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Crystal structure of bis[*S*-hexyl 3-(4-methylbenzylidene)dithiocarbazato-κ^2N^3,S]palladium(II)

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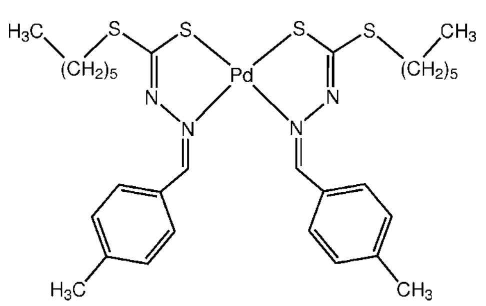
The whole molecule of the title complex, $[Pd(C_{15}H_{21}N_2S_2)_2]$, is generated by twofold rotational symmetry. The palladium(II) atom exhibits a square-planar coordination geometry, and is located on the crystallographic twofold axis that induces a *cis* configuration of the *N*,*S* chelating ligands. In the crystal, molecules stack along the *c*-axis direction and there are no significant intermolecular interactions present. The structure was refined as an inversion twin with a final BASF parameter of 0.34 (2).

Keywords: crystal structure; palladium(II) complex; *cis*-ligand configuration.

CCDC reference: 1046981

1. Related literature

For the crystal structures of the free Schiff base ligand and of its Ni^{II} complex, see: Howlader *et al.* (2015*a*,*b*). For similar bis(dithiocarbazato)Pd complexes with a *cis* configuration of the azomethine N and thiolate S atoms, see: Ali *et al.* (2002); Liu *et al.* (2011); Duan *et al.* (1998); Tampouris *et al.* (2007). For complexes with a *trans* configuration, see: Khaledi & Mohd Ali (2011); Tampouris *et al.* (2007); Tarafder *et al.* (2010).



2. Experimental

2.1. Crystal data

$[Pd(C_{15}H_{21}N_2S_2)_2]$
M_r = 693.32
Monoclinic, $C2$
a = 18.3559 (11) Å
b = 9.6747 (5) Å
c = 10.3368 (6) Å
β = 116.810 (2)°
V = 1638.37 (16) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 7.14 mm^{-1}
T = 173 K
0.25 × 0.16 × 0.11 mm

2.2. Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)
T_{min} = 0.268, T_{max} = 0.507
9318 measured reflections
2710 independent reflections
2121 reflections with $I > 2\sigma(I)$
R_{int} = 0.120

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.091
$wR(F^2)$ = 0.225
S = 1.03
2710 reflections
180 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.07 e Å^{-3}
$\Delta\rho_{min}$ = −1.32 e Å^{-3}
Absolute structure: Flack (1983), 1218 Friedel pairs
Absolute structure parameter: 0.34 (2)

Data collection: *RAPID-AUTO* (Rigaku, 2010); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU5071).

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supporting information

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Crystal structure of bis[*S*-hexyl 3-(4-methylbenzylidene)dithiocarbazato-κ^2N^3,S]palladium(II)

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S1. Synthesis and crystallization

A solution of $PdCl_2$ (0.044 g, 0.25 mmol, 25 mL methanol) was added to a solution of the ligand, *S*-hexyl (*E*)-3-(4-methylbenzylidene)dithiocarbazate (0.147 g, 0.5 mmol, 10 mL methanol). The resulting mixture was stirred at room temperature for 3 h. An orange red precipitate was formed, filtered off, washed with methanol and dried in vacuo over anhydrous $CaCl_2$. Orange red single crystals, suitable for X-ray diffraction, of the compound were obtained by slow evaporation from a mixture of chloroform and acetonitrile (1:1) after 5 days (m.p.: 433 K).

S2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were fixed geometrically (C—H = 0.95 - 0.99 Å) and refined as riding, with U_{iso}(H) =1.2 U_{eq}(C). The rather high R factor is affected by the small crystal dimensions and consequently by low diffraction at high θ angles. The collected data were cut at a resolution of 0.85 Å. The structure was refined as an inversion twin with a final BASF parameter = 0.34 (2).

