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[1,9-Bis(3,5-dimethylpyrazol-1-yl-κN^2)-3,7-dithianonane-$\kappa^2 S,S'$]palladium(II) bis(tetrafluoroborate)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
Disorder in solvent or counterion
R factor = 0.035
wR factor = 0.060
Data-to-parameter ratio = 18.2

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

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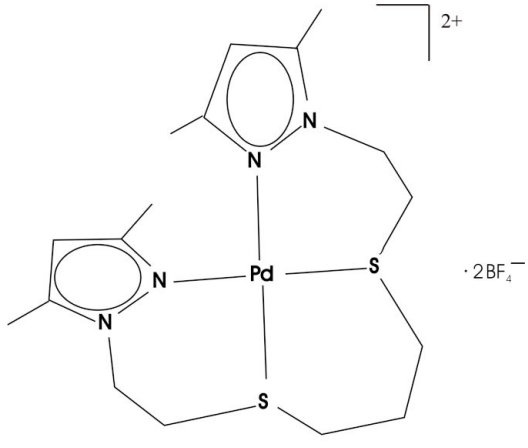
In the crystal structure of the title compound, $[Pd(C_{17}H_{28}N_4S_2)](BF_4)_2$, the Pd^{II} atom is coordinated by one N atom from each of the pyrazolyl groups and the two thioether S atoms in a slightly distorted square-planar geometry.

Comment

The coordination chemistry of semi-labile ligands has been widely studied in recent years (Braunstein & Naud, 2001; Slone *et al.*, 1999; Bader & Lindner, 1991). In our group, bidentate ligands containing two donor centres of different strengths have been prepared: aminoalkylpyrazole (*N,N′*) (Esquius, Pons, Yánez & Ros, 2000; Esquius, Pons, Yánez, Ros, Solans & Font-Bardia, 2000; Esquius, Pons, Yánez, Ros, Mathieu *et al.*, 2002; Esquius, Pons, Yánez, Ros, Solans & Font-Bardia, 2002), phosphinoalkylpyrazole (*N,P*) (Esquius, Pons, Yánez, Ros, Mathieu *et al.*, 2002; Esquius *et al.*, 2003) and thioetheralkylpyrazole (*N,S*) (García-Antón *et al.*, 2002, 2003). Recently, we have reported the crystal structure of the complex [1,8-bis(3,5-dimethyl-1-pyrazolyl-$\kappa^2 N,N'$)-3,7-dithia-$\kappa^2 S,S'$-octane]palladium(II) bis(tetrafluoroborate) $[Pd(bddo)](BF_4)_2$, (II) (García-Antón *et al.*, 2002). As a continuation of our investigations, we now present the X-ray crystal structure of a mononuclear palladium(II) complex with 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn). There is no crystal structure with the 1,9-bis(1-pyrazolyl)-3,7-dithianone moiety in the Cambridge Structural Database (CSD, release of March 2004; Allen, 2002).



(I)

In the title compound, (I), the Pd atom is linked to two N atoms of the pyrazolyl groups and two thioether groups which are *cis* to each other (Fig. 1). The coordination is planar, with atom N2 0.127 (4) Å out of the plane defined by the

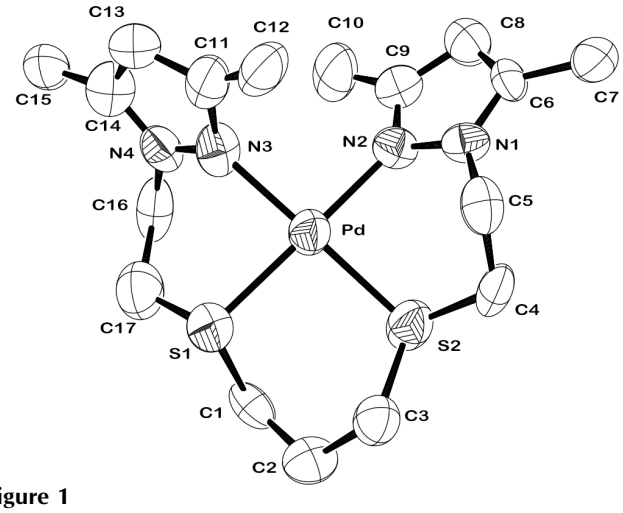


Figure 1
View of the cation in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

