

cis-Bis[1-allyl-3-(2-pyridyl- κ N)thio-ureato- κ S]palladium(II)

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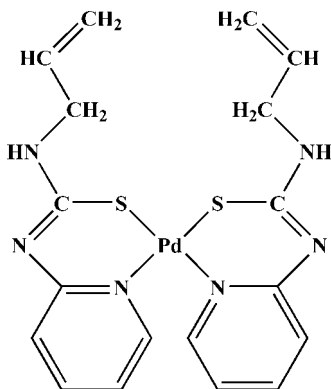
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.022; wR factor = 0.055; data-to-parameter ratio = 14.7.

Yellow plate-like shaped crystals of the title compound, $[\text{Pd}(\text{C}_9\text{H}_{10}\text{N}_3\text{S})_2]$, were obtained by ligand-exchange reaction between palladium(II) acetylacetonate and the corresponding organic reagent at room temperature. The Pd^{II} atom shows a slightly distorted square-planar coordination geometry consisting of two ligand molecules in a *cis* conformation that bind in their thiolic tautomeric form. Weak intermolecular $\text{Pd} \cdots \text{H}$ interactions with $\text{Pd}-\text{H}$ distances of 3.328 (2) Å were observed in the crystal structure. The three-dimensional network of the crystal structure is realized by weak intermolecular $\text{C}-\text{H} \cdots \text{N}$, $\text{N}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{S}$ hydrogen bonds.

Related literature

For a related structure, see: Bon *et al.* (2007). For the anti-tumoral properties of Pd compounds, see: Upadhayaya *et al.* (2009), Hernández *et al.* (2008).



Experimental

Crystal data

$[\text{Pd}(\text{C}_9\text{H}_{10}\text{N}_3\text{S})_2]$
 $M_r = 490.96$
 Monoclinic, $P2_1/c$
 $a = 10.8976$ (6) Å
 $b = 8.9730$ (5) Å
 $c = 21.798$ (1) Å
 $\beta = 113.624$ (2)°

$V = 1952.9$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.18$ mm⁻¹
 $T = 173$ K
 $0.51 \times 0.21 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: numerical (*SADABS*; Bruker, 2005)
 $T_{\text{min}} = 0.583$, $T_{\text{max}} = 0.941$

17417 measured reflections
 4010 independent reflections
 3522 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.055$
 $S = 1.03$
 4010 reflections
 272 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{C3}-\text{H3A} \cdots \text{N2}^{\text{i}}$	0.95	2.64	3.511 (3)	152
$\text{C14}-\text{H14A} \cdots \text{N5}^{\text{ii}}$	0.95	2.57	3.376 (3)	143
$\text{N3}-\text{H3N} \cdots \text{N3}^{\text{iii}}$	0.78 (3)	2.84 (3)	3.425 (4)	133 (2)
$\text{C4}-\text{H4A} \cdots \text{S2}^{\text{iv}}$	0.95	2.98	3.728 (2)	136
$\text{C12}-\text{H12A} \cdots \text{S1}^{\text{v}}$	0.95	3.02	3.910 (2)	156
$\text{C18B}-\text{H18D} \cdots \text{S1}^{\text{vi}}$	0.95	2.95	3.85 (1)	160
$\text{C7}-\text{H7A} \cdots \text{S2}^{\text{iii}}$	0.99	2.85	3.825 (3)	167

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2129).

References

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supplementary materials

Acta Cryst. (2009). E65, m1059 [doi:10.1107/S1600536809029262]

cis-Bis[1-allyl-3-(2-pyridyl- κ N)thioureato- κ S]palladium(II)

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Comment

Palladium complexes with carbothioamide derivatives as organic ligands attract ongoing scientific interest due to their cytotoxic, antitumoral, antifungal and antimicrobial activities (Upadhayaya *et al.* 2009; Hernández *et al.* 2008)

