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A Palladium–Dithiooxamide Complex

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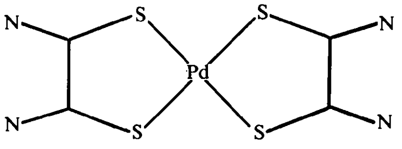
Abstract

Single crystals of bis[dithiooxamido(1−)-*S*,*S*′]-palladium 0.5-methanol solvate 0.5-hydrate, $[\mathrm{Pd}(\mathrm{C_2H_3N_2S_2})_2].0.5\mathrm{CH_3OH}.0.5\mathrm{H_2O}$, are obtained from a methanolic solution of $\mathrm{K_2PdCl_6}$ and dithiooxamide. This complex crystallizes in the monoclinic system (space group $I2/a$). The structure can be described as an array of neutral centrosymmetric $\mathrm{Pd}(L\mathrm{H_3})_2$ molecules (where $L\mathrm{H_3} = \mathrm{C_2H_3N_2S_2}$). Each Pd atom has a near perfect square-planar environment of S atoms. The unsubstituted dithiooxamide molecules are planar and show a *cis* conformation which is observed for the first time in a crystal structure. The methanol molecule is disordered.

Comment

The unsubstituted dithiooxamide ligand $(\mathrm{NH_2})\mathrm{SCCS}(\mathrm{NH_2})$, abbreviated to $L\mathrm{H_4}$, forms metallic complexes with almost all *d*-block transition metals and also with some metals from the *p* block, like Sb, Pb or Bi. However, because of the extremely low solubility of these complexes, it is very difficult to obtain suitable single crystals. A small number of crystallographic studies proved the ligand to be in a *trans* conformation (Mosset, Abboudi & Galy, 1983; Belicchi, Ferrari, Pellizzi & Tarasconi, 1985), but many spectroscopic studies indicate the possibility of a *cis* conformation, particularly with Pd (Hofmans, Desseyn, Aarts & Herman, 1982; Bellaihou, Weyten & Desseyn, 1990).

The structure of the title compound consists of an array of two independent $\mathrm{Pd}(L\mathrm{H_3})_2$ neutral molecules, situated on a centre of symmetry, and solvent molecules (one molecule of water and a disordered molecule of methanol). Around each Pd atom there exists a near perfect square plane involving four S atoms from two ligands, with a mean Pd—S bond length of 2.267 Å (Fig. 1). This characteristic proves that $\mathrm{Pd^{IV}}$ has been reduced to $\mathrm{Pd^{II}}$. Indeed, all complexes in the IV oxidation state which have been studied are octahedral with the low-spin t_{2g}^6 configuration (Greenwood & Earnshaw, 1986). This reduction is not very surprising as $\mathrm{Pd^{IV}}$ complexes are rather sparse and much less stable than those of $\mathrm{Pd^{II}}$.



$\mathrm{Pd}(L\mathrm{H_3})_2$

Perpendicular to this coordination plane, the apical positions are occupied by two other S atoms; they are situated at distances of 3.61 (1) Å for Pd(1) and 3.67 (1) Å for Pd(2). These distances are extremely long and much greater than the sum of the contact radii. However, these very weak interactions lead to a stacking along [010], at distances shorter than the *b* parameter (Fig. 2). The $\mathrm{Pd}(L\mathrm{H_3})_2$ molecules are also held together through hydrogen bonding between O atoms from solvent molecules and amino groups (Table 3).

The most important feature in this structure is the *cis* conformation of the ligand. This is the first time that this conformation, predicted from IR studies, is observed in a crystal structure for the unsubstituted ligand. Thus, the ligand is *S*,*S*′ coordinated to the metal atoms. This situation has already been encountered in Pd complexes with dibenzyl- and dicyclohexyldithiooxamide (Antolini, Fabretti, Franchini, Menabue & Pellacani, 1987). In these three Pd complexes, bond lengths are within the same expected ranges: 2.26–2.30 Å for Pd—S, 1.66–1.74 Å for C—S and 1.28–1.32 Å for C—N. Compared to the free ligand (Wheatley, 1965), the lengthening of the C—S and the shortening of the C—N bonds appear negligible. Torsion angles for S atoms (S—C—C—S) are roughly equal to zero [2 (4) and 4 (4)° in this work, compared to 0.8 and 2.7° for the other Pd complexes]. The dithiooxamide molecules are probably strictly planar, the torsion angles N—C—C—N being equal to 3 (4)°.

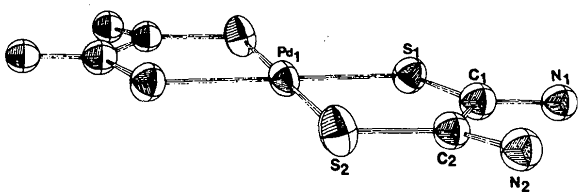


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of a Pd(LH_3)$_2$ molecule.

