

## Bis[*S*-benzyl-3-(4-*n*-octyloxybenzylidene)dithiocarbazato- $\kappa^2N^3,S'$ ]-palladium(II)

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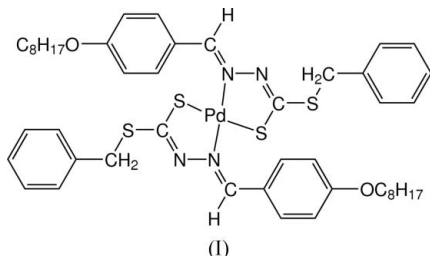
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In the title compound, [Pd(C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>OS<sub>2</sub>)<sub>2</sub>], the Pd<sup>II</sup> atom displays the expected square-planar coordination geometry. However, the *trans* configuration, which allows the Pd<sup>II</sup> atom to be located on a crystallographic inversion centre, is unusual with respect to the *cis* arrangement found in analogous Pd complexes comprising similar *N,S*-chelating ligands.

### Comment

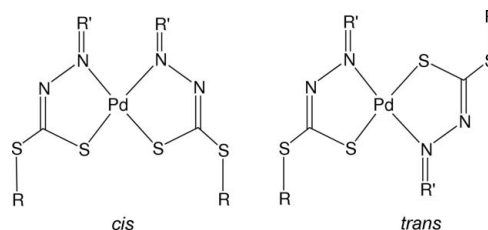
Metal chelates of *S*-alkyl/aryl esters of dithiocarbazate (SBDTC) and their Schiff bases have attracted the interest of researchers for their coordination chemistry and also for their potential use as anticancer compounds (Maurya *et al.*, 2003; How *et al.* 2008; Crouse *et al.*, 2004; Tarafder *et al.*, 2001, 2002; Ali *et al.*, 1992). As a continuation of our interest in *N,S*-donor ligands and their complexes, we have isolated a novel Schiff base of SBDTC, *S*-benzyl-3-[(4-*n*-octyloxyphenyl)methylene]-dithiocarbazate, and its bis-bidentate palladium(II) complex, the title compound, (I).



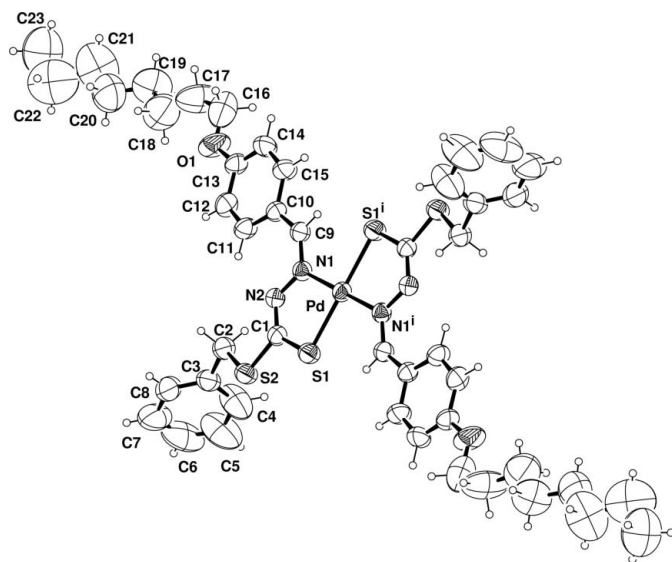
The structure of (I) shows the Pd<sup>II</sup> ion in the expected square-planar donor environment (Fig. 1), with the metal atom on a centre of inversion and the asymmetric unit therefore constituted by half of the molecule. Each of the ligands is coordinated to the metal as a bidentate chelating agent bonding *via* the thiolate S and azomethine N atoms, yielding two five-membered chelate rings. The Pd–N and

Pd–S bond lengths (Table 1) are slightly shorter and longer, respectively, than those observed in Pd complexes containing bis-*N,S*-chelating dithiocarbazate ligands, which fall in the ranges 2.067–2.111 and 2.253–2.268 Å, respectively, as retrieved from the Cambridge Structural Database (CSD, Version 5.31 of November 2009; Allen, 2002). Inside the C–N–N–C group, the bond distances follow the trend found in the other Pd complexes retrieved, indicating that C9–N1 and N2–C1 are double bonds and N1–N2 is a single bond. As described in the *Experimental* section, the octyloxy chain is disordered over two positions, leading to absolute O1–C17–C18–C19 torsion angles of 66.6 (14) and 162.7 (17)° for the two arrangements, corresponding to synclinal and anti-periplanar conformations, respectively. The former is close to that found in the octyloxybenzaldehyde thiosemicarbazone ligand (Islam *et al.*, 2010).

A key interest in bis-*N,S*-bidentate complexes of Ni triad metals is the adoption of *cis versus trans* geometries. A CSD search for the fragment  $M[SC(S)NN]_2$  (where  $M = Ni, Pd$  or  $Pt$ ) indicates that Ni complexes with *N,S*-chelating dithiocarbazate groups adopt either a *cis* (12 entries) or a *trans* geometry (12 entries) with equal probability. By contrast, five out of six Pd complexes have a *cis* configuration, while all five Pt complexes adopt a *trans* arrangement. The unique reported Pd complex with a *trans* geometry is notable in that the *S*-benzylidithiocarbazate ligand has an NH<sub>2</sub> group (Tampouris *et al.* 2007) as the coordinating N atom, rather than an alkyl- or alkylidene-substituted N atom.