The asymmetric unit of the title compound contains one molecule of the complex (Fig. 1). Palladium shows a slightly distorted square-planar coordination geometry with a mean deviation from the plane of 0.0679 (2) Å. Two molecules of the organic ligand chelate the palladium in *cis*-conformation *via* carbothioamide sulfur and pyridine nitrogen atoms. The observed bond lengths of the carbothioamide fragment [C(6)—S(1) 1.752 (2), C(15)—S(2) 1.753 (2), C(6)—N(2) 1.301 (3) and C(15)—N(5) 1.302 (3) Å] indicate the thiolic tautomeric form of the thiourea derivative. The six-membered metallacycle exhibits a non-planar geometry with torsion angles Pd(1)—S(1)—C(6)—N(2) 142.8 (2) and Pd(1)—S(2)—C(15)—N(5) 134.1 (2)°. The allyl substituents of both coordinated ligand molecules are disordered over two positions with occupancies of 0.7 and 0.3, respectively. The crystal structure of the title compound shows weak intermolecular Pd···H interactions with $d(\text{Pd—H}) = 3.328$ Å. The 3-D network is realized by weak C—H···N, N—H···N and C—H···S intermolecular hydrogen bonds (Fig.2, Table 1).

Experimental

Single crystals of title compound were synthesized by a ligand exchange reaction between 5 ml (5×10^{-3} M) of a solution of palladium(II) acetylacetonate in chloroform and 5 ml (10^{-2} M) of an ethanolic solution of the organic ligand. After staying one month in a dark place the layered mixture becomes homogeneous and yellow plate-like shaped crystals were grown.

Refinement

Disorder of both allyl fragments has been observed in the molecular structure of the title compound. Disordered allyl substituents C8, C9 and C17, C18 were treated with occupancies 0.71/0.29 and 0.70/0.30, respectively, and refined with equal ADP for both parts. H atoms bonded to N were located in a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model with C—H = 0.99 Å for CH₂ [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] and C—H = 0.95 Å for CH [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Figures

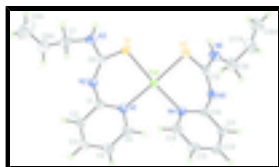


Fig. 1. The title compound showing 50% probability displacement ellipsoids for the non-hydrogen atoms. Only one position is shown for disordered allyl fragments

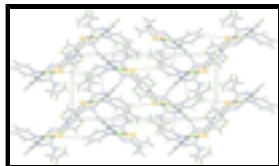


Fig. 2. Crystal packing of title compound, projection down the a axis. Dashed lines indicate hydrogen bonds.

cis-Bis[1-allyl-3-(2-pyridyl- κ N)thioureato- κ S]palladium(II)

Crystal data

[Pd(C ₉ H ₁₀ N ₃ S ₁) ₂]	$F_{000} = 992$
$M_r = 490.96$	$D_x = 1.670 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Melting point: 343 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 10.8976 (6) \text{ \AA}$	Cell parameters from 8451 reflections
$b = 8.9730 (5) \text{ \AA}$	$\theta = 3.0\text{--}26.4^\circ$
$c = 21.798 (1) \text{ \AA}$	$\mu = 1.18 \text{ mm}^{-1}$
$\beta = 113.624 (2)^\circ$	$T = 173 \text{ K}$
$V = 1952.9 (2) \text{ \AA}^3$	Plate, yellow
$Z = 4$	$0.51 \times 0.21 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	4010 independent reflections
Radiation source: fine-focus sealed tube	3522 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.026$
Detector resolution: 8.26 pixels mm^{-1}	$\theta_{\text{max}} = 26.4^\circ$
$T = 173 \text{ K}$	$\theta_{\text{min}} = 2.0^\circ$
φ and ω scans	$h = -13 \rightarrow 13$
Absorption correction: numerical (SADABS; Bruker, 2005)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.583$, $T_{\text{max}} = 0.941$	$l = -26 \rightarrow 27$
17417 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.055$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 1.8761P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
4010 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
272 parameters	$\Delta\rho_{\text{max}} = 0.58 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