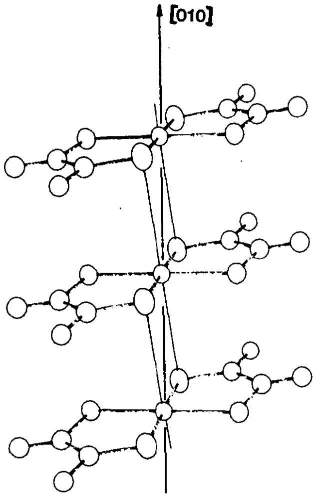


Fig. 2. Stacking along the [010] axis.

Experimental

A methanolic solution (10^{-2} *M*) of dithiooxamide was added, at room temperature with stirring, to a methanolic solution (10^{-2} *M*) of K_2PdCl_6 (molar ratio Pd/LH_4 = 0.5). The precipitation was instantaneous but not complete. The precipitate was filtered off and the solution allowed to crystallize at ambient temperature. Orange needles formed after one week.

Crystal data

$[Pd(C_2H_3N_2S_2)_2]$.-
0.5CH_3OH.0.5H_2O
$M_r = 369.8$
Monoclinic
$I2/a$
$a = 23.39$ (3) Å
$b = 3.9832$ (9) Å
$c = 23.80$ (3) Å
$\beta = 90.46$ (1)°
$V = 2217$ (4) Å^3
$Z = 8$
$D_x = 2.13$ (2) Mg m^{-3}
$D_m = 2.16$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7$-$17°$
$\mu = 2.35$ mm^{-1}
$T = 293$ K
Needle
0.6 × 0.1 × 0.1 mm
Orange

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1764 measured reflections
1265 independent reflections
563 observed reflections [$F_o > 3\sigma(F_o)$]

$R_{int} = 0.0266$
$\theta_{max} = 22°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 4$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity variation: 5%

Refinement

Refinement on *F*
$R = 0.0694$
$wR = 0.0684$
$S = 2.78$
563 reflections
88 parameters
H atoms not located
$w = 2.5388/[\sigma^2(F) + 0.000867F^2]$

$(\Delta/\sigma)_{max} = 0.066$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -1.19$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

For Pd and S, $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$; U_{iso} for other atoms.

	x	y	z	U_{iso}/U_{eq}
Pd(1)	0	0	0	0.042 (3)
Pd(2)	1/4	3/4	3/4	0.044 (3)
S(1)	−0.0967 (3)	0.005 (3)	−0.0040 (3)	0.047 (5)
S(2)	−0.0048 (4)	−0.252 (3)	0.0854 (4)	0.056 (6)
S(3)	0.1622 (4)	0.512 (3)	0.2432 (4)	0.058 (6)
S(4)	0.2549 (4)	0.768 (3)	0.1548 (3)	0.050 (6)
N(1)	−0.170 (1)	−0.265 (3)	0.065 (1)	0.048 (7)
N(2)	−0.095 (1)	−0.504 (4)	0.137 (1)	0.068 (8)
N(3)	0.111 (1)	0.268 (3)	0.153 (1)	0.068 (9)
N(4)	0.183 (1)	0.504 (4)	0.080 (1)	0.054 (7)
C(1)	−0.118 (1)	−0.191 (4)	0.055 (1)	0.044 (9)
C(2)	−0.074 (2)	−0.316 (3)	0.096 (2)	0.06 (1)
C(3)	0.153 (2)	0.438 (3)	0.175 (1)	0.06 (1)
C(4)	0.195 (2)	0.565 (4)	0.132 (1)	0.05 (1)
O*W*†	3/4	0.110 (7)	0	0.06 (1)
O*M*	−0.500 (2)	−0.23 (1)	−0.289 (2)	0.05 (1)
C*M*	0.036 (3)	−0.97 (1)	0.252 (3)	0.06 (2)

† O*W* denotes the water O atom, O*M* and C*M* denote the methanolic O and C atoms, respectively.

Table 2. *Selected geometric parameters* (Å, °)

