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cis-[1,3-Bis(butylsulfanyl)propane-κ^2S,S']-dichloropalladium(II): *meso* and *rac* forms in the same crystal structure

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.046
wR factor = 0.132
Data-to-parameter ratio = 23.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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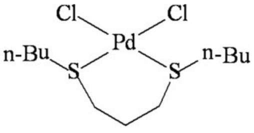
There are two kinds of mononuclear palladium(II) units, *A* (*meso*) and *B* (one enantiomer of a *rac* pair), in the asymmetric unit of the title complex, $[PdCl_2(C_{11}H_{24}S_2)]$. In units *A* and *B*, each central Pd^{II} ion is four-coordinated in a *cis* square-planar geometry and chelated by a 1,3-bis(butylsulfanyl)propane (*L*) molecule to form a six-membered ring. The *L* ligands in the two units adopt *cis* and *trans* configurations, while the S atoms show *R*,*S* and *R*,*R* (*S*,*S*) chirality, respectively.

Comment

Mononuclear (Wang *et al.*, 1992), dinuclear (Errington *et al.*, 1980) and a one-dimensional chain (Xie *et al.*, 2003) structure of some Pd^{II} complexes with dithioether ligands have been characterized by X-ray crystallographic analysis. To gain more insight into the coordination features of analogous complexes, we report here the crystal structure of a new Pd^{II} complex, (I), with the ligand 1,3-bis(butylsulfanyl)propane (*L*).



(I)

As shown in Fig. 1, the asymmetric unit of (I) is composed of two kinds of mononuclear Pd^{II} units (*A* and *B*). Each central Pd^{II} ion is four-coordinated by two S-donor atoms of *L* and two Cl anions in a *cis* square-planar geometry (the sums of the corresponding bond angles are almost 360° in both *A* and *B*). The Pd—S bond lengths are approximately equal [mean value 2.279 (2) Å], as are the Pd—Cl bond lengths [mean value 2.322 (2) Å], and are in the normal ranges (Errington *et al.*, 1980). Although each *L* molecule chelates a Pd^{II} ion by two S-donor atoms and constructs a six-membered ring, the ligands adopt different configurations in units *A* and *B*. In *A*, the six-membered Pd1/S1/S2/C5–C7 chelate ring adopts an envelope form in which atom C6 lies 0.742 (9) Å above the least-squares plane through atoms S1/S2/C5/C7/Pd1. The *L* molecule adopts a *cis* conformation with respect to a pseudo-torsion angle C4—S1···S2—C8 of 0.8 (3)° between the two S—C(butyl) bonds, while the C atoms of both butyl substituents are arranged in an *anti* mode [C1—C2—C3—C4 = −175.6 (8)° and C8—C9—C10—C11 = 168.2 (10)°]. Unit *A* has approximate C_s symmetry, the mirror plane, containing atoms Pd1 and C6, being perpendicular to the least-squares plane. A similar *meso* form can be found in the mononuclear complex *cis*-{*meso*-1,2-bis[alkyl(aryl)sulfinyl]ethane}dichloropalladium(II) (Shao *et al.*, 1989).

Unit *B* has a similar coordination to that of unit *A* but the six-membered chelate ring adopts a chair conformation. The displacements of atoms C17 and Pd2 from the S3/S4/C16/C18 plane are 0.356 (5) and −0.727 (8) Å, respectively. As shown in Fig. 1, ligand *L* in *B* displays a *trans* form, with a corresponding pseudo-torsion angle C15—S3···S4—C19 of −166.6 (3)°, and the substituent butyl groups adopt *gauche* and *anti* modes, respectively [C12—C13—C14—C15 = 71.9 (11)° and C19—C20—C21—C22 = −173.8 (6)°]. Unit *B* does not possess any symmetry. The structure of unit *B* is similar to that observed in the complex $[PdCl_2\{PhS(CH_2)_3SPh\}]$, (II) (Wang *et al.*, 1992), in which the ligand also takes a *trans* form and the Pd^{II} ion adopts a *cis* square-planar geometry. The Pd—S bonds in (I) are slightly shorter than those in (II) [mean 2.284 (3) Å], which can be considered a result of the conjugation of π electrons of the phenyl groups with the empty $d\pi$ orbitals of S atoms in (II) (Cotton & Wilkinson, 1972).

A view of the packing of the molecules in the crystal structure is given in Fig. 2, which also shows the chirality of the S atoms in units *A* and *B*. It is interesting to note that it is rare in analogous complexes that *meso* and racemic units co-exist in the same crystal structure.