Although the Pd and Pt dithiocarbazate complexes are fewer in number, there is a fair indication that these metals prefer a *cis* (Pd) or a *trans* (Pt) geometry, although it should be noted that a broader search of Pd complexes of bis-bidentate ligands with N–C–C–S (nine *cis versus five trans*) or N–N–C–S (10 *cis versus 17 trans*) linkages shows no clear preference. Thus, we can say that (I) represents a rare example of a bis(dithiocarbazato)palladium(II) ion in a *trans*-planar coordination geometry (see scheme above), likely assumed in order to avoid steric clashes between the substituents on the ligand. The (ferrocenyl)ethylidene (Duan *et al.*, 1998) and diazafluorene–dithiocarbazate (Zhou *et al.*, 2007) derivatives, which have bulky groups on the ligand and a *cis* configuration, appear to be stabilized by intramolecular stacking interactions between the cyclopentadienyl planes from different Fe atoms and between the diazafluorene rings, respectively. Since no stacking interaction between phenyl rings is detected in (I), intermolecular packing forces favouring the *trans* geometry appear to be excluded. In the absence of such effects, the stabilization of one configuration over the other may result from the different *trans* influence exerted by the N and S



**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only one conformation of the disordered alkyl chain is shown. [Symmetry code: (i)  $-x, -y + 1, -z$ .]

atoms, induced by the electronic and steric effects of substituent groups on the ligand, which lead to different Pd–N and Pd–S bond energies.

## Experimental

The title compound was prepared by adding a solution of palladium chloride (0.04 g, 0.25 mmol) in methanol (60 ml) to a hot solution of the dithiocarbazate ligand (0.21 g, 0.5 mmol) in ethanol (20 ml). The resulting solution was kept under reflux for 30 min, after which time a brick-red precipitate appeared. The compound was filtered off, washed with hot ethanol, and recrystallized from a mixture of chloroform and ethanol (20:10 v/v) (yield 0.1 g, 40%; m.p. 417 K). In an attempt to grow single crystals, the product was dissolved in a solution of chloroform and toluene (20:5 v/v) and allowed to stand at room temperature. Red microcrystals unsuitable for X-ray study were obtained after 7 d. The compound was then dissolved in a mixture of chloroform and acetone (30:30 v/v) and allowed to stand at room temperature. Very fine flat orange–red crystals of (I) were obtained after 12 d and proved suitable for analysis.

### Crystal data

$[\text{Pd}(\text{C}_{23}\text{H}_{29}\text{N}_2\text{OS}_2)_2]$	$V = 2389.0 (8) \text{ \AA}^3$
$M_r = 933.60$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 16.586 (4) \text{ \AA}$	$\mu = 0.60 \text{ mm}^{-1}$
$b = 14.082 (3) \text{ \AA}$	$T = 293 \text{ K}$
$c = 10.507 (2) \text{ \AA}$	$0.40 \times 0.35 \times 0.12 \text{ mm}$
$\beta = 103.22 (3)^\circ$	

### Data collection

Enraf–Nonius DIP1030 image-plate diffractometer	27894 measured reflections
Absorption correction: part of the refinement model ( $\Delta F$ ) (Parkin <i>et al.</i> , 1995)	4042 independent reflections
$T_{\min} = 0.742, T_{\max} = 0.932$	1977 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.060$

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Pd1–N1	2.034 (3)	N1–N2	1.396 (4)
Pd1–S1	2.2825 (11)	N2–C1	1.287 (4)
N1–C9	1.312 (4)		
N1–Pd1–S1	83.08 (10)		

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	60 restraints
$wR(F^2) = 0.083$	H-atom parameters constrained
$S = 0.77$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
4042 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
277 parameters	

The octyloxy chain proved to be highly disordered. The part of the chain immediately attached to the arene ring (atoms O1 and C16–C18) was split over two conformations, with refined occupancies of 0.568 (8):0.432 (8). Disorder was not modelled for the outer reaches of this chain. Bond-length restraints of 1.50 (2) and 1.40 (2)  $\text{\AA}$  were applied to all C–C and C–O bonds, respectively, within the octyloxy chain. Pseudo-isotropic restraints (Sheldrick, 2008) were applied to the disordered C atoms and to atoms C4, C5 and C6 of the terminal benzyl ring, which also shows some indication of rotational disorder (not modelled). The disordered non-H atoms at lower occupancy were treated isotropically. H atoms were included at calculated positions, with C–H = 0.93 (aromatic), 0.97 (methylene) or 0.96  $\text{\AA}$  (methyl), and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups or  $1.2U_{\text{eq}}(\text{C})$  otherwise.

Data collection: *XPRESS* (MacScience, 2002); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3259). Services for accessing these data are described at the back of the journal.

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