[5-Benzyl-3-phenyl-2-(2-pyridyl-κN)-thiazolidin-4-one-κS]dichloropalladium(II)

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The palladium(II) centre in the title compound, [PdCl$_2$-(C$_{21}$H$_{18}$N$_2$OS)], is coordinated to the pyridyl N atom and to the thiazolidinone S atom of the 5-benzyl-3-phenyl-2-(2-pyridyl)thiazolidin-4-one ligand, resulting in a five-membered chelate ring. Two cis-chloro ligands complete the square-planar coordination environment of the metal. Although the geometry at the Pd centre is essentially planar, the N—Pd—S bite angle of 85.20 (8)° causes deviations in the cis angles from the ideal value of 90°. Opposite enantiomers form one-dimensional chains in the cell via a short S···O intermolecular interaction.

Comment

Thiazolidinones, which have been studied extensively because of their diverse biological activities, can be prepared with a variety of ring substituents in quantitative yields and with high stereoselectivities (de Vries *et al.*, 1997; Tanabe *et al.*, 1995; Singh *et al.*, 1981). Accordingly, thiazolidinone derivatives are good candidates for ligands in transition metal-mediated asymmetric transformations. Pyridyl-substituted thiazolidin-4-ones, in particular, have been used as chiral ligands in the copper(I)-catalyzed asymmetric conjugate addition of diethylzinc to enones (de Vries *et al.*, 1997). However, the hypothetical thiazolidinone metal intermediates were not isolated and the coordination mode(s) of the ligands remained unknown. In fact, few crystallographic studies of transition metal thiazolidin-4-one complexes have been carried out; a search of the Cambridge Structural Database (CSD, Version 5.23 of April 2002; Allen & Kennard, 1993) revealed only eight structures, none involving Pd. Here, we investigate the metal–ligand binding in the title pyridyl-substituted thiazolidin-4-one Pd^{II} complex, (I).

A view of compound (I), showing the coordination geometry at the Pd centre, is presented in Fig. 1, and selected geometric parameters are listed in Table 1. The centrosymmetric space group ($P2_1/c$) requires that both the 1R,2S,5S-(Fig. 1) and 1S,2R,5R-enantiomers are present in the crystal structure.

(I)
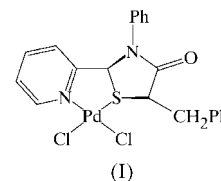
The thiazolidinone ligand is coordinated to the Pd atom in a bidentate fashion, *via* the pyridyl N atom [Pd1—N21 = 2.046 (3) Å] and the thiazolidinone S atom [Pd1—S1 = 2.2605 (9) Å]. Two cis-chloro ligands, at Pd—Cl distances of 2.2883 (10) and 2.3046 (10) Å, complete the somewhat distorted square-planar Pd coordination environment. The cis angles, which sum to 360.0 (1)°, deviate by up to 5° from the ideal value of 90°. All the metal–ligand distances are consistent with literature values for comparable complexes, for example, chloro(2-{6-[2-(methoxycarbonyl)phenylthiomethyl-κS]pyridin-2-yl-κN}-3-oxybenzothiophene-κO)palladium(II) [Pd—N = 2.033 (2) Å, Pd—S = 2.261 (2) Å and Pd—Cl = 2.301 (2) Å; Teixidor *et al.*, 1992].

The bite angle of the *N,S*-bidentate ligand [N21—Pd1—S1 = 85.20 (8)°] is within the range observed for similar systems, including η^3-allyl[2-(phenylthiomethyl-κS)pyridine-κN]palladium(II) perchlorate [N—Pd—S = 84.2 (2)°; Canovese *et al.*, 1998]. The resulting five-membered PdC$_2$NS chelate ring has an envelope conformation, with an S1—C2—C22—N21 torsion angle of 35.3 (4)°. For comparison, the S—C—C—N torsion angle in the related uncoordinated 5-methyl-3-phenyl-2-(2-pyridyl)thiazolidin-4-one molecule, (II), is 88.5 (17)° (Spek *et al.*, 1999). Presumably, coordination of the ligand to the metal forces the pyridyl N atom to bend toward the Pd centre to satisfy the preferred square-planar geometry.

The mean plane of the thiazolidin-4-one ring in (I) is nearly orthogonal to the Pd coordination plane [86.70 (13)°]. The pyridyl and benzyl substituents are positioned on opposite sides of the ring (*trans* relative to one another), directed toward and away from the metal, respectively. The thiazolidinone ring adopts a twisted conformation, and the bond distances and angles within the ring are similar to those observed in (II).

Analysis of the crystal packing in (I) reveals that the two opposite enantiomers are linked into one-dimensional chains by several close contacts along the *c* direction (Table 2). The S1···O41^i [symmetry code: (i) x, $\frac{1}{2} - y$, $\frac{1}{2} + z$] contact of 3.084 (3) Å is considerably shorter than the sum of the van der Waals radii (3.3 Å; Bondi, 1964). Several studies examining similar short contacts between nucleophiles (X) and divalent sulfur (Y—S—Z) have suggested that they arise from electrostatic interactions between S$^{\delta+}$ and $X^{\delta-}$ (Allen *et al.*, 1997; Burling & Goldstein, 1993; Rosenfield *et al.*, 1977). In a metal-coordinated Y—S—Z system, electron donation from S to the

