

We thank BP Research International for a studentship (DJI).

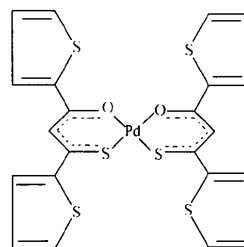
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Pd—S distances are 2.014 (14) and 2.231 (5) Å, respectively. Although the mean *cis* angles around Pd deviate markedly from 90°, its environment is almost exactly planar. In each independent molecule one of the four thiophene rings is disordered by rotation about its bond to the chelate ring. The result is that while three of the thiophene rings are always *endo*, the fourth is *exo* in 50% of the molecules. In neither conformation are there any significant intermolecular Pd··S contacts.

## Comment

We recently reported the analogous 1:2 Pd<sup>II</sup> and Cu<sup>II</sup> complexes of the related ligand 3-hydroxy-1,3-bis(2-thienyl)prop-2-enone: in the Cu complex the orientation of one of the thiophene rings was determined by a specific pattern of Cu··S intermolecular contacts (Baxter, Blake, Gould, Heath & Stephenson, 1993). To our knowledge only three Pd<sup>II</sup> complexes with mixed O,S donor chelates have been structurally characterized: bis(monothiodibenzoyl methane) palladium (Shkol'nikova, Yutal, Shugam & Knyazeva, 1973) and bis(2,2,6,6-tetramethylhept-4-ene-5-thiol-3-onato) palladium (Pope & Boeyens, 1976) occur as *cis* isomers while bis(1,1-diethyl-3-benzoylthioureato) palladium (Fitzl, Beyer, Sieler, Richter, Kaiser & Hoyer, 1977) is the only known example of the *trans* form.



(I)

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## *cis*-Bis[3-sulfido-1,3-bis(2-thienyl)prop-2-enone-O,S]palladium(II)

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## Abstract

Bis[3-sulfido-1,3-bis(2-thienyl)prop-2-enone-O,S]-palladium(II), [Pd(C<sub>11</sub>H<sub>7</sub>OS<sub>3</sub>)<sub>2</sub>], exists as the *cis* isomer with the O donor atom of one ligand opposite the S donor atom of the other. The mean Pd—O and

For the present compound, (I), the crystal studied was composed exclusively of the *cis* form, with two very similar independent molecules in the asymmetric unit. The mean Pd—O and Pd—S distances are 2.014 (14) and 2.231 (5) Å, respectively; the average *cis* angles are 81.5 (3)° for O—Pd—O, 86.7 (1)° for S—Pd—S and 95.9 (2)° for O—Pd—S, the last of these corresponding to the bite angle of the chelate ligand. Although these angles around Pd differ appreciably from 90°, their sum (360.0°) indicates near-planarity. Bond lengths and angles have values close to those found for the other two *cis* complexes. In each independent molecule one of the four thiophene rings is disordered by rotation about its bond to the chelate ring, with the result that while three thiophene rings are always *endo*, the fourth is *exo* in 50% of the molecules. In neither their *endo* or *exo* conformation do the S atoms of the thiophene rings participate in any close Pd··S intermolecular contacts.

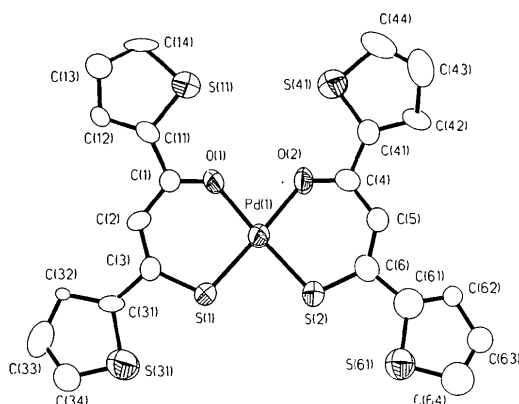


Fig. 1. One of the independent molecules in the asymmetric unit showing the labelling of the non-H atoms. Only one orientation [C(61)—C(64)] of the disordered thiophene ring is shown; the other [C(71)—C(74)] may be generated by rotating the ring *circa* 180° about the C(61)—C(6) bond. Displacement ellipsoids are shown at the 30% probability level.