S3. Comment

In the crystal of the title complex, Fig. 1, the Pd^{II} atom resides on a crystallographic twofold rotational axis and the two chelating Schiff base ligands, in their deprotonated imino thiolate form, coordinate the metal center *via* the azomithine nitrogen atom, N1 and thiolate sulfur atom, S1 in a *cis*-planar configuration (Fig. 1). However, the donor atoms are not coplanar as observed for the corresponding nickel derivative (Howlader *et al.*, 2015*b*), but the square planar geometry presents a slight tetrahedral distortion with displacement of atoms N1 and S1 of ± 0.121 (14) and ∓ 0.134 (6) Å, respectively, from the coordination mean plane. The Pd1–S1 and Pd1—N1 coordination bond distances are of 2.264 (4) and 2.154 (12) Å, respectively, with an N1—Pd1—S1 chelating angle of 83.2 (3)°. These values are in agreement with those observed in similar Pd-bis(dithiocarbazato) complexes, either with a *cis* configuration (Ali *et al.*, 2002; Liu, *et al.*, 2011; Duan *et al.*, 1998; Tampouris *et al.*, 2007) or with a *trans* configuration (Khaledi *et al.*, 2011; Tampouris *et al.*, 2007; Tarafder *et al.*, 2010). It is worth noting that the E conformation about the imine bond N1═C8 [= 1.207 (17) Å; torsion angle N2—N1—C8—C5 = 172.1 (14)°] is different to that observed in the nickel derivative mentioned above, *viz.*1.2 (7)°. This allows an approach between the rings of the methylbenzylidene moieties, with a centroid-to-centroid distance of 4.114 (8) Å, indicating a very weak π-π interaction.

In the crystal, there are no significant intermolecular interactions present. The molecules pack along the *c* axis direction (Fig. 2).

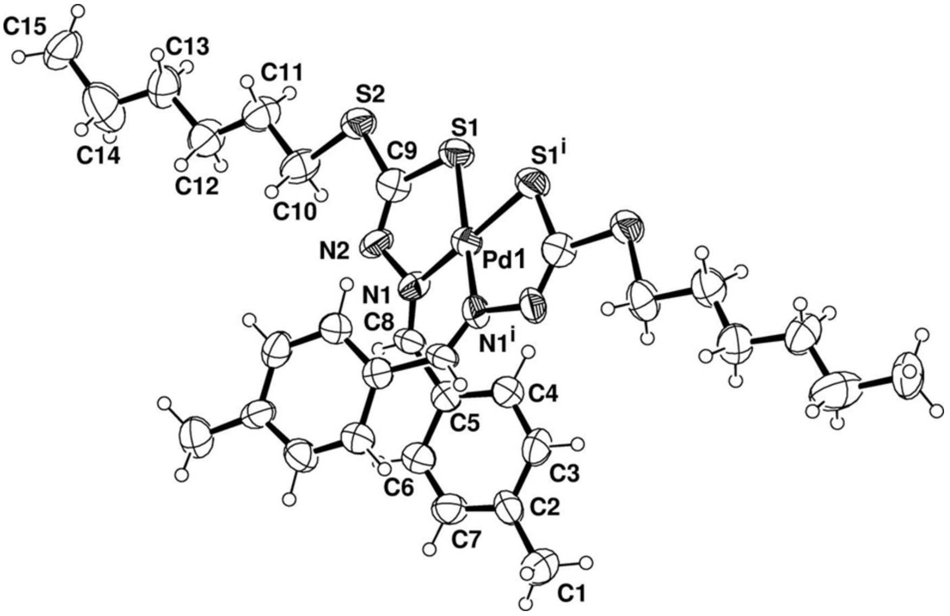

Figure 1

A view of the molecular structure of the title complex, with atom labelling (symmetry code: (i) -*x* + 1, *y*, -*z*). Displacement ellipsoids are drawn at the 50% probability level.