metal-organic compounds

metal cation should enhance this $S^{\delta+} \cdots X^{\delta-}$ interaction. The geometry of the contact observed in (I) is consistent with the directional in-plane approach of $X^{\delta-}$ along the extension of either the Y—S or Z—S bond, which has been reported for Y—S—Z systems (Rosenfield *et al.*, 1977). The carbonyl atom O41^i approaches S1 at a direction of 31.8 (2)° relative to the C2—S1—C5 plane, on the side opposite to the coordinated Pd; the C2—S1$\cdots$O41^i and C5—S1$\cdots$O41^i angles are 66.24 (12) and 140.16 (12)°, respectively.
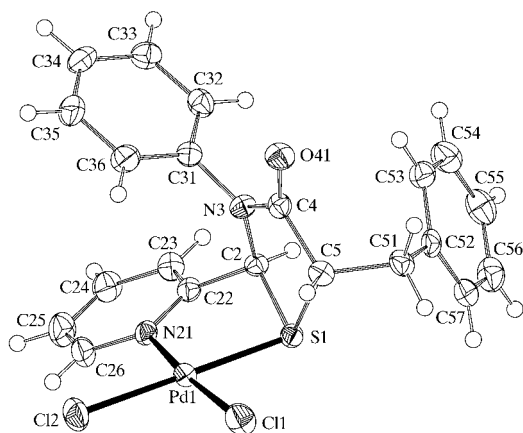

Figure 1
A view of the 1*R*,2*S*,5*S*-enantiomer of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms shown as small spheres of arbitrary radii.

The relatively short C2$\cdots$O41^i and H2$\cdots$O41^i contacts could possibly be considered as soft C—H$\cdots$O hydrogen bonds (Desiraju & Steiner, 1999); however, the small C2—H2$\cdots$O41^i angle of 101° implies that these interactions are fortuitous consequences of the packing determined by $S^{\delta+} \cdots O^{\delta-}$.

Experimental

The title complex was synthesized by the addition of [Pd(CH₃CN)₂- Cl₂] to one equivalent of the 5-benzyl-3-phenyl-2-(2-pyridyl)thia- zolidin-4-one ligand in dichloromethane. Yellow needles of (I) suitable for X-ray analysis were obtained by diffusing hexane into the dichloromethane solution.

Crystal data

[PdCl₂(C₂₁H₁₈N₂OS)]	$D_x = 1.672$ Mg m⁻³
$M_r = 523.73$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 11.1270$ (8) Å	reflections
$b = 15.622$ (1) Å	$\theta = 11.6$–13.9°
$c = 12.470$ (1) Å	$\mu = 1.26$ mm⁻¹
$\beta = 106.28$ (1)°	$T = 198$ (2) K
$V = 2080.8$ (3) Å³	Needle, yellow
$Z = 4$	0.63 × 0.17 × 0.10 mm

Data collection

Enraf–Nonius CAD-4T	$\theta_{max} = 27.5°$
diffractometer	$h = -14 \rightarrow 14$
$\omega/2\theta$ scans	$k = -20 \rightarrow 0$
9970 measured reflections	$l = -16 \rightarrow 16$
4771 independent reflections	3 standard reflections
3403 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.053$	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.039$	$w = 1/[\sigma^2(F_o{}^2) + (0.023P)^2]$
$wR(F^2) = 0.075$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
4771 reflections	$\Delta\rho_{max} = 0.44$ e Å⁻³
253 parameters	$\Delta\rho_{min} = -0.53$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Pd1—N21	2.046 (3)	N3—C2	1.467 (4)
Pd1—S1	2.2605 (9)	N3—C4	1.350 (4)
Pd1—Cl1	2.2883 (10)	C4—C5	1.518 (5)
Pd1—Cl2	2.3046 (10)	S1—C5	1.826 (4)
S1—C2	1.833 (4)	O41—C4	1.217 (4)
N21—Pd1—S1	85.20 (8)	C4—N3—C2	118.2 (3)
S1—Pd1—Cl1	88.70 (4)	N3—C4—C5	113.2 (3)
Cl1—Pd1—Cl2	91.84 (4)	C4—C5—S1	105.5 (2)
N21—Pd1—Cl2	94.26 (8)	O41—C4—N3	124.6 (3)
N21—Pd1—Cl1	173.87 (8)	O41—C4—C5	122.2 (3)
S1—Pd1—Cl2	179.44 (4)	C5—S1—Pd1	104.73 (12)
C5—S1—C2	92.91 (16)	C2—S1—Pd1	95.98 (11)
N3—C2—S1	103.5 (2)		
Pd1—N21—C22—C2	−11.3 (4)	C4—N3—C2—S1	23.6 (4)
S1—C2—C22—N21	35.3 (4)	C2—N3—C4—C5	−9.8 (4)
Pd1—S1—C2—C22	−37.5 (2)	N3—C4—C5—S1	−9.4 (4)
N21—Pd1—S1—C2	25.07 (13)	C2—S1—C5—C4	19.3 (2)
S1—Pd1—N21—C22	−12.3 (2)	C5—S1—C2—N3	−23.6 (2)

Table 2
Intermolecular contact distances (Å).

S1$\cdots$O41^i	3.084 (3)	H2$\cdots$O41^i	2.51
C2$\cdots$O41^i	2.884 (4)		

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

X-ray data were collected using Zr-filtered Mo $K\alpha$ radiation, with a collimator broad enough to accommodate the larger than usual maximum crystal dimension of 0.63 mm (Alexander & Smith, 1962). A correction for absorption was not performed, since 360° ψ scans showed only minor variations in transmission ($T_{min} = 0.822$ and $T_{max} = 0.883$). All H atoms were constrained to idealized geometries and were allowed to ride on their parent C atoms, with C—H distances of 0.95, 0.99 or 1.00 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$. A check for solvent-accessible voids with *PLATON* (Spek, 2002) detected a small void (49 Å³) surrounded by hydrophobic groups at $(\frac{1}{2},0,0)$. However, no residual electron density was found in that region.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF*99 (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *PLATON*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1000). Services for accessing these data are described at the back of the journal.

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