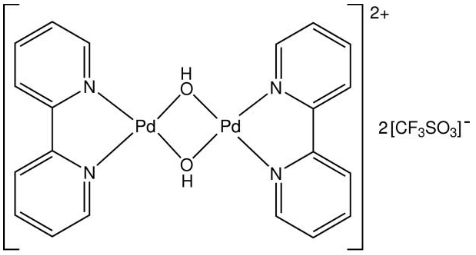
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.004 Å
R factor = 0.027
wR factor = 0.057
Data-to-parameter ratio = 12.9

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

Comment

Dimeric complexes of the general formula $[M(L)(\mu_2\text{-}OH)_2M(L)]^{2+}$ have been proposed for M = Pd and Pt for L = 2,2′-bipyridine and 1,10-phenanthroline (Wimmer *et al.*, 1988, 1989). While this has been confirmed by X-ray crystallography for the M = Pt complexes (Koz'min *et al.*, 1997; Fekl & van Eldik, 1998), the analogous structures for M = Pd are not yet known. The structure of $[Pd(L)(\mu_2\text{-}OH)_2Pd(L)]^{2+}$, where L = 2,2′-bipyridine, is reported here as its trifluoromethanesulfonate salt, (I).



(I)

The molecular structure of the cation in (I) is shown in Fig. 1. The Pd atoms are bridged by two μ_2-OH groups, forming essentially equivalent Pd—O bonds (Table 1). The square-planar coordination geometry about each Pd center is completed by a chelating 2,2′-bipyridine ligand. The intramolecular Pd1⋯Pd2 separation is 3.0834 (3) Å. The dihedral angle between the two PdN_2O_2 least-squares planes is 3.42 (9)°. Indeed, the entire cation is essentially planar, as indicated by the r.m.s. deviation for all non-H atoms of 0.056 Å.

There are several other structures in the literature containing an $N_2Pd(OH)_2PdN_2$ core. The cations in each of $[(Me_2NCH_2CH_2NMe_2)Pd(OH)]_2[ClO_4]_2$ (Shen *et al.*, 2005) and $[(bipyrazine)Pd(OH)]_2[NO_3]_2\cdot 4H_2O$ (Schnebeck *et al.*, 2000) are disposed about a center of inversion, indicating that the central core is strictly planar. By contrast, a butterfly conformation is observed in the cation in $[(4\text{-}MeO\text{-}C_6H_4N{=}C(Me)-C(Me){=}NC_6H_4OMe\text{-}4)Pd(OH)]_2[BF_4]_2\cdot CH_2Cl_2\cdot 0.5THF$ (Kannan *et al.*, 2000). In the two centrosymmetric structures, the hydroxyl H atoms lie above and below the central core, and in the butterfly structure, the hydroxyl H

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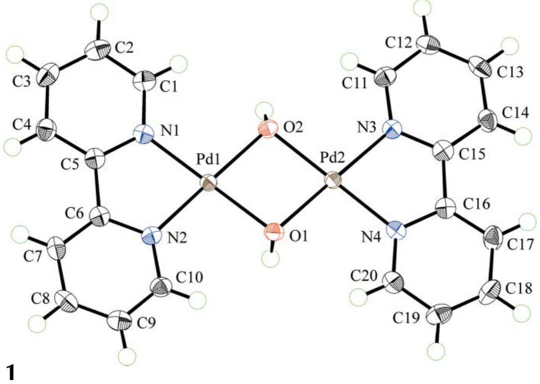

Figure 1
The cation in (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 70% probability level.

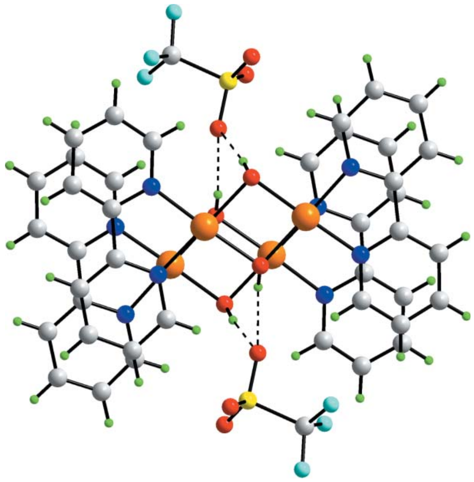

Figure 2
Hydrogen bonding (dashed lines) between centrosymmetric pairs in (I) (Crystal Impact, 2002). Colour code: Pd (orange), F (cyan), O (red), N (blue), C (gray) and H (green).

atoms project laterally from the molecule. A different situation pertains in the structure of (I) in that the hydroxyl H atoms lie to the same side of the molecule, *i.e.* are *syn*. This arrangement allows for hydrogen bonding, as shown in Fig. 2 and detailed in Table 2. Here, centrosymmetrically related molecules are connected *via* hydrogen bonds to O3 belonging to one of the trifluoromethanesulfonate anions (symmetry code $1 - x, 1 - y, 1 - z$). While this has the effect of bringing the aromatic rings in close proximity, the closest distance between ring centroids within this dimeric unit is 3.5775 (15) Å and occurs between the PdN_2C_2 chelate rings. Additional interactions occur between centrosymmetrically related dimers with the result that the shortest distance between two dimers is shorter than the shortest distance within an individual dimeric unit. Thus, the distance between the centroid of the $Pd1N_2C_2$ chelate ring and the $Pd(OH)_2Pd$ core is 3.2405 (14) Å for symmetry code $(-x, 1 - y, 1 - z)$. These associations lead to the formation of columns parallel to the *a* axis, as shown in Fig. 3. As indicated in Table 2, there are many other hydrogen-bond interactions in the structure, primarily of the type C—H···O. The trifluoromethanesulfonate O atoms of one anion, *viz.* O3, O4 and O5, all form C—H···O interactions to provide additional stabilization of the dimer shown in Fig. 2. Links between dimers are afforded by C—H···O interactions involving atom O7 belonging to the second trifluoromethanesulfonate anion. This atom also forms an interaction to the $Pd2N_2C_2$ chelate ring so that the O7···ring centroid distance is 3.068 (3) Å and the angle at O7 is 152.64 (14)°. Links between columns are provided by C—H···O contacts involving the remaining trifluoromethanesulfonate-bound O atoms, *i.e.* O6 and O8. The most prominent contact involving an F atom also provides a link between columns (Table 2).

