

***trans*-Dichloro(1,12-diphenyl-5,8-dioxa-2,11-dithiadodecane-*S,S'*)-palladium(II)**Ki-Min Park,^a Il Yoon,^{a,b} Byeong Soon Yoo,^c Jin Beom Choi,^d Shim Sung Lee^{a,b,*} and Bong Gon Kim^c^aResearch Institute of Natural Sciences, Gyeongsang National University, Chinju 660-701, South Korea, ^bDepartment of Chemistry, Gyeongsang National University, Chinju 660-701, South Korea, ^cDepartment of Chemistry Education, Gyeongsang National University, Chinju 660-701, South Korea, and ^dDepartment of Earth and Environmental Sciences, Gyeongsang National University, Chinju 660-701, South Korea

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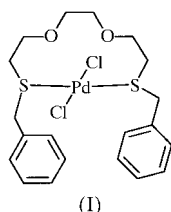
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In the title compound, [PdCl₂(C₂₀H₂₆O₂S₂)], the Pd atom has a distorted square-planar coordination geometry, with Pd–S distances of 2.3121 (18) and 2.3102 (18) Å, Pd–Cl distances of 2.291 (2) and 2.314 (2) Å, and S–Pd–Cl angles of 94.98 (7) and 86.25 (7)°. Upon complexation, an 11-membered ring is formed by the S–Pd–S linkage in the ligand chain.

Comment

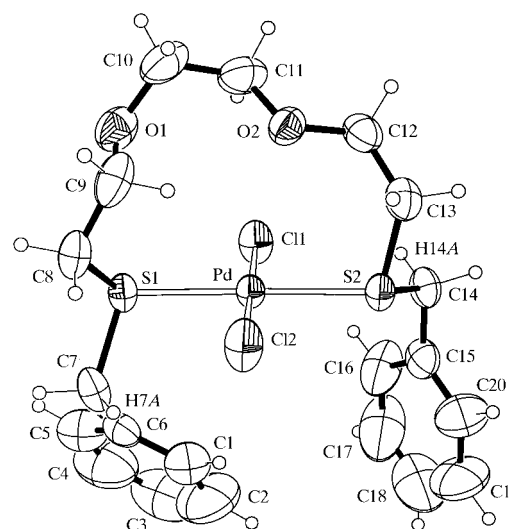
Ligands with mixed O/S donor sets have attracted much interest, especially in recent years (Cameron *et al.*, 1997; Casabó *et al.*, 1995; Grant *et al.*, 1998). According to our preliminary results, the acyclic S₂O₂ donor-type ligand in the title compound shows superior performance as a silver(I) ionophore to its cyclic analog compounds in the areas of solvent extraction, membrane transport and ion-selective electrodes (Lee *et al.*, 2000).

As part of our continuing interest in the complexation properties of cyclic and acyclic oxathia mixed-donor ligands with thiophilic metal ions (Chung *et al.*, 1997; Jung *et al.*, 1999; Yoon *et al.*, 2000), the preparation and crystal structure of the Pd^{II} complex, (I), of an acyclic S₂O₂ donor-type ligand are presented here.



As shown in Fig. 1, the Pd atom is in a *trans*-type square-planar arrangement coordinated by two S atoms of the di-

thiadioxo chelate and two Cl[−] ions. On the other hand, the Pd···O2 distance [3.084 (5) Å] is significantly shorter than that of Pd···O1 [3.750 (6) Å] and is slightly less than the sum of the van der Waals radii (3.10 Å; Huheey *et al.*, 1993) of the atoms concerned. Assuming distorted pseudo-square-pyramidal geometry, the basal square plane consisting of atoms Pd, Cl1, Cl2, S1 and S2 rotates approximately 18° around the S1–Pd–S2 axis, maintaining the Pd–S bond distance. In addition, there are intramolecular interactions between Cl and H atoms attached to C7 and C14 [Cl1···H14A (2.75 Å) and Cl2···H7A (2.94 Å)]. The interactions mentioned above may be related to the asymmetric conformation of the chelate ring, although the chemical diagram suggests that the chelate ring has a chemical twofold axis passing through the midpoint of the O1–C10–C11–O2 bond and the Pd atom.

**Figure 1**

Perspective view of (I) with displacement ellipsoids at the 50% probability level.

The molecular structures of a number of palladium(II) complexes with *trans*-dichloro and sulfur ligands have been determined (Flower & Griffiths, 1978; Clark *et al.*, 1991; Parvez *et al.*, 1995), but, to our knowledge, all of the sulfur ligands in these complexes were monodentate.

A comparison of bond lengths and angles around the Pd atom in the title compound with the corresponding data of other *trans*-dichlorobis(*L*)Pd^{II} complexes, where the ligands (*L*) are monodentate sulfur ligands, such as thiomorpholine-3-one (Flower & Griffiths, 1978), 2,3-dihydrobenzo[*b*]thiophene (Clark *et al.*, 1991), 2,3-dihydromethylbenzo[*b*]thiophene (Clark *et al.*, 1993) and 7-thiabicyclo[2.2.1]heptane (Parvez *et al.*, 1995), reveals that there are no significant differences in the dimensions around the square-planar Pd atom. The dimensions of Pd–S, Pd–Cl and S–Pd–Cl in the above listed *trans*-dichlorobis(*L*)Pd^{II} complexes are in the ranges 2.293–2.330 (3), 2.283–2.309 (3) Å and 84.1–95.9 (1)°, respectively.