3 restraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pd1	0.504182 (15)	0.273165 (18)	0.331038 (7)	0.02144 (6)	
S1	0.48920 (6)	0.26120 (8)	0.43136 (3)	0.03554 (15)	
S2	0.72854 (5)	0.24180 (7)	0.38621 (3)	0.02877 (13)	
N1	0.30161 (17)	0.3217 (2)	0.28592 (8)	0.0226 (4)	
N2	0.22927 (17)	0.1688 (2)	0.35666 (9)	0.0246 (4)	
N3	0.3409 (2)	0.0682 (3)	0.45961 (10)	0.0356 (5)	
N4	0.52967 (17)	0.26693 (19)	0.24180 (8)	0.0216 (4)	
N5	0.73705 (17)	0.4037 (2)	0.27993 (8)	0.0238 (4)	
N6	0.88430 (19)	0.4612 (2)	0.38499 (10)	0.0330 (5)	
C1	0.2066 (2)	0.2704 (2)	0.30613 (10)	0.0231 (4)	
C2	0.0738 (2)	0.3203 (3)	0.27361 (11)	0.0282 (5)	
H2A	0.0067	0.2803	0.2862	0.034*	
C3	0.0396 (2)	0.4252 (3)	0.22420 (11)	0.0303 (5)	
H3A	-0.0500	0.4600	0.2033	0.036*	
C4	0.1382 (2)	0.4802 (3)	0.20512 (11)	0.0299 (5)	
H4A	0.1177	0.5536	0.1710	0.036*	
C5	0.2656 (2)	0.4259 (2)	0.23664 (11)	0.0268 (5)	
H5A	0.3327	0.4633	0.2233	0.032*	
C6	0.3393 (2)	0.1622 (3)	0.41056 (10)	0.0262 (5)	
C7	0.2192 (3)	0.0080 (3)	0.46317 (13)	0.0396 (6)	
H7A	0.2445	-0.0645	0.5005	0.048*	
H7B	0.1673	-0.0461	0.4211	0.048*	
C8A	0.1310 (4)	0.1276 (5)	0.4737 (2)	0.0501 (10)	0.711 (5)
H8AA	0.0885	0.1963	0.4383	0.060*	0.711 (5)
C9A	0.1099 (12)	0.1423 (10)	0.5274 (5)	0.0819 (19)	0.711 (5)
H9AA	0.1507	0.0755	0.5638	0.098*	0.711 (5)
H9AB	0.0534	0.2198	0.5307	0.098*	0.711 (5)
C8B	0.1993 (11)	0.0863 (13)	0.5186 (6)	0.0501 (10)	0.289 (5)
H8BA	0.2630	0.0696	0.5630	0.060*	0.289 (5)
C9B	0.103 (3)	0.173 (3)	0.5105 (16)	0.0819 (19)	0.289 (5)