Pd(1)—S(1)	2.263 (8)	C(1)—N(1)	1.28 (4)
Pd(1)—S(2)	2.270 (9)	C(2)—N(2)	1.31 (5)
Pd(2)—S(3)	2.267 (10)	S(3)—C(3)	1.67 (3)
Pd(2)—S(4)	2.270 (8)	S(4)—C(4)	1.70 (3)
S(1)—C(1)	1.67 (3)	C(3)—C(4)	1.51 (5)
S(2)—C(2)	1.66 (4)	C(3)—N(3)	1.29 (5)
C(1)—C(2)	1.51 (5)	C(4)—N(4)	1.28 (4)
N(1)···O*W*	2.84 (3)	N(3)···O*M*	2.95 (5)
N(2)···O*M*	2.96 (5)	N(4)···O*W*	2.92 (3)
S(1)—Pd(1)—S(2)	89.2 (3)	N(2)—C(2)—S(2)	125.3 (2.1)
S(3)—Pd(2)—S(4)	89.8 (3)	S(3)—C(3)—C(4)	121.2 (2.2)
S(1)—C(1)—C(2)	119.8 (2.1)	S(4)—C(4)—C(3)	118.8 (2.6)
S(2)—C(2)—C(1)	125.3 (2.9)	N(3)—C(3)—C(4)	113.7 (1.9)
N(1)—C(1)—C(2)	116.2 (2.4)	N(4)—C(4)—C(3)	116.0 (2.5)
N(2)—C(2)—C(1)	114.1 (2.0)	N(3)—C(3)—S(3)	125.1 (2.0)
N(1)—C(1)—S(1)	123.8 (2.1)	N(4)—C(4)—S(4)	125.2 (2.0)

Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976). Program used to prepare material for publication: *PLATON*92 (Spek, 1992). The methanol molecule is disordered.

Lists of structure factors and anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Benzenethiolato-κS)triphenyltin(IV), [Sn(C$_6$H$_5$S)(C$_6$H$_5$)$_3$] (I), and Bis(benzenethiolato-κS)diphenyltin(IV), [Sn(C$_6$H$_5$S)$_2$(C$_6$H$_5$)$_2$] (II)

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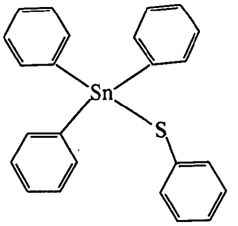
Abstract

The structures of the title compounds, [(Ph)$_3$Sn(SPh)] (I) and [(Ph)$_2$Sn(SPh)$_2$] (II), where Ph = C$_6$H$_5$, have been determined by single-crystal X-ray diffraction experiments. In both, the Sn atom has a coordination number of four. The first compound presents a quite regular tetrahedral geometry about the Sn atom, while in the second a greater distortion from the ideal angle of 109.5° is observed. The atomic distances and angles in the phenyl rings are in good agreement with those of a regular hexagon, larger distortions being observed in the second compound.

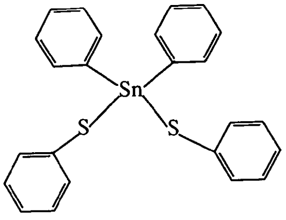
Comment

Crystallographic studies of compounds of the R_xSn(SPh)$_y$ family form part of our research. These compounds are fragments of heterobimetallic complexes, since their reactions with Nb compounds result in Nb—Sn bonds. Heterobimetallic complexes, especially those containing sulfur, are of considerable interest because of their applications in several catalytic processes (Müller, Watkins & Dahl, 1976; Kwart, Schuit & Gates, 1980). Understanding the structural differences between the Sn ligands can be useful in the study of the properties of these complexes.

The two related structures [(Ph)$_3$Sn(SPh)] (I) and [(Ph)$_2$Sn(SPh)$_2$] (II) have been determined by single-crystal X-ray diffraction. Similar structures containing Sn—C and Sn—S bonds have been reported elsewhere (Chieh & Trotter, 1970; Clarke, Cradwick & Wardell, 1973).



(I)



(II)

The Sn—C bond lengths obtained in the present work are all in good agreement with one another. The mean values, 2.138 (3) in (I) and 2.127 (2) Å in (II), are comparable to 2.144 (14) Å in [(Ph)$_4$Sn] (Chieh & Trotter, 1970) and 2.126 Å in [(Ph)$_3$Sn(SC$_6$H$_4$-p-^{t}Bu)] (Clarke *et al.*, 1973). The Sn—S and S—C bond lengths in compounds (I) and (II) also agree with those obtained by Clarke *et al.* (1973) [2.413(3) and 1.784 (9) Å, respectively].

All phenyl rings were refined without any constraints. Values of distances and angles in the rings show no significant differences from those of a perfect hexagon.

Substitution of Ph groups by SPh groups in the structure causes a greater distortion from regular tetrahedral geometry about the Sn atom. This can be seen by comparing the values of angles around Sn in compound (II) [from 102.4 (2) to 119.3 (2)°], in compound (I) [from 106.4 (1) to 112.4 (1)°] and in [(Ph)$_4$Sn] [from 108.8 (4) to 110.8 (9)° (Chieh & Trotter, 1970)]. We also observe that the introduction of SPh groups leads to structures of lower symmetry, since the crystal systems are tetragonal for [(Ph)$_4$Sn] (Chieh & Trotter, 1970), monoclinic for [(Ph)$_3$Sn(SPh)] and triclinic for [(Ph)$_2$Sn(SPh)$_2$].