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Diacetonitrile(2,2′-bipyridine-κ^2N,N')palladium(II) bis(trifluoromethanesulfonate)

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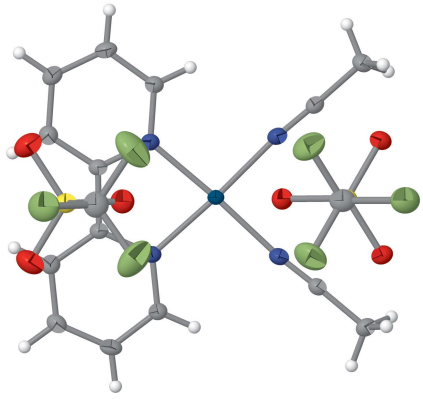
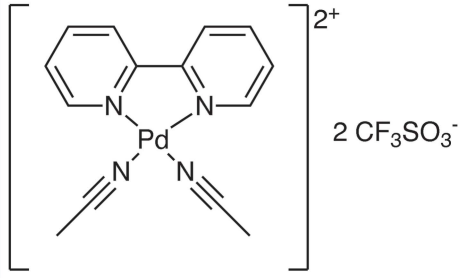
Structural data: full structural data are available from iucrdata.iucr.org

In the title complex, $[Pd(C_{10}H_8N_2)(CH_3CN)_2](CF_3SO_3)_2$ or $[Pd(bipy)(CH_3CN)_2](CF_3SO_3)_2$, the palladium(II) ion is fourfold coordinated by two acetonitrile molecules and a bidentate 2,2′-bipyridine ligand in a distorted square-planar geometry.

3D view



Chemical scheme



Structure description

Palladium(II) complexes of 2,2′-bipyridine continue to be investigated due to their application in catalysis (Kitanosono *et al.*, 2021) and remarkable antiproliferative activity against cancer cells (Fatahian-Nezhad *et al.*, 2021; Tabrizi *et al.*, 2020; Icsel *et al.*, 2015). Our research group has been exploring the synthesis of palladium(II) and copper(II) complexes containing various ancillary ligands. With that in mind, herein, we report the synthesis and structure of the title complex, an excellent starting material for synthesizing novel palladium complexes.

The asymmetric unit contains only half of the title complex due to the presence of a vertical plane of symmetry along the *a* axis that bisects the bond between the pyridine rings, C1—C1^{i}, and the Pd1, O1, F1, O3, and F4 atoms. The title complex exhibits a Pd^{II} ion in a distorted square-planar coordination environment defined by two N atoms of the bidentate 2,2′-bipyridine ligand and one nitrogen from each of the two coordinated acetonitrile molecules. Two trifluoromethanesulfonate ions sit outside the coordination sphere of the title complex balancing the charge of the metal (Fig. 1). The Pd—N1 and Pd—N2 bond lengths of 1.999 (2) Å and 2.012 (3) Å, respectively, are in good agreement with the only comparable palladium(II) 2,2′-bipyridine complex, a tetrafluoroborate salt, (1.993 and 2.004 Å) currently available in the CSD (Groom *et al.*, 2016; version 5.43 with update of September 2022; refcode WEFCAL; Nesper *et al.*, 1993). The N—Pd—N angles

Table 1
Selected geometric parameters (Å, °).

Pd1—N1	1.999 (2)	Pd1—N2	2.012 (3)
N1^{i}—Pd1—N1	81.82 (14)	N1—Pd1—N2	176.99 (9)
N1—Pd1—N2^{i}	95.18 (11)	N2—Pd1—N2^{i}	87.83 (14)

Symmetry code: (i) $x, -y+\frac{3}{2}, z$.

also correlate well with the previously referenced complex, with differences of less than one degree in all cases. All relevant bonds and angles are presented in Table 1.

In the molecular packing of the title complex, the palladium(II) complex ions align in layers along the *b*-axis orienting their coordinated acetonitrile toward the same direction, with the trifluoromethanesulfonate ions occupying the gaps between layers, as shown in Fig. 2. Meanwhile, adjacent layers alternate the orientation of the coordinated acetonitrile molecules. No directional supramolecular interactions are present in the crystal packing of the title compound.

