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Chloro(diethyl dithiophosphato-*S*,*S*′)(triphenylphosphine-*P*)palladium(II)

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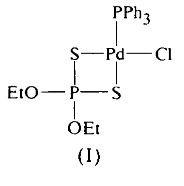
Abstract

The structure of the title compound, [PdCl($C_4H_{10}O_2PS_2$)($C_{18}H_{15}P$)], is reported. There are two independent molecules in the asymmetric unit. The coordination around the Pd atom in each molecule is distorted square planar. Both molecules have nearly the same conformation, except for the orientation of the ethyl groups on the dithiophosphate ligand. Bond lengths and angles are typical of related Pd and Pt complexes.

Comment

The chemistry of palladium(II) and platinum(II) with dithio ligands, such as xanthate, dithiocarbamate and dithiophosphates, is well developed. However, the chemistry of these metals in the +1 oxidation state with these ligands has not received much attention. Thus, in order to obtain palladium(I) complexes, we explored the redox reaction involving palladium(0) and palladium(II) complexes. In all these reactions, however, only palladium(II) complexes were found. The crystal structure of the title compound, (I), has been determined and is presented here.



(I)

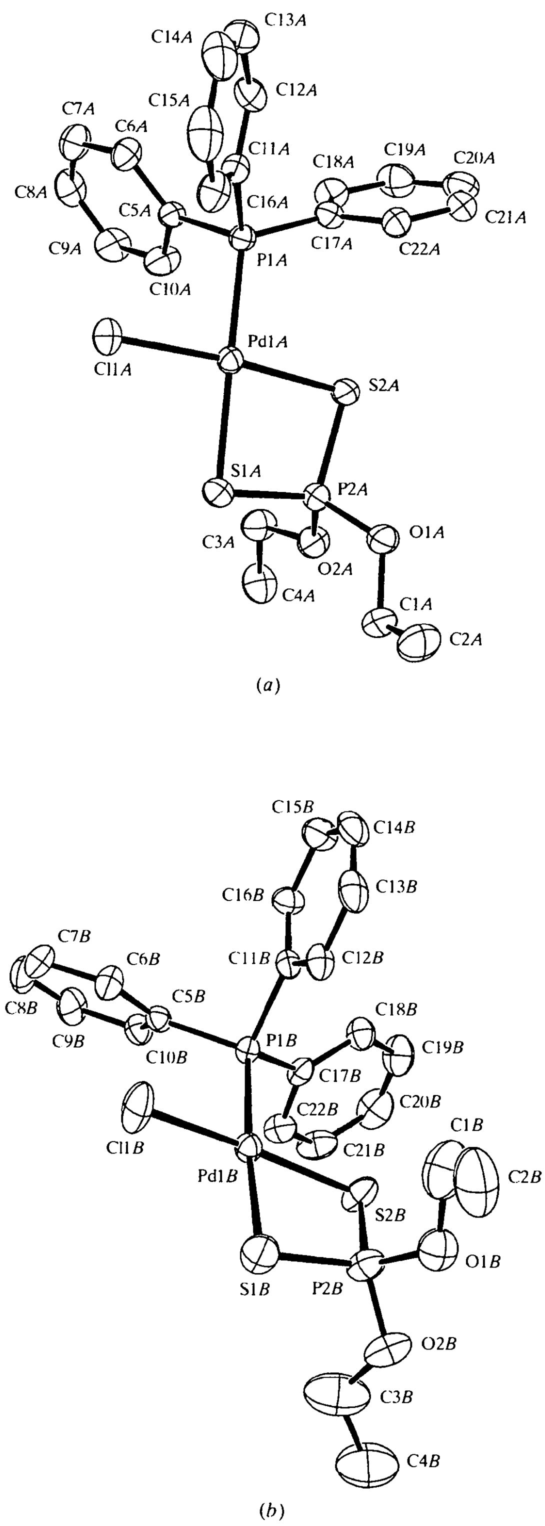


Fig. 1. The structure of (*a*) molecule *A* and (*b*) molecule *B*, showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity.