supplementary materials

H9BA	0.0377	0.1924	0.4668	0.098*	0.289 (5)
H9BB	0.0962	0.2199	0.5481	0.098*	0.289 (5)
C10	0.6369 (2)	0.3219 (2)	0.23255 (10)	0.0230 (4)	
C11	0.6465 (2)	0.3015 (3)	0.17078 (11)	0.0332 (5)	
H11A	0.7189	0.3452	0.1635	0.040*	
C12	0.5531 (3)	0.2197 (3)	0.12094 (12)	0.0377 (6)	
H12A	0.5613	0.2041	0.0797	0.045*	
C13	0.4457 (2)	0.1597 (3)	0.13180 (11)	0.0350 (5)	
H13A	0.3798	0.1013	0.0984	0.042*	
C14	0.4373 (2)	0.1868 (3)	0.19154 (11)	0.0289 (5)	
H14A	0.3628	0.1476	0.1984	0.035*	
C15	0.7807 (2)	0.3775 (2)	0.34392 (10)	0.0240 (4)	
C16	0.9495 (2)	0.5766 (3)	0.36190 (13)	0.0380 (6)	
H16A	0.9016	0.6715	0.3598	0.046*	
H16B	0.9375	0.5515	0.3156	0.046*	
C17A	1.0931 (6)	0.6027 (8)	0.4014 (4)	0.0486 (15)	0.700 (9)
H17A	1.1296	0.6914	0.3918	0.058*	0.700 (9)
C18A	1.1731 (5)	0.5195 (7)	0.4466 (3)	0.0540 (13)	0.700 (9)
H18A	1.1419	0.4294	0.4581	0.065*	0.700 (9)
H18B	1.2645	0.5473	0.4691	0.065*	0.700 (9)
C17B	1.0811 (14)	0.6032 (17)	0.4263 (6)	0.037 (3)	0.300 (9)
H17B	1.0745	0.6469	0.4645	0.044*	0.300 (9)
C18B	1.2000 (13)	0.5671 (16)	0.4290 (7)	0.0540 (13)	0.300 (9)
H18C	1.2085	0.5233	0.3912	0.065*	0.300 (9)
H18D	1.2775	0.5847	0.4687	0.065*	0.300 (9)
H6N	0.904 (2)	0.452 (3)	0.4237 (13)	0.027 (7)*	
H3N	0.404 (3)	0.072 (3)	0.4936 (13)	0.038 (8)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01747 (9)	0.02785 (10)	0.01790 (9)	-0.00036 (7)	0.00594 (6)	0.00161 (6)
S1	0.0235 (3)	0.0626 (4)	0.0191 (3)	-0.0085 (3)	0.0070 (2)	-0.0001 (3)
S2	0.0197 (3)	0.0401 (3)	0.0239 (3)	0.0029 (2)	0.0061 (2)	0.0081 (2)
N1	0.0208 (9)	0.0246 (9)	0.0209 (9)	0.0000 (7)	0.0067 (7)	0.0016 (7)
N2	0.0226 (9)	0.0260 (9)	0.0244 (9)	-0.0010 (8)	0.0086 (7)	0.0030 (7)
N3	0.0307 (11)	0.0493 (13)	0.0246 (10)	0.0025 (10)	0.0089 (9)	0.0118 (9)
N4	0.0207 (9)	0.0228 (9)	0.0203 (9)	-0.0008 (7)	0.0071 (7)	0.0007 (7)
N5	0.0204 (9)	0.0259 (10)	0.0247 (9)	-0.0012 (7)	0.0084 (7)	0.0003 (7)
N6	0.0257 (11)	0.0419 (12)	0.0250 (11)	-0.0068 (9)	0.0035 (9)	-0.0041 (9)
C1	0.0230 (11)	0.0212 (10)	0.0240 (10)	-0.0029 (9)	0.0082 (9)	-0.0029 (8)
C2	0.0198 (11)	0.0314 (12)	0.0317 (12)	-0.0025 (9)	0.0086 (9)	0.0007 (9)
C3	0.0205 (11)	0.0319 (13)	0.0320 (12)	0.0035 (9)	0.0038 (9)	0.0020 (10)
C4	0.0302 (12)	0.0273 (12)	0.0272 (11)	0.0008 (10)	0.0064 (9)	0.0053 (9)
C5	0.0253 (11)	0.0292 (12)	0.0253 (11)	-0.0022 (9)	0.0093 (9)	0.0022 (9)
C6	0.0241 (11)	0.0323 (12)	0.0244 (11)	0.0032 (9)	0.0120 (9)	0.0011 (9)
C7	0.0474 (16)	0.0395 (14)	0.0343 (13)	-0.0108 (12)	0.0188 (12)	0.0048 (11)
C8A	0.042 (2)	0.068 (3)	0.049 (2)	0.0008 (19)	0.0275 (18)	0.005 (2)

C9A	0.133 (4)	0.060 (5)	0.081 (7)	0.006 (4)	0.072 (5)	0.018 (3)
C8B	0.042 (2)	0.068 (3)	0.049 (2)	0.0008 (19)	0.0275 (18)	0.005 (2)
C9B	0.133 (4)	0.060 (5)	0.081 (7)	0.006 (4)	0.072 (5)	0.018 (3)
C10	0.0230 (11)	0.0209 (10)	0.0247 (10)	0.0013 (8)	0.0091 (9)	0.0024 (8)
C11	0.0315 (13)	0.0446 (15)	0.0269 (12)	-0.0040 (11)	0.0153 (10)	0.0024 (10)
C12	0.0433 (15)	0.0479 (15)	0.0233 (12)	-0.0028 (12)	0.0148 (11)	-0.0041 (10)
C13	0.0388 (14)	0.0365 (14)	0.0238 (11)	-0.0081 (11)	0.0064 (10)	-0.0074 (10)
C14	0.0263 (12)	0.0299 (12)	0.0275 (11)	-0.0055 (10)	0.0077 (9)	-0.0019 (9)
C15	0.0191 (10)	0.0245 (11)	0.0281 (11)	0.0034 (9)	0.0094 (9)	-0.0023 (9)
C16	0.0321 (13)	0.0382 (14)	0.0427 (14)	-0.0109 (11)	0.0139 (11)	-0.0101 (11)
C17A	0.033 (3)	0.045 (3)	0.063 (4)	-0.013 (2)	0.014 (3)	-0.002 (3)
C18A	0.038 (3)	0.059 (4)	0.054 (3)	-0.009 (2)	0.0074 (19)	0.005 (2)
C17B	0.039 (6)	0.035 (5)	0.045 (7)	-0.015 (4)	0.026 (6)	-0.011 (5)
C18B	0.038 (3)	0.059 (4)	0.054 (3)	-0.009 (2)	0.0074 (19)	0.005 (2)