Synthesis and crystallization

Silver trifluoromethanesulfonate (0.154 g, 0.600 mmol) was added to a 40.0 ml acetonitrile suspension of (2,2′-bipyridine)dichloropalladium(II) (0.100 g, 0.300 mmol). The resulting solution was filtrated using a 0.45 mm PTFE syringe filter and heated at 323 K to reduce the volume to 10.0 ml. Crystals suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether over the saturated acetonitrile solution of the title complex at 277 K.

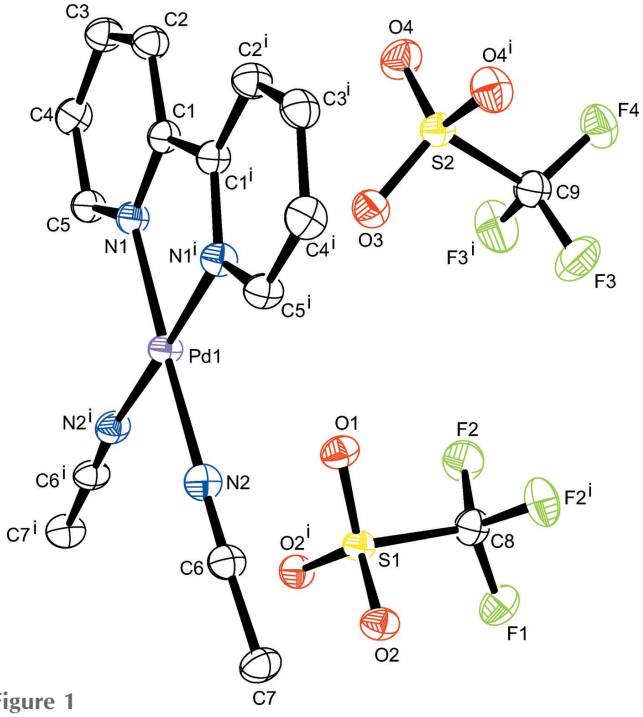


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level; H atoms are omitted for clarity. Symmetry code: (i) $x, -y+\frac{3}{2}, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Pd(C_{10}H_8N_2)(C_2H_3N)_2](CF_3O_3S)_2$
M_r	642.83
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	100
a, b, c (Å)	9.2732 (3), 12.5307 (2), 10.0983 (3)
β (°)	110.627 (3)
V (Å^3)	1098.20 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	9.49
Crystal size (mm)	0.15 × 0.13 × 0.09
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.746, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10720, 2318, 2234
R_{int}	0.048
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.093, 1.09
No. of reflections	2318
No. of parameters	174
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.75, −0.93

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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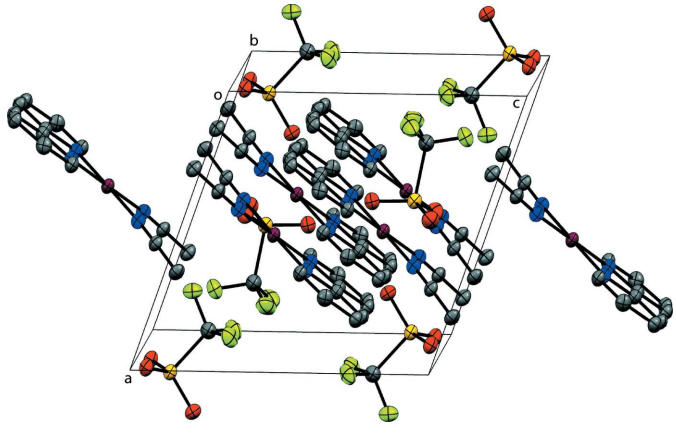

Figure 2
Perspective view of the packing structure of the title complex; H atoms are omitted for clarity.