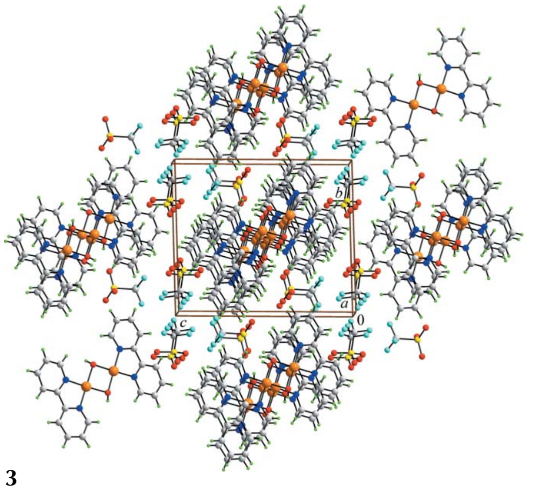

Figure 3
The crystal packing in (I), viewed approximately down the *a* axis. Colour codes as for Fig. 2.

Experimental

The complex was prepared by adding $Ag(CF_3SO_3)$ (0.462 g, 1.80 mmol) to an aqueous suspension (100 ml) of Pd(2,2′-bipyridine)Cl_2 (0.300 mg, 0.900 mmol); pH = 4.23. The mixture was heated at 333 K for 16 h and then filtered to remove AgCl at which stage the pH was 2.64. The solution was concentrated to approximately 5 ml by slow evaporation at 323 K. As the solution cooled, X-ray diffraction quality crystals formed; pH 1.91. Melting occurred in two stages so that the crystals turned black between 528 and 543 K and melted in the range 554–556 K.

Crystal data

$[Pd_2(OH)_2(C_{10}H_8N_2)_2](CF_3O_3S)_2$
$M_r = 857.32$
Triclinic, $P\overline{1}$
$a = 7.6162$ (1) Å
$b = 12.7248$ (2) Å
$c = 14.6448$ (2) Å
$\alpha = 86.626$ (1)°
$\beta = 84.153$ (1)°
$\gamma = 75.610$ (1)°
$V = 1366.79$ (3) Å^3

$Z = 2$
$D_x = 2.083$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24414 reflections
$\theta = 2.1$–25.6°
$\mu = 1.57$ mm^{-1}
$T = 153$ (2) K
Block, yellow
0.30 × 0.20 × 0.15 mm

Data collection

Rigaku R-AXIS SPIDER diffractometer
ω scans
Absorption correction: numerical (Katayama, 1986; Paturle & Coppens, 1988)
$T_{min} = 0.754$, $T_{max} = 0.918$
42226 measured reflections

5114 independent reflections
4826 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 25.6°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.057$
$S = 1.18$
5114 reflections
397 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0188P)^2 + 2.6048P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—O1	2.0228 (19)	Pd2—O1	2.0233 (19)
Pd1—O2	2.0195 (19)	Pd2—O2	2.0249 (19)
Pd1—N1	1.994 (2)	Pd2—N3	1.992 (2)
Pd1—N2	1.988 (2)	Pd2—N4	1.993 (2)
O1—Pd1—O2	80.45 (8)	O1—Pd2—N3	177.71 (8)
O1—Pd1—N1	177.66 (8)	O1—Pd2—N4	97.94 (9)
O1—Pd1—N2	98.02 (9)	O2—Pd2—N3	100.55 (9)
O2—Pd1—N1	100.12 (9)	O2—Pd2—N4	174.91 (8)
O2—Pd1—N2	175.69 (8)	N3—Pd2—N4	81.03 (9)
N1—Pd1—N2	81.25 (9)	Pd1—O1—Pd2	99.29 (8)
O1—Pd2—O2	80.30 (8)	Pd1—O2—Pd2	99.35 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1o···O3	0.84	1.94	2.772 (3)	174
O2—H2o···O3^{i}	0.84	2.06	2.858 (3)	158
C1—H1···O4^{i}	0.95	2.47	3.201 (4)	133
C3—H3···F3^{ii}	0.95	2.54	3.439 (3)	157
C4—H4···O7^{iii}	0.95	2.28	3.218 (4)	168
C7—H7···O7^{iii}	0.95	2.46	3.392 (4)	168
C8—H8···O6^{iv}	0.95	2.40	3.245 (4)	148
C11—H11···O3^{i}	0.95	2.57	3.438 (3)	151
C12—H12···O8^{v}	0.95	2.47	3.280 (4)	143
C20—H20···O5	0.95	2.60	3.356 (4)	137

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1, y+1, z$; (iii) $-x, -y+1, -z+1$; (iv) $x, y, z-1$; (v) $-x+1, -y+1, -z+2$.

H atoms were included in the riding-model approximation, with C—H = 0.95 Å and O—H = 0.84 Å, and with U_{iso}(H) = $1.2U_{eq}$(C) and $1.5U_{eq}$(O).

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *TwinSolve* (Rigaku, 2002); data reduction: *TwinSolve*; program(s) used to solve structure: *PATTY* in *DIRDIF92* (Beurskens *et al.*, 1992); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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