Geometric parameters (Å, °)

Pd1—N1	2.0713 (17)	C7—H7A	0.9900
Pd1—N4	2.0730 (17)	C7—H7B	0.9900
Pd1—S1	2.2598 (6)	C8A—C9A	1.288 (7)
Pd1—S2	2.2686 (6)	C8A—H8AA	0.9500
S1—C6	1.752 (2)	C9A—H9AA	0.9500
S2—C15	1.753 (2)	C9A—H9AB	0.9500
N1—C1	1.358 (3)	C8B—C9B	1.261 (17)
N1—C5	1.358 (3)	C8B—H8BA	0.9500
N2—C6	1.301 (3)	C9B—H9BA	0.9500
N2—C1	1.374 (3)	C9B—H9BB	0.9500
N3—C6	1.357 (3)	C10—C11	1.404 (3)
N3—C7	1.463 (3)	C11—C12	1.367 (3)
N3—H3N	0.78 (3)	C11—H11A	0.9500
N4—C10	1.355 (3)	C12—C13	1.392 (4)
N4—C14	1.359 (3)	C12—H12A	0.9500
N5—C15	1.302 (3)	C13—C14	1.363 (3)
N5—C10	1.376 (3)	C13—H13A	0.9500
N6—C15	1.353 (3)	C14—H14A	0.9500
N6—C16	1.455 (3)	C16—C17A	1.471 (7)
N6—H6N	0.79 (2)	C16—C17B	1.572 (13)
C1—C2	1.405 (3)	C16—H16A	0.9900
C2—C3	1.365 (3)	C16—H16B	0.9900
C2—H2A	0.9500	C17A—C18A	1.265 (9)
C3—C4	1.389 (3)	C17A—H17A	0.9500
C3—H3A	0.9500	C18A—H18A	0.9500
C4—C5	1.368 (3)	C18A—H18B	0.9500
C4—H4A	0.9500	C17B—C18B	1.31 (2)
C5—H5A	0.9500	C17B—H17B	0.9500
C7—C8B	1.487 (11)	C18B—H18C	0.9500
C7—C8A	1.519 (5)	C18B—H18D	0.9500
N1—Pd1—N4	94.48 (7)	C9A—C8A—H8AA	117.8
N1—Pd1—S1	89.59 (5)	C7—C8A—H8AA	117.8