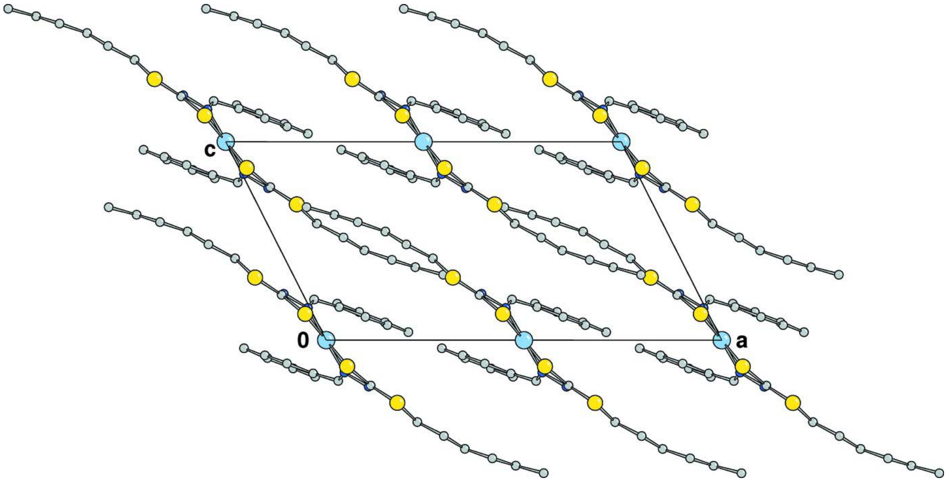

Figure 2

Crystal packing of the title complex viewed along the *b* axis.

Bis[*S*-hexyl 3-(4-methylbenzylidene)dithiocarbazato-κ^2N^3,*S*]palladium(II)

Crystal data

$[Pd(C_{15}H_{21}N_2S_2)_2]$
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Hall symbol: C 2y
a = 18.3559 (11) Å
b = 9.6747 (5) Å
c = 10.3368 (6) Å

β = 116.810 (2)°
V = 1638.37 (16) Å^3
Z = 2
F(000) = 720
D_x = 1.405 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54187 Å
θ = 4.8–67.0°

μ = 7.14 mm^{-1}	Prism, orange
T = 173 K	0.25 × 0.16 × 0.11 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	9318 measured reflections
Radiation source: fine-focus sealed tube	2710 independent reflections
Graphite monochromator	2121 reflections with $I > 2\sigma(I)$
Detector resolution: 10.000 pixels mm^{-1}	$R_{\rm int}$ = 0.120
ω scans	$\theta_{\rm max}$ = 65.1°, $\theta_{\rm min}$ = 4.8°
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)	$h = -21 \rightarrow 21$
$T_{\rm min}$ = 0.268, $T_{\rm max}$ = 0.507	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.091	$w = 1/[\sigma^2(F_o^2) + (0.1251P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.225	$(\Delta/\sigma)_{\rm max}$ < 0.001
S = 1.03	$\Delta\rho_{\rm max}$ = 2.07 e Å^{-3}
2710 reflections	$\Delta\rho_{\rm min}$ = −1.32 e Å^{-3}
180 parameters	Absolute structure: Flack (1983), 1218 Friedel pairs
1 restraint	Absolute structure parameter: 0.34 (2)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Pd1	0.5000	0.5495	0.0000	0.0607 (4)
S1	0.4807 (3)	0.3802 (4)	0.1325 (5)	0.0725 (11)
S2	0.4003 (2)	0.3956 (4)	0.3156 (4)	0.0726 (9)
N1	0.4949 (7)	0.6818 (12)	0.1634 (13)	0.060 (3)
N2	0.4526 (9)	0.6244 (17)	0.2347 (16)	0.071 (4)
C1	0.7185 (10)	1.1510 (17)	0.0408 (17)	0.087 (4)
H1A	0.7670	1.1034	0.0465	0.130*
H1B	0.7353	1.2327	0.1036	0.130*
H1C	0.6839	1.1796	−0.0594	0.130*
C2	0.6712 (6)	1.0545 (19)	0.0900 (11)	0.063 (3)
C3	0.6745 (8)	0.9122 (16)	0.0758 (15)	0.072 (4)
H3	0.7083	0.8746	0.0369	0.086*