Funding information

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full crystallographic data

IUCrData (2022). **7**, x221151 [https://doi.org/10.1107/S2414314622011518]

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Crystal data

$[Pd(C_{10}H_8N_2)(C_2H_3N)_2](CF_3O_3S)_2$
M_r = 642.83
Monoclinic, $P12_1/m1$
a = 9.2732 (3) Å
b = 12.5307 (2) Å
c = 10.0983 (3) Å
β = 110.627 (3)°
V = 1098.20 (6) Å^3
Z = 2
$F(000)$ = 636
D_x = 1.944 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 5466 reflections
θ = 4.7–75.7°
μ = 9.49 mm^{-1}
T = 100 K
Block, clear colourless
0.15 × 0.13 × 0.09 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2020)
T_{min} = 0.746, T_{max} = 1.000
10720 measured reflections
2318 independent reflections
2234 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 76.3°, θ_{min} = 4.7°
h = −11→11
k = −11→15
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.093
S = 1.09
2318 reflections
174 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.5328P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.75 e Å^{-3}
$\Delta\rho_{min}$ = −0.93 e Å^{-3}
Extinction correction: *SHELXL2018/3* (Sheldrick, 2015*b*), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00084 (18)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.45413 (3)	0.750000	0.68769 (3)	0.01791 (13)
S1	0.95842 (11)	0.750000	0.87020 (10)	0.0194 (2)
S2	0.58391 (11)	0.750000	0.25835 (10)	0.0222 (2)
F1	1.2500 (3)	0.750000	0.8920 (3)	0.0318 (6)
F2	1.0991 (2)	0.66371 (16)	0.7117 (2)	0.0362 (5)
F4	0.8145 (3)	0.750000	0.1642 (3)	0.0343 (6)
F3	0.8599 (2)	0.83614 (19)	0.3585 (2)	0.0455 (5)
O2	0.9882 (2)	0.84692 (17)	0.9529 (2)	0.0240 (4)
O1	0.8188 (3)	0.750000	0.7478 (3)	0.0250 (6)
O3	0.5802 (4)	0.750000	0.3998 (3)	0.0276 (6)
O4	0.5311 (3)	0.65247 (18)	0.1802 (2)	0.0332 (5)
N1	0.3443 (3)	0.64555 (19)	0.5361 (2)	0.0201 (5)
N2	0.5598 (3)	0.8614 (2)	0.8330 (3)	0.0220 (5)
C1	0.2630 (3)	0.6910 (2)	0.4102 (3)	0.0192 (5)
C5	0.3494 (3)	0.5388 (2)	0.5486 (3)	0.0218 (6)
H5	0.405311	0.508152	0.635496	0.026*
C4	0.2733 (4)	0.4734 (2)	0.4351 (3)	0.0254 (6)
H4	0.277737	0.399608	0.445345	0.030*
C6	0.6305 (3)	0.9177 (2)	0.9187 (3)	0.0219 (6)
C2	0.1852 (3)	0.6298 (2)	0.2937 (3)	0.0241 (6)
H2	0.129953	0.662005	0.207740	0.029*
C3	0.1905 (3)	0.5194 (2)	0.3063 (3)	0.0248 (6)
H3	0.138764	0.476742	0.228681	0.030*
C7	0.7208 (4)	0.9927 (2)	1.0251 (3)	0.0255 (6)
H7A	0.688876	1.064212	0.994367	0.038*
H7B	0.827941	0.984372	1.038591	0.038*
H7C	0.705270	0.979190	1.112678	0.038*
C9	0.7904 (5)	0.750000	0.2872 (5)	0.0285 (9)
C8	1.1090 (5)	0.750000	0.7920 (5)	0.0265 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.02209 (19)	0.01259 (19)	0.01685 (19)	0.000	0.00414 (13)	0.000
S1	0.0234 (5)	0.0146 (5)	0.0189 (4)	0.000	0.0057 (4)	0.000
S2	0.0243 (5)	0.0181 (5)	0.0229 (5)	0.000	0.0067 (4)	0.000
F1	0.0236 (13)	0.0283 (14)	0.0400 (14)	0.000	0.0067 (11)	0.000
F2	0.0426 (11)	0.0326 (10)	0.0392 (11)	−0.0031 (9)	0.0217 (9)	−0.0121 (8)
F4	0.0387 (15)	0.0366 (15)	0.0341 (14)	0.000	0.0210 (12)	0.000