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There are two independent molecules of (I) in the asymmetric unit. The coordination around the Pd atom in each molecule is distorted square planar. Atoms Pd1*A* and Pd1*B* deviate by 0.041 and 0.071 Å from their coordination planes, defined by P1*A*, Cl1*A*, S1*A*, S2*A* and Pd1*A*, and P1*B*, Cl1*B*, S1*B*, S2*B* and Pd1*B*, respectively. Both molecules have nearly the same conformation, except for the orientation of the ethyl groups (Table 1). The dithiophosphate moiety is asymmetrically chelated, as reported for $[Pd(S_2PPh_2)(S_2PPh_2)(PPh_3)]$ (Fackler *et al.*, 1982), $[PtMe\{S_2P(O^iPr)_2\}(AsPh_3)]$ (Jain *et al.*, 1994) and $[Pt\{S_2P(OEt)_2\}\{Ph_2AsCH_2CH_2P(S)Ph_2\}]$ (Colton *et al.*, 1988). However, in the case of $[Pd(SMe)(S_2CNMe_2)(PEt_3)]$ (Reger & Collins, 1995), the dithiocarbamate ligand is symmetrically chelated. The two Pd—S bond distances are within the normal Pd—S range of 2.2–2.5 Å (Reger & Collins, 1995; Fackler *et al.*, 1982). The Pd—P bond length is normal and is less than the radius sum. The P—S bond lengths indicate partial double-bond character. Although the S—Pd—S and S—P—S angles in the two molecules are similar, other angles around the Pd atom are significantly different. The Pd—P—C angles, ranging from 108.7 (2) to 117.2 (2)°, have an average value of 113.4 (2)°, which is larger than the ideal value of 109.5°, while all the C—P—C bond angles, ranging from 102.9 (3) to 107.1 (3)°, are smaller than the ideal tetrahedral angle. The deviation from normal tetrahedral angles has been observed previously in free and coordinated phosphine ligands of this type and is explained on the basis of valence-shell electron-pair repulsion (VSEPR) energy (Houlton *et al.*, 1990).

Experimental

The title compound was prepared using the method of Cornock & Stephenson (1977), and yellow crystals suitable for X-ray crystallography were obtained by evaporation from a solution in acetone–hexane (m.p. 393 K). Analysis found: C 45.0, H 4.2%; calculated: C 44.9, H 4.3%; ^1H NMR ($CDCl_3$, δ, p.p.m.): 1.35 (*t*, 6 Hz, 6H, OCH_2Me), 4.06–4.24 (*m*, 4H, OCH_2), 7.41–7.51 (*m*, 15H, Ph); $^{31}P\{^1H\}$ ($CDCl_3$, δ, p.p.m.): 30.22 (*s*, PPh_3), 100.78 [*s*, $S_2P(OEt)_2$].

Crystal data

$[PdCl(C_4H_{10}O_2PS_2)(C_{18}H_{15}P)]$
$M_r = 589.36$
Monoclinic
$P2_1/a$
$a = 18.178 (3)$ Å
$b = 9.233 (4)$ Å
$c = 30.904 (7)$ Å
$\beta = 101.30 (1)°$
$V = 5086 (3)$ Å^3
$Z = 8$
$D_x = 1.539$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.7–18.5°$
$\mu = 1.141$ mm^{-1}
$T = 293 (2)$ K
Pillar
0.44 × 0.25 × 0.19 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.552$, $T_{max} = 0.809$
8923 measured reflections
8923 independent reflections

6826 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 36$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.217$
$S = 1.070$
8923 reflections
541 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1660P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.007$
$\Delta\rho_{max} = 0.765$ e Å^{-3}
$\Delta\rho_{min} = -0.819$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pd1*A*—P1*A*	2.265 (2)	Pd1*B*—P1*B*	2.279 (2)
Pd1*A*—Cl1*A*	2.306 (2)	Pd1*B*—Cl1*B*	2.304 (2)
Pd1*A*—S2*A*	2.308 (2)	Pd1*B*—S2*B*	2.311 (2)
Pd1*A*—S1*A*	2.391 (2)	Pd1*B*—S1*B*	2.364 (2)
S1*A*—P2*A*	1.985 (3)	S1*B*—P2*B*	1.979 (3)
S2*A*—P2*A*	2.002 (2)	S2*B*—P2*B*	2.009 (3)
P2*A*—O1*A*	1.567 (5)	P2*B*—O2*B*	1.562 (6)
P2*A*—O2*A*	1.568 (5)	P2*B*—O1*B*	1.557 (7)
O1*A*—C1*A*	1.470 (9)	O1*B*—C1*B*	1.49 (2)
O2*A*—C3*A*	1.474 (9)	O2*B*—C3*B*	1.43 (2)
P1*A*—Pd1*A*—Cl1*A*	89.24 (7)	P1*B*—Pd1*B*—Cl1*B*	94.69 (8)
P1*A*—Pd1*A*—S2*A*	94.79 (6)	P1*B*—Pd1*B*—S2*B*	92.60 (6)
Cl1*A*—Pd1*A*—S2*A*	175.37 (7)	Cl1*B*—Pd1*B*—S2*B*	171.61 (8)
P1*A*—Pd1*A*—S1*A*	177.91 (7)	P1*B*—Pd1*B*—S1*B*	175.53 (8)
Cl1*A*—Pd1*A*—S1*A*	91.75 (7)	Cl1*B*—Pd1*B*—S1*B*	88.46 (9)
S2*A*—Pd1*A*—S1*A*	84.15 (6)	S2*B*—Pd1*B*—S1*B*	84.04 (8)
P2*A*—S1*A*—Pd1*A*	84.65 (8)	P2*B*—S1*B*—Pd1*B*	84.88 (9)
P2*A*—S2*A*—Pd1*A*	86.51 (8)	P2*B*—S2*B*—Pd1*B*	85.66 (9)
O1*A*—P2*A*—O2*A*	101.0 (3)	O2*B*—P2*B*—O1*B*	97.3 (4)
O1*A*—P2*A*—S1*A*	115.0 (2)	O2*B*—P2*B*—S1*B*	114.1 (3)
O2*A*—P2*A*—S1*A*	113.9 (2)	O1*B*—P2*B*—S1*B*	114.2 (3)
O1*A*—P2*A*—S2*A*	108.2 (2)	O2*B*—P2*B*—S2*B*	114.1 (3)
O2*A*—P2*A*—S2*A*	114.6 (2)	O1*B*—P2*B*—S2*B*	114.2 (3)
S1*A*—P2*A*—S2*A*	104.37 (11)	S1*B*—P2*B*—S2*B*	103.42 (13)
S1*A*—P2*A*—O1*A*—C1*A*	67.7 (6)	S1*B*—P2*B*—O1*B*—C1*B*	−59.0 (8)
S1*A*—P2*A*—O2*A*—C3*A*	52.6 (6)	S1*B*—P2*B*—O2*B*—C3*B*	52.0 (10)
S2*A*—P2*A*—O1*A*—C1*A*	−176.1 (6)	S2*B*—P2*B*—O1*B*—C1*B*	59.8 (8)
S2*A*—P2*A*—O2*A*—C3*A*	−67.5 (6)	S2*B*—P2*B*—O2*B*—C3*B*	−66.6 (10)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1097). Services for accessing these data are described at the back of the journal.

