cis-Dichlorido(6,11-dihydrodibenzo[b,f][1,4]-dithiocine-κ²S,S′)palladium(II)

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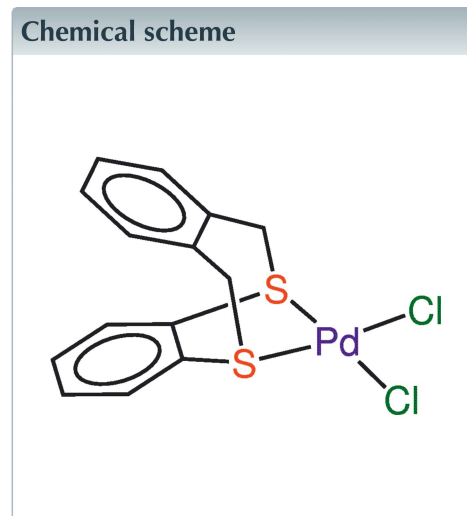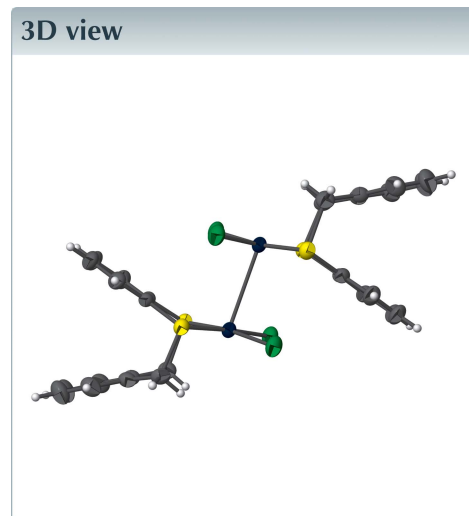
In the title compound, [PdCl$_2$(C$_{14}$H$_{12}$S$_2$)], the Pd^{II} atom features a square-planar coordination to the two S atoms of the dithiocine ligand and two Cl$^-$ ions. The dithiocine ligand forms a pair of metallacycle rings, with seven (C$_4$S$_2$Pd) and five (C$_2$S$_2$Pd) members, respectively. The benzylic part of the molecule is oriented away from the Pd atom, as a consequence of the boat conformation adopted by the chelating ligand. The geometry for both S-donor atoms is consistent with sp^3 hybridization.

3D view

Chemical scheme

Structure description

Good quality crystals for X-ray diffraction analysis of the complex [PdCl$_2$(κ^2-S$_2$C$_{14}$H$_{12}$)] were obtained by slow diffusion of two concentrated solutions of the reactants in CH$_2$Cl$_2$ separated by a phase of pure CH$_2$Cl$_2$, at room temperature (293–298 K). In the complex (Fig. 1), the Pd^{II} atom lies at the centre of a slightly distorted square-planar [S$_2$Cl$_2$] donor set, with the 1,4-dithiocine ligand coordinating in a bidentate fashion. The asymmetric character of this ligand gives rise to a pair of metallacycle rings with five and seven members. The bond angles at S1 and S4 indicate that these atoms retain a quasi-tetrahedral hybridization. The Pd—S bond lengths, 2.2638 (8) and 2.2749 (8) Å, are similar to comparable Pd—S distances found in other thioether complexes (e.g. Tiburcio et al., 2002). The 6,8,6 system of the dithiocine ligand adopts a boat-like conformation, allowing the formation of a weak intramolecular π–π interaction, the distance between the centroids of the benzene rings being 3.854 (2) Å. However, these rings are not parallel, and are inclined at a dihedral angle of 46.5 (2)°.

The molecules are staggered in the triclinic crystal, so the Cl and S atoms of one molecule are rotated by 180° with respect to the neighbouring molecule, forming
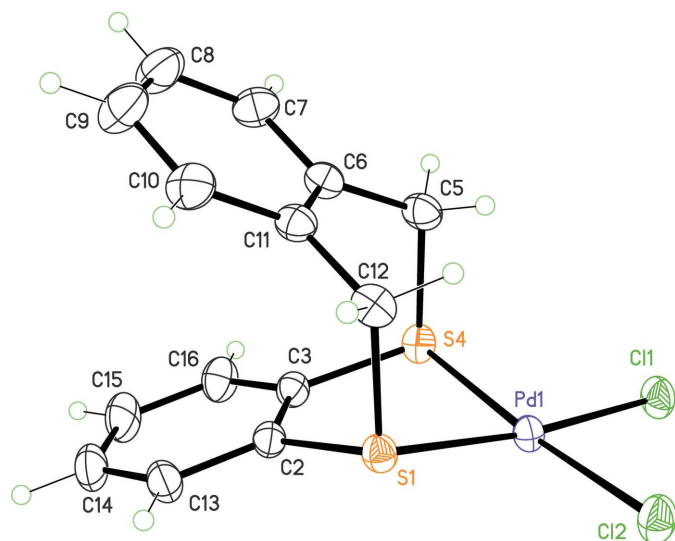
Figure 1
The structure of the title compound, with displacement ellipsoids for non-H atoms at the 30% probability level.