C4	0.6290 (7)	0.8236 (13)	0.1178 (14)	0.062 (3)
H4	0.6339	0.7262	0.1124	0.075*
C5	0.5759 (7)	0.8797 (13)	0.1679 (13)	0.061 (3)
C6	0.5741 (8)	1.0255 (14)	0.1841 (14)	0.070 (4)
H6	0.5412	1.0656	0.2234	0.084*
C7	0.6196 (8)	1.1052 (14)	0.1431 (14)	0.071 (3)
H7	0.6161	1.2025	0.1509	0.085*
C8	0.5215 (8)	0.7962 (12)	0.2045 (14)	0.062 (3)
H8	0.5048	0.8378	0.2700	0.074*
C9	0.4449 (11)	0.4926 (16)	0.2274 (18)	0.059 (4)
C10	0.3742 (9)	0.529 (2)	0.4125 (15)	0.080 (5)
H10A	0.4242	0.5722	0.4885	0.096*
H10B	0.3406	0.6025	0.3449	0.096*
C11	0.3247 (9)	0.4534 (18)	0.4821 (16)	0.081 (4)
H11A	0.2809	0.3981	0.4062	0.097*
H11B	0.3617	0.3886	0.5571	0.097*
C12	0.2885 (8)	0.545 (2)	0.5472 (14)	0.081 (3)
H12A	0.2580	0.6183	0.4765	0.097*
H12B	0.3327	0.5904	0.6324	0.097*
C13	0.2311 (9)	0.4735 (19)	0.5952 (19)	0.091 (5)
H13A	0.1951	0.4112	0.5161	0.109*
H13B	0.2642	0.4148	0.6800	0.109*
C14	0.1813 (12)	0.559 (3)	0.632 (2)	0.133 (7)
H14A	0.1500	0.6224	0.5504	0.160*
H14B	0.2165	0.6168	0.7170	0.160*
C15	0.1205 (10)	0.475 (2)	0.670 (2)	0.110 (6)
H15A	0.0888	0.5391	0.6982	0.165*
H15B	0.1512	0.4118	0.7499	0.165*
H15C	0.0835	0.4224	0.5845	0.165*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0664 (7)	0.0506 (7)	0.0761 (7)	0.000	0.0419 (5)	0.000
S1	0.093 (3)	0.051 (2)	0.095 (3)	0.001 (2)	0.062 (2)	0.004 (2)
S2	0.084 (2)	0.059 (2)	0.092 (2)	−0.0072 (17)	0.0542 (19)	0.0009 (17)
N1	0.055 (6)	0.057 (7)	0.076 (7)	−0.011 (5)	0.037 (6)	0.006 (5)
N2	0.067 (8)	0.072 (9)	0.091 (9)	−0.027 (7)	0.050 (7)	−0.017 (7)
C1	0.081 (9)	0.094 (12)	0.096 (11)	−0.013 (8)	0.048 (9)	0.004 (8)
C2	0.063 (6)	0.054 (7)	0.073 (6)	0.014 (9)	0.032 (5)	−0.003 (9)
C3	0.063 (8)	0.084 (11)	0.086 (9)	0.003 (7)	0.048 (7)	−0.002 (7)
C4	0.058 (6)	0.048 (7)	0.082 (8)	0.003 (5)	0.034 (6)	0.003 (6)
C5	0.060 (7)	0.052 (7)	0.076 (8)	0.000 (6)	0.036 (6)	0.001 (5)
C6	0.076 (7)	0.053 (10)	0.093 (8)	0.001 (7)	0.048 (7)	−0.005 (6)
C7	0.074 (8)	0.055 (8)	0.080 (9)	−0.004 (6)	0.032 (7)	0.011 (6)
C8	0.079 (8)	0.030 (6)	0.096 (9)	0.006 (6)	0.057 (7)	0.005 (6)
C9	0.068 (9)	0.052 (9)	0.063 (9)	−0.004 (7)	0.034 (7)	0.000 (6)
C10	0.085 (8)	0.090 (14)	0.081 (8)	−0.017 (10)	0.053 (7)	0.007 (9)

C11	0.084 (9)	0.083 (11)	0.086 (10)	−0.009 (8)	0.048 (8)	0.002 (8)
C12	0.084 (7)	0.088 (9)	0.081 (7)	−0.019 (12)	0.047 (6)	−0.019 (12)
C13	0.082 (10)	0.104 (12)	0.109 (12)	0.010 (9)	0.063 (9)	0.002 (9)
C14	0.162 (16)	0.118 (16)	0.150 (15)	0.043 (19)	0.098 (14)	−0.003 (17)
C15	0.106 (12)	0.112 (14)	0.160 (17)	−0.024 (10)	0.102 (13)	−0.010 (11)

Geometric parameters (Å, º)