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trans-Diaqua(*C*-*meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N)-nickel(II) dichloride

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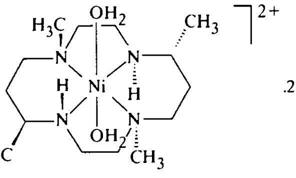
Abstract

The crystal structure of the title compound, $[Ni(C_{14}H_{32}N_4)(H_2O)_2]Cl_2$, has been determined by X-ray diffraction. The Ni^{II} ion lies on an inversion center and is six-coordinate in a distorted octahedral geometry, with the four N atoms of the macrocyclic ligand equatorial and the two water molecules axial. The tetradentate macrocyclic ligand adopts a configuration having two six-membered rings in a chair form and two five-membered rings in a *gauche* form.

Comment

The nickel(II) complex of *C*-*meso*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane, as with other tetraaza ligands, exists in equilibrium as a mixture of blue (paramagnetic, octahedral) and yellow (diamagnetic, square-planar) forms (Anichini *et al.*, 1977). Miyamura *et al.* (1987) reported the crystal structure of the square-planar species. In the present study, we report the isolation and X-ray structure of the *trans*-diaqua form, (I).



(I)

The title complex is octahedral around the metal center. An inversion center exists on the Ni^{II} ion. Two water molecules coordinate axially to the central Ni^{II} ion. The Ni^{II} ion and the four ligand N atoms are exactly coplanar. The ligand skeleton of the title complex takes the most stable *trans*-III conformation designated by Bosnich *et al.* (1965), with the two six-membered rings in a chair form and the two five-membered rings in a *gauche* form. The Ni1—N2 distance [2.069 (3) Å] is essentially equivalent to those found in *trans*-[Ni(1,4,8,11-tetraazacyclotetradecane)X_2] [2.067 (2) Å for X = Cl (Ito *et al.*, 1984), and 2.050 (5) and 2.060 (6) Å for X = NO_3 (Boeyens & Hancock, 1984)] and *trans*-[Ni(1,4,8,11-tetraazacyclotetradecane)-(OH_2)]Cl_2 [2.072 (2) Å; Mochizuki & Kondo, 1995]. The Ni1—N1 distance of 2.113 (3) Å is considerably longer than Ni1—N2, and this value is similar to those in *cis*-(nitrato-*O*,*O*′)(*C*-*rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)-Ni^{II}(NO_3) [2.134 (2) Å; Panneerselvam *et al.*, 1999].

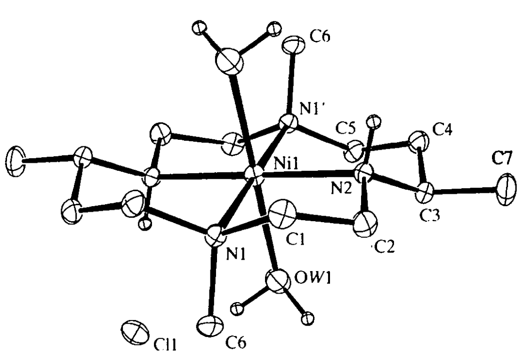


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms are shown only on the amine N atoms and the water ligands.

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