centrosymmetric pairs (Fig. 2). The resulting Pd···Pd distance is rather short, 3.2234 (5) Å, slightly shorter than twice the van der Waals radius of Pd (3.26 Å; Bondi, 1964). Such a short intermolecular contact is however not exceptional, and Pd···Pd separations around 3 Å without any formal σ-bond formation have been reported previously (*e.g.* Karhu *et al.*, 2016; Pullen *et al.*, 1998). The arrangement of the molecules in the crystal avoids the formation of intermolecular π-stacking in the solid state.

Synthesis and crystallization

Unfortunately the title complex is insoluble in all common solvents and decomposes with loss of the ligand in dimethylsulfoxide and dimethylformamide. Therefore, normal synthesis and recrystallization was not possible. In addition, the insolubility of the complex precluded its characterization by standard NMR techniques.
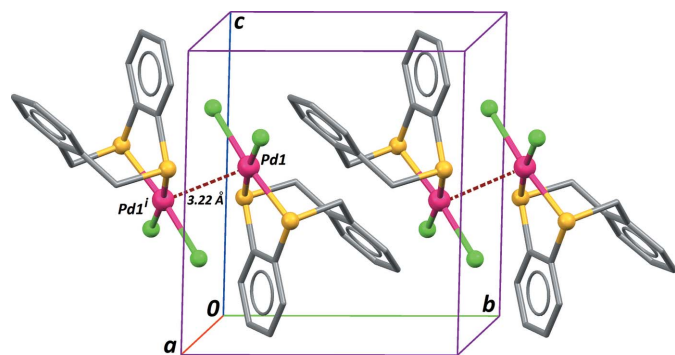

Figure 2
Part of the crystal structure, emphasizing short Pd···Pd distances (dashed lines). H atoms are omitted for clarity [symmetry code: (i) $1 - x$, $-y$, $1 - z$].

Table 1
Experimental details.

Crystal data	
Chemical formula	$[PdCl_2(C_{14}H_{12}S_2)]$
M_r	421.66
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	297
a, b, c (Å)	8.1594 (6), 9.2419 (6), 10.4393 (7)
α, β, γ (°)	82.454 (6), 77.443 (6), 82.281 (4)
V (Å^3)	757.16 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.84
Crystal size (mm)	$0.20 \times 0.12 \times 0.10$
Data collection	
Diffractometer	Bruker P4
Absorption correction	ψ scan (*XSCANS*; Bruker, 1997)
T_{min}, T_{max}	0.304, 0.337
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4833, 4021, 3154
R_{int}	0.024
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.682
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.076, 1.03
No. of reflections	4021
No. of parameters	173
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.53

Computer programs: *XSCANS* (Bruker, 1997), *SHELXS2013* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

To overcome this difficulty, we used an alternative method based on the slow diffusion of CH_2Cl_2 solutions containing each of the reagents, and separated by a phase of pure CH_2Cl_2. The reaction involves the direct displacement of SMe_2 from the complex $[PdCl_2(SMe_2)_2]$ (Jasper *et al.*, 1994) with the chelating ligand $S_2C_{14}H_{12}$ (Schroth *et al.*, 1964).

In an H-shaped vessel with the vertical glass tubes open at the upper-ends and connected with a horizontal tube, $[PdCl_2(SMe_2)_2]$ (150 mg, 0.5 mmol) dissolved in 25 ml of CH_2Cl_2 was placed in one vertical arm, and $S_2C_{14}H_{12}$ (122 mg, 0.5 mmol) dissolved in 25 ml of CH_2Cl_2 in the other. The top level of both solutions was around 3 cm below the horizontal glass tube. Pure CH_2Cl_2 was then layered until the solvent level reached one cm above the horizontal glass tube. The system was left aside for 3 days, affording orange crystals suitable for structural studies. Analysis, found: C 39.6, H 2.3, S 15.6%; calculated for $C_{14}H_{12}Cl_2PdS_2$: C 39.9, H 2.9, S 15.2%. IR (ν, cm^{-1}): 2944 (*m*), 1485 (*m*), 1460 (*s*), 1237 (*m*), 779 (*s*), 668 (*s*), 326 (*s*), 295 (*m*), 287(*s*).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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full crystallographic data