supplementary materials

N4—Pd1—S1	174.63 (5)	C8A—C9A—H9AA	120.0
N1—Pd1—S2	174.24 (5)	C8A—C9A—H9AB	120.0
N4—Pd1—S2	88.44 (5)	H9AA—C9A—H9AB	120.0
S1—Pd1—S2	87.80 (2)	C9B—C8B—C7	124.2 (18)
C6—S1—Pd1	101.25 (7)	C9B—C8B—H8BA	117.9
C15—S2—Pd1	98.20 (7)	C7—C8B—H8BA	117.9
C1—N1—C5	118.27 (18)	C8B—C9B—H9BA	120.0
C1—N1—Pd1	125.52 (14)	C8B—C9B—H9BB	120.0
C5—N1—Pd1	115.82 (14)	H9BA—C9B—H9BB	120.0
C6—N2—C1	123.98 (19)	N4—C10—N5	123.65 (18)
C6—N3—C7	123.1 (2)	N4—C10—C11	119.71 (19)
C6—N3—H3N	116 (2)	N5—C10—C11	116.58 (19)
C7—N3—H3N	116 (2)	C12—C11—C10	120.9 (2)
C10—N4—C14	118.47 (18)	C12—C11—H11A	119.5
C10—N4—Pd1	125.27 (14)	C10—C11—H11A	119.5
C14—N4—Pd1	115.87 (14)	C11—C12—C13	118.8 (2)
C15—N5—C10	123.16 (18)	C11—C12—H12A	120.6
C15—N6—C16	124.1 (2)	C13—C12—H12A	120.6
C15—N6—H6N	116.6 (18)	C14—C13—C12	118.5 (2)
C16—N6—H6N	118.9 (18)	C14—C13—H13A	120.8
N1—C1—N2	124.70 (19)	C12—C13—H13A	120.8
N1—C1—C2	119.55 (19)	N4—C14—C13	123.6 (2)
N2—C1—C2	115.73 (19)	N4—C14—H14A	118.2
C3—C2—C1	121.2 (2)	C13—C14—H14A	118.2
C3—C2—H2A	119.4	N5—C15—N6	117.3 (2)
C1—C2—H2A	119.4	N5—C15—S2	129.22 (17)
C2—C3—C4	118.8 (2)	N6—C15—S2	113.46 (16)
C2—C3—H3A	120.6	N6—C16—C17A	117.6 (3)
C4—C3—H3A	120.6	N6—C16—C17B	101.3 (5)
C5—C4—C3	118.3 (2)	N6—C16—H16A	107.9
C5—C4—H4A	120.8	C17A—C16—H16A	107.9
C3—C4—H4A	120.8	C17B—C16—H16A	100.7
N1—C5—C4	123.8 (2)	N6—C16—H16B	107.9
N1—C5—H5A	118.1	C17A—C16—H16B	107.9
C4—C5—H5A	118.1	C17B—C16—H16B	130.2
N2—C6—N3	117.1 (2)	H16A—C16—H16B	107.2
N2—C6—S1	129.58 (17)	C18A—C17A—C16	127.0 (6)
N3—C6—S1	113.29 (17)	C18A—C17A—H17A	116.5
N3—C7—C8B	107.4 (4)	C16—C17A—H17A	116.5
N3—C7—C8A	112.9 (2)	C17A—C18A—H18A	120.0
N3—C7—H7A	109.0	C17A—C18A—H18B	120.0
C8B—C7—H7A	74.1	H18A—C18A—H18B	120.0
C8A—C7—H7A	109.0	C18B—C17B—C16	122.2 (12)
N3—C7—H7B	109.0	C18B—C17B—H17B	118.9
C8B—C7—H7B	140.3	C16—C17B—H17B	118.9
C8A—C7—H7B	109.0	C17B—C18B—H18C	120.0
H7A—C7—H7B	107.8	C17B—C18B—H18D	120.0
C9A—C8A—C7	124.3 (5)	H18C—C18B—H18D	120.0
N1—Pd1—S1—C6	42.71 (9)	C6—N3—C7—C8B	-106.2 (5)

