

cis-Dichloro(5,8-dioxa-2,11-dithia-[12]-*o*-cyclophane)palladium(II)

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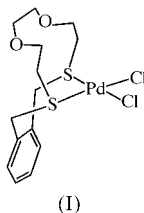
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The preparation and crystal structure of the title compound, *cis*-dichloro[6,9-dioxa-3,12-dithiabicyclo[12.4.0]octadeca-14-,16,18(1)-triene-*S,S'*]palladium(II), [PdCl₂(C₁₄H₂₀O₂S₂)], are described. The Pd atom has a square-planar environment, coordinated to two S atoms of the dithiadioxa macrocycle and to two Cl⁻ ions. The non-coordinating O atoms are oriented away from the metal coordination plane. Upon complexation, a bicyclic chelate structure, which consists of a seven- and an eleven-membered ring, is formed.

Comment

The coordination chemistry of oxathia macrocycles is an intensive area of study and complexes with numerous transition metals are known. As part of our continuing interest in the properties of both cyclic and acyclic oxathia ligands (Jung *et al.*, 1999; Lee *et al.*, 1995; Chung *et al.*, 1997), the preparation and crystal structure of a Pd^{II} complex with an O₂S₂ donor-type macrocycle based on a monobenzo subunit, (I), are described.



The title compound crystallizes in the monoclinic space group *P*2₁/*c*. As shown in Fig. 1, the Pd atom essentially has a square-planar environment and lies above the coordination plane at a perpendicular distance of 0.0882 (4) Å.

The macrocycle adopts a conformation in which two O donors are in *endo* and the two S donors in *exo* orientations (Fig. 1). Therefore, the macrocycle shows a *syn* conformation to facilitate coordination to the Pd atom by two S atoms while

preserving the two *cis*-Pd—Cl bonds. A similar conformation of the donors has been reported for the oxathia macrocycles in the free and complexed form with the Pd^{II} ion (Blake *et al.*, 1995; Lai *et al.*, 1997; Kickham & Loeb, 1994). Otherwise, two O atoms are oriented away from the Pd centre, precluding any Pd—O interaction. In fact, the distance from Pd to the O1 atom is 3.787 (3) Å and to the O2 atom is 4.0008 (27) Å, greater than the sum of the van der Waals radii (3.10 Å; Huheey *et al.*, 1993). Seven- and 11-membered bicyclic rings are formed through Pd—S chelation.

The Pd—S bond lengths are 2.3109 (7) and 2.3069 (7) Å and the Pd—Cl lengths are 2.3161 (8) and 2.3132 (7) Å. These compare well with those (Pd—S 2.301–2.317 Å and Pd—Cl 2.318–2.330 Å) found in the Pd^{II} complex of 2,17-dioxa-5,14-dithia[6,6](1,2)cyclophane (Lai *et al.*, 1997).

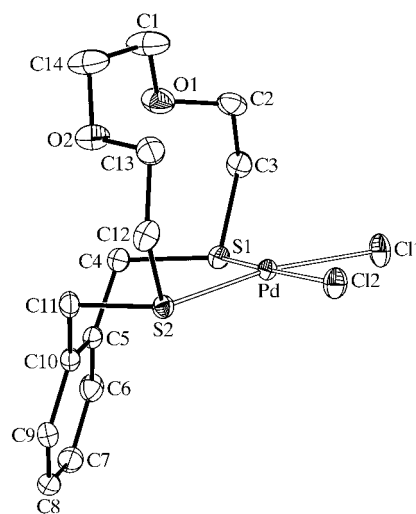


Figure 1

Perspective view of (I) with the atom numbering; displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

It is noted that the S—Pd—S bond angle of 104.46 (3)° is significantly larger than the Cl—Pd—Cl bond angle of 89.58 (3)°. The large difference in the two bond angles is believed to be a result of the conformational steric demand of the bicyclic rings consisting of a seven- and an eleven-membered ring formed by the chelating of Pd^{II} to two S atoms.

Experimental

The macrocycle was prepared in our laboratory by the coupling reaction of α,α' -dibromo-*o*-xylene and the corresponding dithiol under high dilution conditions and the synthetic details will be reported elsewhere. The title compound was prepared by the reaction of equimolar amounts of the macrocycle and [PdCl₂(PhCN)₂] in benzene. The yellow precipitate that formed immediately was filtered off and recrystallized from acetonitrile by slow evaporation to give orange single crystals suitable for X-ray analysis (decomposition 505–507 K).

Crystal data

[PdCl₂(C₁₄H₂₀O₂S₂)]
M_r = 461.72
 Monoclinic, *P*2₁/*c*
a = 8.1698 (4) Å
b = 14.3745 (7) Å
c = 14.9238 (8) Å
 β = 99.6490 (10)°
V = 1727.81 (15) Å³
Z = 4

D_x = 1.775 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 10 792 reflections
 θ = 1.98–28.28°
 μ = 1.625 mm⁻¹
T = 298 (2) K
 Plate, orange
 0.40 × 0.30 × 0.08 mm

Data collection

Siemens SMART CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.476, *T_{max}* = 0.878
 10 792 measured reflections

4119 independent reflections
 3758 reflections with *I* > 2σ(*I*)
R_{int} = 0.032
 θ_{\max} = 28.28°
h = -9 → 10
k = -19 → 15
l = -19 → 19

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.032
wR (*F*²) = 0.082
S = 1.050
 4119 reflections
 190 parameters
 H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 1.9613P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.94 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.87 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Pd—S2	2.3069 (7)	Pd—Cl2	2.3132 (7)
Pd—S1	2.3109 (7)	Pd—Cl1	2.3161 (8)
S2—Pd—S1	104.46 (3)	S2—Pd—Cl1	169.74 (3)
S2—Pd—Cl2	82.87 (3)	S1—Pd—Cl1	82.88 (3)
S1—Pd—Cl2	172.35 (3)	Cl2—Pd—Cl1	89.58 (3)
C2—C3—S1—Pd	38.8 (3)	C10—C11—S2—Pd	-63.4 (3)
C5—C4—S1—Pd	68.9 (2)	C13—C12—S2—Pd	-45.5 (3)

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SHELXTL (Siemens, 1996); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1097). Services for accessing these data are described at the back of the journal.

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