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cis-Dichlorido(6,11-dihydrodibenzo[*b*,*f*][1,4]dithiocine-$\kappa^2 S,S'$)palladium(II)

Crystal data

[PdCl$_2$(C$_{14}$H$_{12}$S$_2$)]
$M_r = 421.66$
Triclinic, $P\bar{1}$
$a = 8.1594$ (6) Å
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$\alpha = 82.454$ (6)°
$\beta = 77.443$ (6)°
$\gamma = 82.281$ (4)°
$V = 757.16$ (9) Å^3

$Z = 2$
$F(000) = 416$
$D_x = 1.849$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 78 reflections
$\theta = 4.2$–13.0°
$\mu = 1.84$ mm^{-1}
$T = 297$ K
Prism, orange
$0.20 \times 0.12 \times 0.10$ mm

Data collection

Bruker P4
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: ψ scan
    (XSCANS; Bruker, 1997)
$T_{min} = 0.304$, $T_{max} = 0.337$
4833 measured reflections

4021 independent reflections
3154 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 29.0°$, $\theta_{min} = 2.0°$
$h = -11 \rightarrow 1$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.076$
$S = 1.03$
4021 reflections
173 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant
    direct methods
Secondary atom site location: difference Fourier
    map

Hydrogen site location: inferred from
    neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 0.1995P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: SHELXL2014
    (Sheldrick, 2015),
    Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.0065 (6)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Pd1	0.35201 (3)	0.13119 (2)	0.53585 (2)	0.03134 (9)
Cl1	0.53384 (11)	0.19942 (9)	0.65447 (8)	0.04461 (19)
Cl2	0.22036 (11)	−0.02243 (9)	0.71175 (7)	0.04510 (19)
S1	0.16909 (9)	0.09097 (8)	0.41133 (7)	0.03249 (16)
C2	0.2749 (4)	0.1462 (3)	0.2468 (3)	0.0325 (6)
C3	0.3975 (4)	0.2410 (3)	0.2291 (3)	0.0344 (6)
S4	0.44874 (10)	0.30113 (8)	0.36954 (7)	0.03602 (17)
C5	0.2777 (4)	0.4545 (3)	0.4108 (3)	0.0423 (7)
H5A	0.2218	0.4351	0.5023	0.051*
H5B	0.3294	0.5447	0.4024	0.051*
C6	0.1470 (4)	0.4776 (3)	0.3273 (3)	0.0378 (7)
C7	0.1456 (5)	0.6017 (4)	0.2347 (4)	0.0501 (8)
H7A	0.2266	0.6661	0.2259	0.060*
C8	0.0265 (6)	0.6306 (4)	0.1563 (4)	0.0635 (11)
H8A	0.0262	0.7146	0.0965	0.076*
C9	−0.0912 (5)	0.5350 (4)	0.1669 (4)	0.0631 (11)
H9A	−0.1700	0.5533	0.1127	0.076*
C10	−0.0943 (4)	0.4115 (4)	0.2574 (4)	0.0497 (8)
H10A	−0.1753	0.3478	0.2634	0.060*
C11	0.0223 (4)	0.3809 (3)	0.3400 (3)	0.0370 (6)
C12	0.0040 (4)	0.2501 (3)	0.4414 (3)	0.0382 (7)
H12A	−0.1054	0.2169	0.4469	0.046*
H12B	0.0045	0.2812	0.5265	0.046*
C13	0.2340 (5)	0.0954 (4)	0.1402 (3)	0.0434 (7)
H13A	0.1516	0.0316	0.1526	0.052*
C14	0.3192 (5)	0.1420 (4)	0.0135 (3)	0.0530 (9)
H14A	0.2939	0.1088	−0.0595	0.064*
C15	0.4399 (5)	0.2364 (5)	−0.0035 (3)	0.0564 (10)
H15A	0.4953	0.2669	−0.0885	0.068*
C16	0.4815 (5)	0.2877 (4)	0.1032 (3)	0.0483 (8)
H16A	0.5636	0.3518	0.0906	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.03337 (13)	0.03475 (13)	0.02738 (12)	−0.00566 (9)	−0.00776 (8)	−0.00404 (8)
Cl1	0.0515 (5)	0.0503 (4)	0.0394 (4)	−0.0137 (4)	−0.0192 (4)	−0.0062 (3)
Cl2	0.0531 (5)	0.0495 (4)	0.0346 (4)	−0.0177 (4)	−0.0102 (3)	0.0033 (3)
S1	0.0341 (4)	0.0341 (3)	0.0307 (3)	−0.0084 (3)	−0.0069 (3)	−0.0035 (3)
C2	0.0301 (14)	0.0380 (14)	0.0283 (13)	0.0034 (12)	−0.0066 (11)	−0.0060 (11)
C3	0.0327 (15)	0.0390 (15)	0.0293 (13)	0.0003 (12)	−0.0039 (12)	−0.0034 (11)
S4	0.0319 (4)	0.0434 (4)	0.0340 (4)	−0.0104 (3)	−0.0071 (3)	−0.0017 (3)
C5	0.0458 (19)	0.0360 (15)	0.0486 (18)	−0.0084 (14)	−0.0117 (15)	−0.0101 (13)
C6	0.0365 (16)	0.0370 (15)	0.0393 (15)	−0.0033 (13)	−0.0041 (13)	−0.0081 (12)
C7	0.052 (2)	0.0377 (17)	0.059 (2)	−0.0087 (16)	−0.0092 (17)	0.0014 (15)