F3	0.0350 (11)	0.0549 (13)	0.0496 (13)	−0.0183 (10)	0.0187 (10)	−0.0220 (11)
O2	0.0303 (11)	0.0174 (10)	0.0225 (10)	0.0003 (8)	0.0069 (8)	−0.0030 (8)
O1	0.0236 (14)	0.0221 (15)	0.0248 (14)	0.000	0.0030 (11)	0.000
O3	0.0294 (16)	0.0280 (16)	0.0267 (15)	0.000	0.0113 (13)	0.000
O4	0.0362 (12)	0.0276 (12)	0.0357 (12)	−0.0069 (10)	0.0127 (10)	−0.0090 (9)
N1	0.0230 (11)	0.0161 (11)	0.0202 (11)	−0.0015 (9)	0.0065 (9)	0.0007 (9)
N2	0.0247 (12)	0.0168 (12)	0.0235 (12)	0.0027 (10)	0.0070 (10)	0.0021 (10)
C1	0.0212 (13)	0.0152 (14)	0.0207 (13)	−0.0006 (11)	0.0070 (11)	−0.0001 (10)
C5	0.0257 (14)	0.0171 (14)	0.0209 (13)	−0.0009 (11)	0.0061 (11)	0.0011 (11)
C4	0.0312 (15)	0.0154 (13)	0.0294 (14)	−0.0029 (12)	0.0104 (12)	−0.0021 (11)
C6	0.0251 (14)	0.0174 (14)	0.0205 (13)	0.0012 (11)	0.0045 (11)	0.0029 (11)
C2	0.0263 (14)	0.0219 (15)	0.0221 (13)	−0.0006 (12)	0.0060 (11)	0.0007 (11)
C3	0.0279 (14)	0.0214 (15)	0.0240 (13)	−0.0018 (12)	0.0078 (11)	−0.0048 (11)
C7	0.0281 (15)	0.0195 (14)	0.0249 (14)	−0.0041 (12)	0.0043 (12)	−0.0025 (12)
C9	0.028 (2)	0.029 (2)	0.027 (2)	0.000	0.0092 (18)	0.000
C8	0.028 (2)	0.022 (2)	0.029 (2)	0.000	0.0104 (18)	0.000

Geometric parameters (Å, º)

Pd1—N1^{i}	1.999 (2)	N1—C1	1.354 (4)
Pd1—N1	1.999 (2)	N1—C5	1.343 (4)
Pd1—N2	2.012 (3)	N2—C6	1.130 (4)
Pd1—N2^{i}	2.012 (3)	C1—C1^{i}	1.480 (5)
S1—O2^{i}	1.444 (2)	C1—C2	1.376 (4)
S1—O2	1.444 (2)	C5—H5	0.9300
S1—O1	1.441 (3)	C5—C4	1.383 (4)
S1—C8	1.830 (4)	C4—H4	0.9300
S2—O3	1.441 (3)	C4—C3	1.382 (4)
S2—O4^{i}	1.443 (2)	C6—C7	1.451 (4)
S2—O4	1.444 (2)	C2—H2	0.9300
S2—C9	1.833 (5)	C2—C3	1.389 (4)
F1—C8	1.341 (5)	C3—H3	0.9300
F2—C8	1.335 (3)	C7—H7A	0.9600
F4—C9	1.338 (5)	C7—H7B	0.9600
F3—C9	1.331 (3)	C7—H7C	0.9600
N1^{i}—Pd1—N1	81.82 (14)	C5—C4—H4	120.5
N1^{i}—Pd1—N2	95.18 (11)	C3—C4—C5	119.0 (3)
N1—Pd1—N2^{i}	95.18 (11)	C3—C4—H4	120.5
N1—Pd1—N2	176.99 (9)	N2—C6—C7	178.1 (3)
N1^{i}—Pd1—N2^{i}	176.99 (9)	C1—C2—H2	120.5
N2—Pd1—N2^{i}	87.83 (14)	C1—C2—C3	119.0 (3)
O2—S1—O2^{i}	114.47 (17)	C3—C2—H2	120.5
O2^{i}—S1—C8	103.28 (12)	C4—C3—C2	119.4 (3)
O2—S1—C8	103.28 (12)	C4—C3—H3	120.3
O1—S1—O2	115.28 (10)	C2—C3—H3	120.3
O1—S1—O2^{i}	115.28 (11)	C6—C7—H7A	109.5
O1—S1—C8	102.79 (19)	C6—C7—H7B	109.5