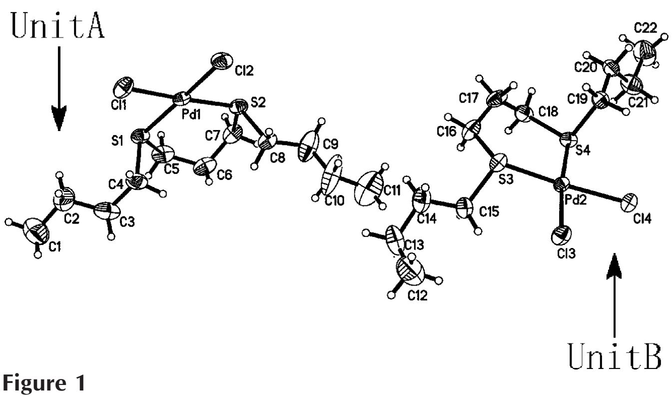


Figure 1
The asymmetric unit of the title complex, (I), with displacement ellipsoids at the 30% probability level.

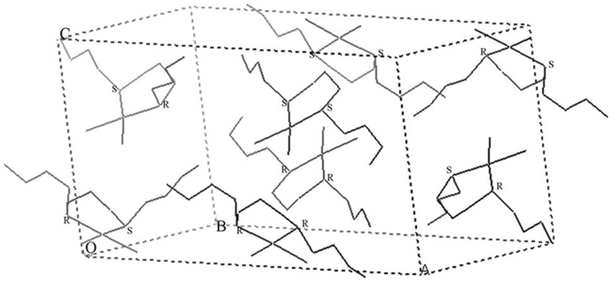


Figure 2
The crystal packing of (I), showing the stacking of the molecules and the chirality of the S atoms. H atoms have been omitted for clarity.

Experimental

The ligand 1,3-bis(butylsulfanyl)propane (*L*) was prepared according to the reported procedure of Shao *et al.* (1984) and the product was characterized by NMR, IR and elemental analyses. A solution containing a 1:1 molar ratio of $PdCl_2$ (0.2 mmol) and *L* (0.2 mmol) in acetonitrile/chloroform (5 ml, 1:1) was stirred for 1 h at room temperature, and then the mixture was filtered. Yellow single crystals suitable for X-ray investigation were obtained from the filtrate by slow evaporation of the solvent. FT–IR (KBr pellet, cm^{-1}): 2956 (*s*), 2929 (*s*), 1465 (*m*), 1418 (*m*), 1170 (*m*), 837 (*w*), 742 (*w*), 472 (*w*). Analysis calculated for the title complex (%): C 33.22, H 6.08%; found: C 33.07, H 6.02%.

Crystal data

$[PdCl_2(C_{11}H_{24}S_2)]$
$M_r = 397.76$
Monoclinic, $P2_1/c$
$a = 23.142\ (12)$ Å
$b = 12.221\ (6)$ Å
$c = 12.031\ (6)$ Å
$\beta = 94.484\ (9)°$
$V = 3392\ (3)$ Å^3
$Z = 8$

$D_x = 1.558$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 991 reflections
$\theta = 2.4$–$26.2°$
$\mu = 1.63$ mm^{-1}
$T = 293\ (2)$ K
Block, yellow
0.20 × 0.18 × 0.14 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.668$, $T_{max} = 0.795$
19 045 measured reflections

6923 independent reflections
3957 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 26.4°$
$h = -28 \rightarrow 28$
$k = -15 \rightarrow 12$
$l = -15 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.132$
$S = 1.08$
6923 reflections
293 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.6086P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—S1	2.2731 (18)	Pd2—S4	2.2776 (17)
Pd1—S2	2.284 (2)	Pd2—S3	2.283 (2)
Pd1—Cl1	2.317 (2)	Pd2—Cl3	2.3229 (17)
Pd1—Cl2	2.3211 (18)	Pd2—Cl4	2.3276 (19)
S1—Pd1—S2	101.01 (7)	S4—Pd2—S3	99.44 (7)
S1—Pd1—Cl1	83.24 (8)	S4—Pd2—Cl3	173.84 (6)
S2—Pd1—Cl1	175.71 (7)	S3—Pd2—Cl3	86.69 (7)
S1—Pd1—Cl2	173.61 (7)	S4—Pd2—Cl4	83.75 (7)
S2—Pd1—Cl2	84.21 (7)	S3—Pd2—Cl4	171.90 (6)
Cl1—Pd1—Cl2	91.51 (7)	Cl3—Pd2—Cl4	90.10 (7)

H atoms were included in calculated positions and treated as riding atoms: C—H = 0.96 Å for CH_3 with $U_{iso}(H) = 1.5U_{eq}(C)$, and C—H = 0.97 Å for CH_2 with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

*ORTEP*II (Johnson, 1976) and *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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