Experimental

The ligand used in this work was synthesized in this laboratory and the synthetic procedure will be described elsewhere. The title compound was prepared by the reaction of equimolar amounts of the ligand and $[\text{PdCl}_2(\text{PhCN})_2]$ in benzene. The yellow precipitate that formed immediately was filtered off and recrystallized from acetonitrile by slow evaporation to give orange single crystals (decomposition 411–413 K).

Crystal data

$[\text{PdCl}_2(\text{C}_{20}\text{H}_{26}\text{O}_2\text{S}_2)]$	$D_x = 1.573 \text{ Mg m}^{-3}$
$M_r = 539.83$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 13914 reflections
$a = 22.155 (2) \text{ \AA}$	$\theta = 0.94\text{--}28.31^\circ$
$b = 7.7440 (8) \text{ \AA}$	$\mu = 1.244 \text{ mm}^{-1}$
$c = 13.6293 (15) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 102.906 (2)^\circ$	Plate, orange
$V = 2279.2 (4) \text{ \AA}^3$	$0.4 \times 0.3 \times 0.1 \text{ mm}$
$Z = 4$	

Data collection

Bruker CCD area-detector diffractometer	5520 independent reflections
φ and ω scans	3499 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.073$
$T_{\text{min}} = 0.601$, $T_{\text{max}} = 0.928$	$\theta_{\text{max}} = 28.31^\circ$
13914 measured reflections	$h = -29 \rightarrow 28$
	$k = -10 \rightarrow 9$
	$l = -17 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0863P)^2 + 8.8015P]$
$R[F^2 > 2\sigma(F^2)] = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.20$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.061$	$\Delta\rho_{\text{max}} = 1.46 \text{ e \AA}^{-3}$
5520 reflections	$\Delta\rho_{\text{min}} = -1.40 \text{ e \AA}^{-3}$
244 parameters	
H-atom parameters constrained	

Table 1

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

Pd—Cl1	2.291 (2)	Pd—S1	2.3121 (18)
Pd—S2	2.3102 (18)	Pd—Cl2	2.314 (2)
Cl1—Pd—S2	94.98 (7)	S2—Pd—Cl2	85.40 (7)
Cl1—Pd—S1	86.25 (7)	S1—Pd—Cl2	93.39 (7)
S1—C8—C9—O1	55.6 (8)	O2—C12—C13—S2	80.6 (8)
O1—C10—C11—O2	-71.7 (11)		

H atoms were added at calculated positions (C—H 0.97 \AA) and refined using a riding model. H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they were attached. Since the large positive (1.46 e \AA^{-3}) and negative (-1.40 e \AA^{-3}) difference Fourier peaks are located at short distances from Pd (1.06 and 0.88 \AA , respectively), these peaks can be attributed to ghosts of the heavy Pd atom.

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: OB1036). Services for accessing these data are described at the back of the journal.

References

- Cameron, B. R., Loeb, S. J. & Yap, G. P. A. (1997). *Inorg. Chem.* **36**, 5498–5504.
- Casabó, J., Teixidor, F., Escriche, L., Vinas, C. & Pérez-Jiménez, C. (1995). *Adv. Mater.* **7**, 238–247.
- Chung, S., Kim, W., Park, S. B., Yoon, I., Lee, S. S. & Sung, D. D. (1997). *Chem. Commun.* pp. 965–966.
- Clark, P. D., Fait, J. F., Jones, C. G. & Kirk, M. J. (1991). *Can. J. Chem.* **69**, 590–598.
- Clark, P. D., Kirk, M. J. & Parvez, M. (1993). *Can. J. Chem.* **71**, 199–205.
- Flower, J. M. & Griffiths, A. (1978). *Acta Cryst.* **B34**, 1711–1712.
- Grant, G. J., Galas, D. F., Jones, M. W., Loveday, K. D., Pennington, W. T., Schimek, G. L., Eagle, C. T. & Vanderveer, D. G. (1998). *Inorg. Chem.* **37**, 5299–5305.
- Huheey, J. E., Keiter, E. A. & Keiter, R. E. (1993). *Inorganic Chemistry: Principles of Structures and Reactivity*, 4th ed., p. 292. New York: Harper Collins.
- Jung, J. H., Yoon, I., Park, K. J., Lee, S. S., Choi, K. S. & Park, S. B. (1999). *Microchem. J.* **63**, 100–108.
- Lee, B. L., Lee, Y. H., Jung, J. H., Park, K.-M. & Lee, S. S. (2000). *Microchem. J.* In the press.
- Parvez, M., Primak, A. & Clark, P. D. (1995). *Acta Cryst.* **C51**, 1099–1102.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Siemens (1996). *SMART*, *SAINTE* (Version 4.0) and *SHELXTL* (Version 5.03). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Yoon, I., Yoo, B. S., Lee, S. S. & Kim, B. G. (2000). *Acta Cryst.* **C56**, 758–759.