remaining four atoms. The mean Pd—S bond length is 2.283 (7) Å, greater than the value of 2.247 (1) Å observed in (II) (García-Antón *et al.*, 2002). This is explained by the fact that the S···S length is greater in the title compound [3.3288 (16) Å] than in (II) (3.169 Å) and the Pd atom tries to maintain the same bite parameter (1.4). [The bite parameter is defined as the distance between the donor atoms of the chelate divided by the metal–donor atom distance (Kepert, 1977)]. As a result, the S—Pd—S angle [93.58 (6)°] in the title compound is greater than in (II) [89.76 (8)°], while the N—Pd—N angle [93.84 (15)°] is smaller than the value of 97.4 (2)° observed in $[Pd(bddo)](BF_4)_2$.

The six-membered Pd/S/C/C/N/N rings have boat conformations, with the Pd and one C atom out of the plane defined by the remaining four atoms, while the six-membered Pd/S/C/C/C/S ring has a twist-boat conformation with a C_s(C1—C2) asymmetry parameter of 44.4 (3)°.

Experimental

A solution of $AgBF_4$ (0.86 mmol) was added dropwise with vigorous stirring to a solution of $[PdCl_2$(1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane)] (0.43 mmol) in CH_2Cl_2 (10 ml) and CH_3OH (10 ml). The reaction was carried out in the dark to prevent reduction of Ag^I to Ag^0. After 5 min, stirring was stopped and AgCl was filtered off. When the volume of the resultant solution had been reduced to roughly 5 ml, the product precipitated as a yellow solid. This solid was filtered and washed with dichloromethane. Crystals of (I) were obtained by evaporation of a methanol solution.

Crystal data

$[Pd(C_{17}H_{28}N_4S_2)](BF_4)_2$	D_x = 1.731 Mg m^{-3}
M_r = 632.57	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8324 reflections
a = 11.7590 (10) Å	θ = 2.9–30.0°
b = 18.6500 (10) Å	μ = 1.01 mm^{-1}
c = 11.8800 (10) Å	T = 293 (2) K
β = 111.29 (2)°	Prism, yellow
V = 2427.5 (5) Å^3	0.20 × 0.07 × 0.07 mm
Z = 4	

Data collection

Marresearch MAR345 image-plate diffractometer	2400 reflections with $I > 2\sigma(I)$
	R_{int} = 0.093
φ scans	θ_{max} = 30.0°
Absorption correction: none	$h = -15 \rightarrow 15$
9639 measured reflections	$k = 0 \rightarrow 26$
6465 independent reflections	$l = 0 \rightarrow 15$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.035	$w = 1/[\sigma^2(F_o^2) + (0.0062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.060	$(\Delta/\sigma)_{max} < 0.001$
S = 1.15	$\Delta\rho_{max}$ = 0.59 e Å^{-3}
5502 reflections	$\Delta\rho_{min}$ = −0.71 e Å^{-3}
303 parameters	

Table 1
Selected geometric parameters (Å, °).

Pd—N2	2.022 (4)	Pd—S1	2.2761 (15)
Pd—N3	2.059 (4)	Pd—S2	2.2900 (16)
N2—Pd—N3	93.84 (15)	N2—Pd—S2	86.81 (12)
N2—Pd—S1	176.85 (12)	N3—Pd—S2	179.10 (12)
N3—Pd—S1	85.81 (11)	S1—Pd—S2	93.58 (6)

The systematic absences were not used in the refinement. The small volume of the crystal resulted in the low ratio of observed/unique reflections. Disordered F atoms in one BF_4 ion were refined isotropically with bond lengths and angles restrained to be equal with an effective standard uncertainty of 0.02. The occupancy factors of the disordered atoms were assumed to be 0.5 according to the height of peaks in the Fourier synthesis. H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined using a riding model with $U_{iso} = 1.2U_{eq}$(C). The shortest C11—C12 and C14—C15 bond lengths and the high displacement parameters of the methyl C atoms suggest possible disorder of atoms C12 and C15.

Data collection: *MARXDS* (Klein, 2000); cell refinement: *MARXDS*; data reduction: *MARSCALE* (Klein, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1998); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1998); molecular graphics: *ORTEP*-3 (Farrugia, 2003); software used to prepare material for publication: *SHELXL*97 and *CIFTAB* (Sheldrick, 1998).

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