## Experimental

The title complex was prepared by the reaction of the protonated ligand with K<sub>2</sub>PdCl<sub>4</sub> in CHCl<sub>3</sub>. The crystals were grown from CHCl<sub>3</sub>.

### Crystal data

[Pd(C<sub>11</sub>H<sub>7</sub>OS<sub>3</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 609.09

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 20.596 (8) Å

*b* = 10.622 (5) Å

*c* = 21.523 (9) Å

β = 99.35 (3)°

*V* = 4646 (3) Å<sup>3</sup>

*Z* = 8

*D<sub>x</sub>* = 1.742 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 30 reflections

θ = 15–16°

μ = 1.357 mm<sup>-1</sup>

*T* = 293 (2) K

Column

0.50 × 0.20 × 0.10 mm

Reddish brown

### Data collection

Stoe Stadi-4 four-circle diffractometer

ω–2θ scans

Absorption correction: none

6055 measured reflections

6055 independent reflections

2521 observed reflections

[*I* > 2σ(*I*)]

θ<sub>max</sub> = 22.49°

*h* = –22 → 21

*k* = 0 → 11

*l* = 0 → 23

3 standard reflections

frequency: 120 min

intensity variation: 2%

### Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.0603

*wR*(*F*<sup>2</sup>) = 0.1167

*S* = 1.140

(Δ/σ)<sub>max</sub> = 0.68

Δρ<sub>max</sub> = 0.91 e Å<sup>-3</sup>

Δρ<sub>min</sub> = –0.55 e Å<sup>-3</sup>

Extinction correction: none

6052 reflections

489 parameters

H-atom parameters not refined

Calculated weights

$$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Pd1	0.65563 (5)	0.09040 (10)	0.33234 (4)	0.0476 (3)
S1	0.6871 (2)	0.2159 (3)	0.4152 (2)	0.0631 (11)
S2	0.5814 (2)	0.0092 (3)	0.3860 (2)	0.0592 (10)
O1	0.7204 (4)	0.1563 (8)	0.2807 (3)	0.056 (2)
O2	0.6294 (4)	–0.0144 (8)	0.2537 (3)	0.055 (2)
C1	0.7655 (6)	0.2366 (11)	0.2931 (5)	0.037 (3)
C2	0.7789 (5)	0.3148 (11)	0.3472 (5)	0.040 (3)
C3	0.7488 (5)	0.3147 (10)	0.3996 (5)	0.039 (3)
C4	0.5920 (6)	–0.1102 (12)	0.2447 (5)	0.040 (3)
C5	0.5487 (5)	–0.1536 (11)	0.2837 (5)	0.043 (3)
C6	0.5384 (5)	–0.1070 (11)	0.3417 (5)	0.044 (3)
C11	0.8093 (5)	0.2502 (11)	0.2453 (4)	0.044 (3)
S11	0.7926 (2)	0.1518 (4)	0.1813 (2)	0.0782 (12)
C12	0.8616 (5)	0.3336 (10)	0.2400 (5)	0.040 (3)
C13	0.8856 (6)	0.3074 (12)	0.1842 (6)	0.063 (4)
C14	0.8531 (6)	0.2171 (14)	0.1488 (5)	0.081 (5)
C31	0.7708 (5)	0.4086 (10)	0.4490 (4)	0.036 (3)
S31	0.7373 (2)	0.4107 (4)	0.5167 (2)	0.0990 (15)
C32	0.8191 (4)	0.5069 (8)	0.4481 (4)	0.021 (2)
C33	0.8202 (6)	0.5761 (11)	0.5049 (6)	0.085 (5)
C34	0.7809 (6)	0.5377 (11)	0.5434 (5)	0.063 (4)
C41	0.5948 (5)	–0.1796 (10)	0.1860 (5)	0.041 (3)