S2—Pd1—S1—C6	-142.43 (8)	C6—N3—C7—C8A	-63.7 (3)
N4—Pd1—S2—C15	47.84 (9)	N3—C7—C8A—C9A	-112.2 (8)
S1—Pd1—S2—C15	-136.00 (7)	C8B—C7—C8A—C9A	-22.0 (10)
N4—Pd1—N1—C1	143.98 (17)	N3—C7—C8B—C9B	113.5 (19)
S1—Pd1—N1—C1	-32.53 (17)	C8A—C7—C8B—C9B	8.4 (18)
N4—Pd1—N1—C5	-43.35 (16)	C14—N4—C10—N5	-179.6 (2)
S1—Pd1—N1—C5	140.15 (15)	Pd1—N4—C10—N5	-7.2 (3)
N1—Pd1—N4—C10	140.26 (17)	C14—N4—C10—C11	3.2 (3)
S2—Pd1—N4—C10	-34.78 (16)	Pd1—N4—C10—C11	175.61 (16)
N1—Pd1—N4—C14	-47.14 (16)	C15—N5—C10—N4	36.3 (3)
S2—Pd1—N4—C14	137.82 (15)	C15—N5—C10—C11	-146.4 (2)
C5—N1—C1—N2	-177.9 (2)	N4—C10—C11—C12	-3.8 (4)
Pd1—N1—C1—N2	-5.4 (3)	N5—C10—C11—C12	178.9 (2)
C5—N1—C1—C2	3.2 (3)	C10—C11—C12—C13	1.7 (4)
Pd1—N1—C1—C2	175.69 (15)	C11—C12—C13—C14	0.8 (4)
C6—N2—C1—N1	35.3 (3)	C10—N4—C14—C13	-0.7 (3)
C6—N2—C1—C2	-145.8 (2)	Pd1—N4—C14—C13	-173.80 (19)
N1—C1—C2—C3	-3.3 (3)	C12—C13—C14—N4	-1.4 (4)
N2—C1—C2—C3	177.6 (2)	C10—N5—C15—N6	176.7 (2)
C1—C2—C3—C4	1.5 (3)	C10—N5—C15—S2	-0.6 (3)
C2—C3—C4—C5	0.3 (3)	C16—N6—C15—N5	-0.5 (3)
C1—N1—C5—C4	-1.4 (3)	C16—N6—C15—S2	177.21 (18)
Pd1—N1—C5—C4	-174.65 (18)	Pd1—S2—C15—N5	-45.9 (2)
C3—C4—C5—N1	-0.4 (4)	Pd1—S2—C15—N6	136.77 (15)
C1—N2—C6—N3	172.1 (2)	C15—N6—C16—C17A	-148.5 (4)
C1—N2—C6—S1	-6.3 (3)	C15—N6—C16—C17B	-165.4 (6)
C7—N3—C6—N2	-17.4 (3)	N6—C16—C17A—C18A	13.5 (10)
C7—N3—C6—S1	161.29 (19)	C17B—C16—C17A—C18A	61.2 (18)
Pd1—S1—C6—N2	-37.2 (2)	N6—C16—C17B—C18B	112.2 (14)
Pd1—S1—C6—N3	144.37 (16)	C17A—C16—C17B—C18B	-25.9 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C3—H3A...N2 ⁱ	0.95	2.64	3.511 (3)	152
C14—H14A...N5 ⁱⁱ	0.95	2.57	3.376 (3)	143
N3—H3N...N3 ⁱⁱⁱ	0.78 (3)	2.84 (3)	3.425 (4)	133 (2)
C4—H4A...S2 ^{iv}	0.95	2.98	3.728 (2)	136
C12—H12A...S1 ^v	0.95	3.02	3.910 (2)	156
C18B—H18D...S1 ^{vi}	0.95	2.95	3.85 (1)	160
C7—H7A...S2 ⁱⁱⁱ	0.99	2.85	3.825 (3)	167

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

Fig. 1

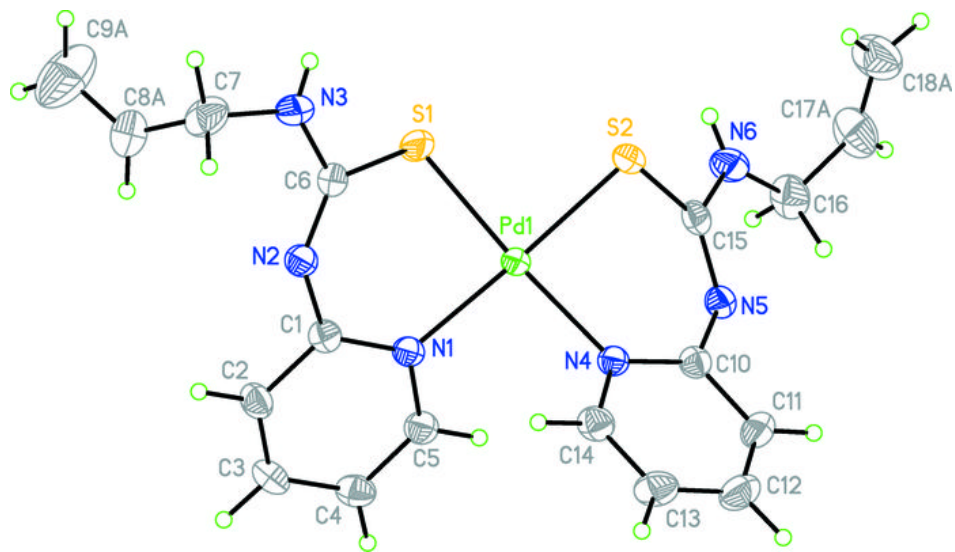


Fig. 2

