Bis(O-ethyl dithiocarbonato-κ^2S,S')-palladium(II)

Irene Ara,[a]***** **Fatima El Bahij,**[a]**†** **Mohamed Lachkar**[b] **and Najib Ben Larbi**[b]

[a]Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza CSIC, 50009 Zaragoza, Spain, and [b]Département de Chimie, Faculté des Sciences Dhar-Mehraz, Université Sidi Mohamed Ben Abdellah, BP 1796 (Atlas), 30000 Fes, Morocco

Correspondence e-mail: irene.ara@posta.unizar.es

The Pd atom in the title compound, $[Pd(C_3H_5OS_2)_2]$, lies on an inversion center and adopts a square-planar coordination geometry defined by the four S atoms of the two dithiocarbonate (xanthate) ligands. In the solid state, the molecules aggregate into layers in which the rows of molecules alternate their orientation to allow each Pd atom to interact with two symmetry-equivalent S atoms of the xanthate ligands of adjacent molecules, generating a pseudo-octahedral environment around each Pd atom. This weak interaction of 3.3579 (7) Å can be classified as a closed-shell electrostatic intermolecular interaction.

Comment

Xanthate ligands can act as monodentate, bidentate or bridging ligands to two or even three metal centers, which leads to a variety of complexes. Although the structural features of these ligands have been extensively studied, one feature that is not very well represented in the literature is their involvement in intermolecular interactions. Such interactions are the basis for crystal engineering, their nature and strength determining their competitive importance in forming different crystal packings (Desiraju, 1995). The S atom is a weak donor atom but can interact with acceptors to help define the crystal packing of the molecules (Xue et al., 2003). In metal xanthates, the intermolecular distances are long enough in most cases to preclude any kind of interaction (Eisenberg, 1970); in other cases, the intermolecular distances have not been explored. In the title complex, (I), the intermolecular interactions are not negligible and contribute to the shaping of the supramolecular array. Although (I) was first synthesized in 1945 (Bulmer & Mann, 1945) and its structure is known to be square planar, as are the structures of $[Ni(S_2COEt)_2]$ or $[Pt(S_2COEt)_2]$ (Watt &

† On leave from the Université Sidi Mohamed Ben Abdellah, BP 1796 (Atlas), 30000 Fes, Morocco.

McCormick, 1965), a description of the crystal packing of (I) has not been reported to date.

(I)
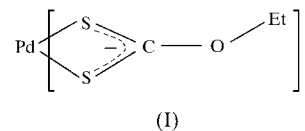
In (I), the Pd atom, which is located at a center of inversion, is coordinated by two equivalent xanthate groups, each group behaving as a bidentate ligand through two S atoms (Fig. 1). The two Pd—S distances are not significantly different, and the S—C, C—O and O—C distances have the usual lengths (Table 1). The S1···S2 bite distance is 2.8542 (11) Å, which is somewhat longer than the distances found in other related complexes of group 10 metals, which range from 2.81 to 2.84 Å (Chen & Fackler, 1978; Chan et al., 1982). Considerable strain within the four-membered 1,1-dithiolate chelate is evidenced by a significant deviation from ideal square-planar coordination, the bite angle of the xanthate group being 75.47 (3)°. All non-H atoms of the molecule of (I) are coplanar (the mean deviation from the plane is 0.01 Å).

The supramolecular structure of (I) consists of a two-dimensional array of molecules (Fig 2). In each layer, rows of molecules alternate their orientations and lie at an angle of 72.77 (2)° to each other. This configuration allows each Pd atom to interact with two equivalent S1 atoms of neighboring
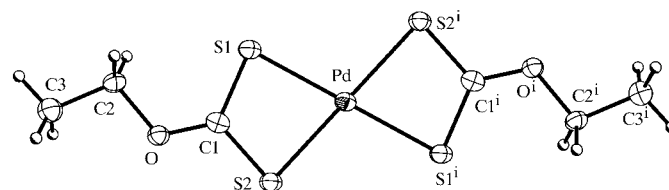

Figure 1
The structure of (I), showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1 - x$, $-y$, $1 - z$.]
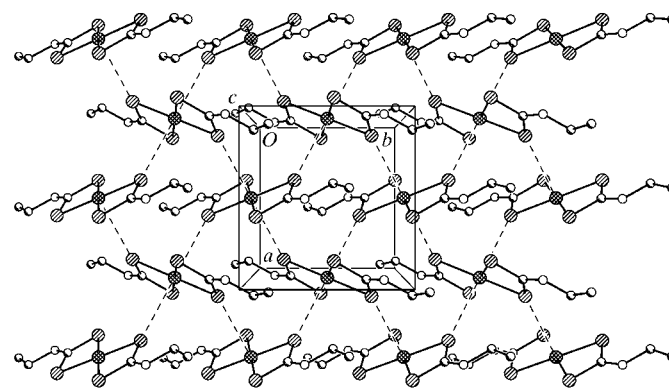