S41	0.6473 (2)	–0.1283 (4)	0.1383 (2)	0.0800 (13)
C42	0.5605 (5)	–0.2894 (11)	0.1639 (5)	0.048 (4)
C43	0.5801 (6)	–0.3248 (11)	0.1056 (6)	0.084 (5)
C44	0.6253 (2)	–0.2485 (4)	0.0873 (2)	0.081 (5)
C61†	0.4865 (2)	–0.1752 (4)	0.3728 (2)	0.076 (25)
S61†	0.4892 (2)	–0.1554 (4)	0.4525 (2)	0.075 (3)
C62†	0.4352 (2)	–0.2503 (4)	0.3473 (2)	0.035 (9)
C63†	0.3980 (2)	–0.2913 (4)	0.3939 (2)	0.056 (30)
C64†	0.4214 (2)	–0.2486 (4)	0.4517 (2)	0.091 (20)
C71†	0.4885 (2)	–0.1644 (4)	0.3746 (2)	0.036 (16)
S71†	0.4268 (2)	–0.2512 (4)	0.3310 (2)	0.079 (3)
C72†	0.4851 (2)	–0.1662 (4)	0.4367 (2)	0.029 (8)
C73†	0.4301 (2)	–0.2412 (4)	0.4492 (2)	0.052 (14)
C74†	0.3954 (2)	–0.2903 (4)	0.3980 (2)	0.109 (37)
Pd1′	0.17606 (5)	0.34962 (10)	0.19442 (5)	0.0461 (3)
S1′	0.2581 (2)	0.2870 (3)	0.1461 (2)	0.0608 (11)
S2′	0.1481 (2)	0.4782 (3)	0.11262 (15)	0.0552 (10)
O1′	0.1967 (4)	0.2298 (8)	0.2684 (3)	0.053 (2)
O2′	0.1035 (4)	0.4029 (8)	0.2407 (3)	0.053 (2)
C1′	0.2954 (5)	0.1556 (11)	0.1832 (6)	0.046 (3)
C2′	0.2811 (6)	0.1038 (11)	0.2383 (5)	0.043 (3)
C3′	0.2384 (6)	0.1395 (11)	0.2779 (6)	0.040 (3)
C4′	0.0576 (6)	0.4825 (11)	0.2285 (6)	0.041 (3)
C5′	0.0444 (6)	0.5525 (10)	0.1705 (6)	0.043 (3)
C6′	0.0771 (6)	0.5515 (10)	0.1204 (5)	0.039 (3)
C11′	0.3466 (5)	0.1060 (11)	0.1496 (5)	0.059 (4)
S11′	0.4009 (2)	–0.0057 (4)	0.1862 (2)	0.102 (2)
C12′	0.3590 (5)	0.1388 (9)	0.0885 (4)	0.028 (3)
C13′	0.4120 (7)	0.0637 (13)	0.0755 (6)	0.079 (5)
C14′	0.4374 (6)	–0.0139 (13)	0.1209 (6)	0.085 (5)
C31′	0.2399 (6)	0.0770 (11)	0.3397 (5)	0.054 (4)
S31′	0.1876 (2)	0.1309 (4)	0.3881 (2)	0.0790 (13)
C32′	0.2795 (6)	–0.0201 (11)	0.3666 (6)	0.056 (4)
C33′	0.2670 (7)	–0.0443 (13)	0.4268 (7)	0.085 (5)
C34′	0.2191 (8)	0.0254 (13)	0.4451 (5)	0.090 (6)
C41′	0.0163 (5)	0.5055 (10)	0.2765 (4)	0.040 (3)
S41′	0.0306 (2)	0.4097 (4)	0.34231 (15)	0.0645 (11)
C42′	–0.0329 (5)	0.5935 (10)	0.2793 (4)	0.038 (3)

C43'	-0.0564 (5)	0.5772 (10)	0.3381 (5)	0.053 (4)
C44'	-0.0280 (2)	0.4831 (4)	0.3736 (2)	0.058 (4)
C61'†	0.0455 (2)	0.6421 (4)	0.0682 (2)	0.089 (15)
S61'†	0.0971 (2)	0.6876 (4)	0.0169 (2)	0.060 (3)
C62'†	-0.0189 (2)	0.6660 (4)	0.0444 (2)	0.028 (7)
C63'†	-0.0256 (2)	0.7219 (4)	-0.0166 (2)	0.078 (17)
C64'†	0.0320 (2)	0.7394 (4)	-0.0366 (2)	0.077 (11)
C71'†	0.0512 (2)	0.6252 (4)	0.0626 (2)	0.005 (6)
S71'†	-0.0328 (2)	0.6410 (4)	0.0432 (2)	0.061 (3)
C72'†	0.0829 (2)	0.7045 (4)	0.0197 (2)	0.109 (17)
C73'†	0.0386 (2)	0.7642 (4)	-0.0209 (2)	0.052 (8)
C74'†	-0.0246 (2)	0.7430 (4)	-0.0165 (2)	0.051 (14)

† Site occupancy = 0.5.