Pd1—N1	2.154 (12)	C6—C7	1.337 (16)
Pd1—N1^{i}	2.154 (12)	C6—H6	0.9500
Pd1—S1	2.264 (4)	C7—H7	0.9500
Pd1—S1^{i}	2.264 (4)	C8—H8	0.9500
S1—C9	1.777 (17)	C10—C11	1.573 (19)
S2—C9	1.747 (16)	C10—H10A	0.9900
S2—C10	1.829 (18)	C10—H10B	0.9900
N1—C8	1.208 (16)	C11—C12	1.44 (2)
N1—N2	1.404 (17)	C11—H11A	0.9900
N2—C9	1.282 (15)	C11—H11B	0.9900
C1—C2	1.511 (19)	C12—C13	1.52 (2)
C1—H1A	0.9800	C12—H12A	0.9900
C1—H1B	0.9800	C12—H12B	0.9900
C1—H1C	0.9800	C13—C14	1.41 (2)
C2—C7	1.381 (16)	C13—H13A	0.9900
C2—C3	1.39 (2)	C13—H13B	0.9900
C3—C4	1.397 (18)	C14—C15	1.56 (3)
C3—H3	0.9500	C14—H14A	0.9900
C4—C5	1.403 (16)	C14—H14B	0.9900
C4—H4	0.9500	C15—H15A	0.9800
C5—C6	1.423 (17)	C15—H15B	0.9800
C5—C8	1.460 (16)	C15—H15C	0.9800
N1—Pd1—N1^{i}	107.1 (6)	N2—C9—S2	124.7 (15)
N1—Pd1—S1	83.2 (3)	N2—C9—S1	125.6 (15)
N1^{i}—Pd1—S1	168.1 (3)	S2—C9—S1	109.6 (9)
N1—Pd1—S1^{i}	168.1 (3)	C11—C10—S2	105.5 (13)
N1^{i}—Pd1—S1^{i}	83.2 (3)	C11—C10—H10A	110.6
S1—Pd1—S1^{i}	87.3 (2)	S2—C10—H10A	110.6
C9—S1—Pd1	95.1 (5)	C11—C10—H10B	110.6
C9—S2—C10	101.8 (7)	S2—C10—H10B	110.6
C8—N1—N2	114.2 (12)	H10A—C10—H10B	108.8
C8—N1—Pd1	131.8 (10)	C12—C11—C10	114.0 (15)
N2—N1—Pd1	114.0 (9)	C12—C11—H11A	108.7
C9—N2—N1	115.8 (16)	C10—C11—H11A	108.7
C2—C1—H1A	109.5	C12—C11—H11B	108.7
C2—C1—H1B	109.5	C10—C11—H11B	108.7
H1A—C1—H1B	109.5	H11A—C11—H11B	107.6
C2—C1—H1C	109.5	C11—C12—C13	113.9 (18)
H1A—C1—H1C	109.5	C11—C12—H12A	108.8

H1B—C1—H1C	109.5	C13—C12—H12A	108.8
C7—C2—C3	117.7 (14)	C11—C12—H12B	108.8
C7—C2—C1	121.0 (16)	C13—C12—H12B	108.8
C3—C2—C1	121.2 (12)	H12A—C12—H12B	107.7
C2—C3—C4	120.9 (12)	C14—C13—C12	116.7 (19)
C2—C3—H3	119.5	C14—C13—H13A	108.1
C4—C3—H3	119.5	C12—C13—H13A	108.1
C3—C4—C5	119.4 (12)	C14—C13—H13B	108.1
C3—C4—H4	120.3	C12—C13—H13B	108.1
C5—C4—H4	120.3	H13A—C13—H13B	107.3
C4—C5—C6	118.9 (11)	C13—C14—C15	112 (2)
C4—C5—C8	123.5 (11)	C13—C14—H14A	109.1
C6—C5—C8	117.6 (11)	C15—C14—H14A	109.1
C7—C6—C5	118.9 (12)	C13—C14—H14B	109.1
C7—C6—H6	120.5	C15—C14—H14B	109.1
C5—C6—H6	120.5	H14A—C14—H14B	107.8
C6—C7—C2	124.0 (14)	C14—C15—H15A	109.5
C6—C7—H7	118.0	C14—C15—H15B	109.5
C2—C7—H7	118.0	H15A—C15—H15B	109.5
N1—C8—C5	129.2 (12)	C14—C15—H15C	109.5
N1—C8—H8	115.4	H15A—C15—H15C	109.5
C5—C8—H8	115.4	H15B—C15—H15C	109.5

Symmetry code: (i) −*x*+1, *y*, −*z*.