Figure 2
Packing diagram of (I), viewed along the c axis, showing the intermolecular Pd···S interactions (dashed lines).

metal-organic compounds

centrosymmetrically related molecules, thereby giving an $S1^{ii} \cdots Pd \cdots S^{iii}$ angle of 180° [symmetry codes: (ii) $\frac{1}{2} - x$, $y - \frac{1}{2}$, z; (iii) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$]. The $Pd \cdots S1^{ii}$ distance of 3.3579 (7) Å is considerably shorter than the sum of the van der Waals radii (3.8 Å; Whuler *et al.*, 1980) of these atoms. Considering these $Pd \cdots S$ contacts, the Pd atom lies in a pseudo-octahedral coordination environment, with a tetragonal distortion of four short and two long $Pd \cdots S$ distances. The $S1 - Pd \cdots S1^{iii}$ and $S2 - Pd \cdots S1^{iii}$ angles are 87.92 (1) and 78.72 (2)°, respectively. These intermolecular contacts can be classified as closed-shell electrostatic interactions rather than donor–acceptor interactions, because the distance is closer to the limit of the van der Waals contacts than to true $Pd - S$ bond lengths and there is no significant distortion of the geometry of the formal complex (Bertolasi *et al.*, 2001). The structure of (I) is comparable to that of the arylxanthate derivative, $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ (Chen & Fackler, 1978). In these two structures, the geometric parameters around the Pd atoms are very similar, but in the latter, the PdS_4 groups form a plane perpendicular to the plane of the phenyl ring. This conformation precludes any intermolecular interactions, the nearest $Pd \cdots S$ distance being 5.834 Å.

Experimental

Compound (I) (yield 82%, m.p. 424 K) was prepared according to the procedure of Bulmer & Mann (1945), using $[Zn(S_2COEt)_2]$ and $[PdCl_2(C_4H_8S)_2]$ as starting materials. Analysis found: C 20.43, H 2.75, S 36.30%; calculated: C 20.67, H 2.87, S 36.71%. Single crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the complex at room temperature.

Crystal data

$[Pd(C_3H_5OS_2)_2]$
$M_r = 348.78$
Orthorhombic, *Pbca*
$a = 7.4958$ (6) Å
$b = 7.1942$ (6) Å
$c = 20.7522$ (18) Å
$V = 1119.09$ (16) Å^3
$Z = 4$
$D_x = 2.070$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 2030 reflections
$\theta = 3.9-27.6°$
$\mu = 2.37$ mm^{-1}
$T = 100$ (2) K
Plate, orange
$0.36 \times 0.20 \times 0.12$ mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.483$, $T_{max} = 0.764$
6401 measured reflections

1324 independent reflections
992 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 28.3°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 7$
$l = -27 \rightarrow 24$

Table 1
Selected geometric parameters (Å, °).

Pd—S1	2.3271 (8)	O—C1	1.304 (3)
Pd—S2	2.3363 (8)	O—C2	1.463 (3)
S1—C1	1.693 (3)	C2—C3	1.496 (4)
S2—C1	1.700 (3)		
S1^i—Pd—S1	180	C1—S2—Pd	84.78 (10)
S1—Pd—S2	75.47 (3)	C1—O—C2	117.6 (2)
C1—S1—Pd	85.24 (11)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.057$
$S = 0.92$
1324 reflections
61 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *XCIF* in *SHELXTL*.

References

Bertolasi, V., Gilli, P., Ferretti, V. & Gilli, G. (2001). *New J. Chem.* **25**, 408–415.
Bruker (1999). *SAINT-Plus*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SMART* (Version 5.611) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Bulmer, G. & Mann, F. G. (1945). *J. Chem. Soc.* pp. 666–674.
Chan, L. T., Chen, H. W., Fackler, J. P. Jr, Masters, A. F. & Pan, W. H. (1982). *Inorg. Chem.* **21**, 4291–4295.
Chen, H. W. & Fackler, J. P. Jr (1978). *Inorg. Chem.* **17**, 22–26.
Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.
Eisenberg, R. (1970). *Prog. Inorg. Chem.* **12**, 295–369.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Watt, C. W. & McCormick, B. J. (1965). *J. Inorg. Nucl. Chem.* **27**, 898–900.
Whuler, A., Brouty, C. & Spinat, P. (1980). *Acta Cryst.* B36, 1267–1269.
Xue, G., Xu, W., Yu, W.-T. & Fang, Q. (2003). *Acta Cryst.* C59, m27–m29.