C8	0.072 (3)	0.050 (2)	0.068 (3)	−0.001 (2)	−0.027 (2)	0.0104 (19)
C9	0.058 (2)	0.059 (2)	0.075 (3)	0.000 (2)	−0.031 (2)	0.007 (2)
C10	0.0361 (17)	0.0513 (19)	0.065 (2)	−0.0034 (15)	−0.0160 (16)	−0.0080 (17)
C11	0.0316 (15)	0.0366 (15)	0.0426 (16)	−0.0010 (12)	−0.0059 (13)	−0.0087 (12)
C12	0.0276 (15)	0.0435 (16)	0.0426 (16)	−0.0077 (13)	0.0001 (13)	−0.0093 (13)
C13	0.0475 (19)	0.0481 (17)	0.0381 (16)	−0.0024 (15)	−0.0134 (14)	−0.0124 (14)
C14	0.060 (2)	0.068 (2)	0.0325 (16)	0.005 (2)	−0.0153 (16)	−0.0127 (16)
C15	0.057 (2)	0.080 (3)	0.0262 (15)	−0.002 (2)	−0.0005 (15)	−0.0045 (16)
C16	0.0433 (19)	0.064 (2)	0.0342 (16)	−0.0081 (17)	−0.0020 (14)	0.0008 (15)

Geometric parameters (Å, º)

Pd1—S4	2.2638 (8)	C7—H7A	0.9300
Pd1—S1	2.2749 (8)	C8—C9	1.367 (6)
Pd1—Cl1	2.3211 (8)	C8—H8A	0.9300
Pd1—Cl2	2.3257 (8)	C9—C10	1.382 (5)
Pd1—Pd1[i]	3.2234 (5)	C9—H9A	0.9300
S1—C2	1.789 (3)	C10—C11	1.396 (5)
S1—C12	1.866 (3)	C10—H10A	0.9300
C2—C13	1.383 (4)	C11—C12	1.499 (4)
C2—C3	1.384 (4)	C12—H12A	0.9700
C3—C16	1.386 (4)	C12—H12B	0.9700
C3—S4	1.782 (3)	C13—C14	1.395 (5)
S4—C5	1.873 (3)	C13—H13A	0.9300
C5—C6	1.495 (5)	C14—C15	1.371 (5)
C5—H5A	0.9700	C14—H14A	0.9300
C5—H5B	0.9700	C15—C16	1.388 (5)
C6—C7	1.400 (4)	C15—H15A	0.9300
C6—C11	1.416 (4)	C16—H16A	0.9300
C7—C8	1.380 (5)		
S4—Pd1—S1	86.69 (3)	C8—C7—H7A	119.3
S4—Pd1—Cl1	88.30 (3)	C6—C7—H7A	119.3
S1—Pd1—Cl1	173.68 (3)	C9—C8—C7	119.7 (3)
S4—Pd1—Cl2	172.50 (3)	C9—C8—H8A	120.2
S1—Pd1—Cl2	90.62 (3)	C7—C8—H8A	120.2
Cl1—Pd1—Cl2	93.88 (3)	C8—C9—C10	120.6 (4)
S4—Pd1—Pd1[i]	97.81 (2)	C8—C9—H9A	119.7
S1—Pd1—Pd1[i]	100.64 (2)	C10—C9—H9A	119.7
Cl1—Pd1—Pd1[i]	83.85 (2)	C9—C10—C11	121.1 (4)
Cl2—Pd1—Pd1[i]	89.56 (2)	C9—C10—H10A	119.5
C2—S1—C12	100.75 (13)	C11—C10—H10A	119.5
C2—S1—Pd1	103.05 (10)	C10—C11—C6	118.6 (3)
C12—S1—Pd1	101.42 (10)	C10—C11—C12	117.9 (3)
C13—C2—C3	121.1 (3)	C6—C11—C12	123.5 (3)
C13—C2—S1	120.4 (2)	C11—C12—S1	115.9 (2)
C3—C2—S1	118.5 (2)	C11—C12—H12A	108.3
C2—C3—C16	120.4 (3)	S1—C12—H12A	108.3