O3—S2—O4^{i}	114.85 (11)	C6—C7—H7C	109.5
O3—S2—O4	114.85 (11)	H7A—C7—H7B	109.5
O3—S2—C9	103.35 (19)	H7A—C7—H7C	109.5
O4^{i}—S2—O4	115.7 (2)	H7B—C7—H7C	109.5
O4^{i}—S2—C9	102.76 (12)	F4—C9—S2	111.1 (3)
O4—S2—C9	102.75 (12)	F3—C9—S2	111.4 (2)
C1—N1—Pd1	114.14 (18)	F3^{i}—C9—S2	111.4 (2)
C5—N1—Pd1	126.1 (2)	F3—C9—F4	107.2 (2)
C5—N1—C1	119.8 (2)	F3^{i}—C9—F4	107.2 (2)
C6—N2—Pd1	173.7 (2)	F3—C9—F3^{i}	108.4 (4)
N1—C1—C1^{i}	114.85 (15)	F1—C8—S1	111.4 (3)
N1—C1—C2	121.3 (2)	F2^{i}—C8—S1	111.2 (2)
C2—C1—C1^{i}	123.82 (17)	F2—C8—S1	111.2 (2)
N1—C5—H5	119.3	F2—C8—F1	107.3 (2)
N1—C5—C4	121.4 (3)	F2^{i}—C8—F1	107.3 (2)
C4—C5—H5	119.3	F2^{i}—C8—F2	108.2 (3)
Pd1—N1—C1—C1^{i}	−3.37 (19)	O4—S2—C9—F4	60.23 (11)
Pd1—N1—C1—C2	177.7 (2)	O4^{i}—S2—C9—F4	−60.23 (11)
Pd1—N1—C5—C4	−177.6 (2)	O4—S2—C9—F3^{i}	−59.2 (3)
O2^{i}—S1—C8—F1	−59.77 (10)	O4^{i}—S2—C9—F3	59.2 (3)
O2—S1—C8—F1	59.77 (10)	O4^{i}—S2—C9—F3^{i}	−179.6 (2)
O2^{i}—S1—C8—F2^{i}	−179.4 (2)	O4—S2—C9—F3	179.6 (2)
O2—S1—C8—F2^{i}	−59.9 (3)	N1—C1—C2—C3	0.1 (4)
O2—S1—C8—F2	179.4 (2)	N1—C5—C4—C3	0.1 (4)
O2^{i}—S1—C8—F2	59.9 (3)	C1—N1—C5—C4	0.1 (4)
O1—S1—C8—F1	180.000 (1)	C1^{i}—C1—C2—C3	−178.68 (19)
O1—S1—C8—F2	−60.3 (2)	C1—C2—C3—C4	0.1 (4)
O1—S1—C8—F2^{i}	60.3 (2)	C5—N1—C1—C1^{i}	178.68 (19)
O3—S2—C9—F4	180.000 (1)	C5—N1—C1—C2	−0.2 (4)
O3—S2—C9—F3	−60.6 (2)	C5—C4—C3—C2	−0.2 (4)
O3—S2—C9—F3^{i}	60.6 (2)		

Symmetry code: (i) x, $-y+3/2$, z.