C2—C3—S4	119.5 (2)	C11—C12—H12B	108.3
C16—C3—S4	120.1 (3)	S1—C12—H12B	108.3
C3—S4—C5	102.25 (14)	H12A—C12—H12B	107.4
C3—S4—Pd1	103.28 (10)	C2—C13—C14	118.5 (3)
C5—S4—Pd1	98.12 (11)	C2—C13—H13A	120.8
C6—C5—S4	115.1 (2)	C14—C13—H13A	120.8
C6—C5—H5A	108.5	C15—C14—C13	120.2 (3)
S4—C5—H5A	108.5	C15—C14—H14A	119.9
C6—C5—H5B	108.5	C13—C14—H14A	119.9
S4—C5—H5B	108.5	C14—C15—C16	121.5 (3)
H5A—C5—H5B	107.5	C14—C15—H15A	119.3
C7—C6—C11	118.6 (3)	C16—C15—H15A	119.3
C7—C6—C5	118.6 (3)	C3—C16—C15	118.3 (3)
C11—C6—C5	122.7 (3)	C3—C16—H16A	120.8
C8—C7—C6	121.4 (3)	C15—C16—H16A	120.8
C12—S1—C2—C13	−96.8 (3)	C7—C8—C9—C10	1.4 (7)
Pd1—S1—C2—C13	158.7 (2)	C8—C9—C10—C11	−0.1 (6)
C12—S1—C2—C3	82.9 (2)	C9—C10—C11—C6	−1.4 (5)
Pd1—S1—C2—C3	−21.6 (2)	C9—C10—C11—C12	176.2 (3)
C13—C2—C3—C16	0.3 (5)	C7—C6—C11—C10	1.6 (5)
S1—C2—C3—C16	−179.4 (2)	C5—C6—C11—C10	−179.9 (3)
C13—C2—C3—S4	−178.9 (2)	C7—C6—C11—C12	−175.9 (3)
S1—C2—C3—S4	1.4 (3)	C5—C6—C11—C12	2.7 (5)
C2—C3—S4—C5	−81.8 (3)	C10—C11—C12—S1	109.4 (3)
C16—C3—S4—C5	99.0 (3)	C6—C11—C12—S1	−73.1 (3)
C2—C3—S4—Pd1	19.7 (3)	C2—S1—C12—C11	−10.0 (3)
C16—C3—S4—Pd1	−159.5 (2)	Pd1—S1—C12—C11	95.8 (2)
C3—S4—C5—C6	3.7 (3)	C3—C2—C13—C14	−0.1 (5)
Pd1—S4—C5—C6	−101.9 (2)	S1—C2—C13—C14	179.7 (2)
S4—C5—C6—C7	−108.3 (3)	C2—C13—C14—C15	−0.3 (5)
S4—C5—C6—C11	73.2 (4)	C13—C14—C15—C16	0.3 (6)
C11—C6—C7—C8	−0.3 (5)	C2—C3—C16—C15	−0.3 (5)
C5—C6—C7—C8	−178.9 (3)	S4—C3—C16—C15	178.9 (3)
C6—C7—C8—C9	−1.2 (6)	C14—C15—C16—C3	0.0 (6)

Symmetry code: (i) −x+1, −y, −z+1.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5B···Cl1[ii]	0.97	2.69	3.654 (3)	172
C12—H12A···Cl2[iii]	0.97	2.96	3.678 (3)	132

Symmetry codes: (ii) −x+1, −y+1, −z+1; (iii) −x, −y, −z+1.