Table 2. Selected geometric parameters (Å, °)

Pd1—O1	1.997 (8)	Pd1'—O1'	2.028 (8)
Pd1—O2	2.024 (8)	Pd1'—O2'	2.008 (8)
Pd1—S1	2.237 (4)	Pd1'—S1'	2.225 (4)
Pd1—S2	2.233 (4)	Pd1'—S2'	2.229 (3)
S1—C3	1.724 (11)	S1'—C1'	1.726 (12)
S2—C6	1.716 (12)	S2'—C6'	1.689 (12)
O1—C1	1.257 (12)	O1'—C3'	1.283 (12)
O2—C4	1.273 (13)	O2'—C4'	1.263 (12)
C1—C2	1.420 (14)	C1'—C2'	1.382 (14)
C1—C11	1.483 (14)	C1'—C11'	1.469 (14)
C2—C3	1.372 (13)	C2'—C3'	1.374 (14)
C3—C31	1.475 (13)	C3'—C31'	1.483 (15)
C4—C5	1.398 (14)	C4'—C5'	1.440 (15)
C4—C41	1.472 (14)	C4'—C41'	1.462 (14)
C5—C6	1.391 (14)	C5'—C6'	1.360 (14)
C6—C71	1.470 (12)	C6'—C71'	1.494 (11)
C6—C61	1.531 (12)	C6'—C61'	1.541 (12)
O1—Pd1—O2	80.7 (3)	O2'—Pd1'—O1'	82.2 (3)
O1—Pd1—S2	176.9 (2)	O2'—Pd1'—S1'	178.0 (3)
O2—Pd1—S2	96.2 (2)	O1'—Pd1'—S1'	95.8 (3)
O1—Pd1—S1	95.9 (2)	O2'—Pd1'—S2'	95.8 (2)
O2—Pd1—S1	176.2 (3)	O1'—Pd1'—S2'	177.1 (3)
S2—Pd1—S1	87.22 (13)	S1'—Pd1'—S2'	86.13 (13)
C3—S1—Pd1	109.5 (4)	C1'—S1'—Pd1'	109.9 (5)
C6—S2—Pd1	109.0 (4)	C6'—S2'—Pd1'	108.7 (4)
C1—O1—Pd1	131.0 (7)	C3'—O1'—Pd1'	130.0 (8)
C4—O2—Pd1	129.8 (7)	C4'—O2'—Pd1'	132.6 (8)
O1—C1—C2	127.7 (11)	C2'—C1'—C11'	123.3 (11)
O1—C1—C11	115.5 (10)	C2'—C1'—S1'	125.3 (10)
C2—C1—C11	116.9 (10)	C11'—C1'—S1'	111.3 (9)
C3—C2—C1	128.2 (11)	C3'—C2'—C1'	132.0 (12)
C2—C3—C31	117.7 (10)	O1'—C3'—C2'	126.1 (12)
C2—C3—S1	127.4 (9)	O1'—C3'—C31'	113.1 (11)
C31—C3—S1	114.9 (8)	C2'—C3'—C31'	120.7 (11)
O2—C4—C5	127.0 (11)	O2'—C4'—C5'	123.8 (11)
O2—C4—C41	115.1 (10)	O2'—C4'—C41'	117.8 (11)
C5—C4—C41	117.9 (11)	C5'—C4'—C41'	118.5 (11)
C6—C5—C4	128.9 (12)	C6'—C5'—C4'	129.4 (11)
C5—C6—C71	120.3 (10)	C5'—C6'—C71'	120.1 (10)
C5—C6—C61	116.3 (10)	C5'—C6'—C61'	111.7 (10)
C5—C6—S2	127.8 (10)	C5'—C6'—S2'	129.1 (10)
C71—C6—S2	111.7 (7)	C71'—C6'—S2'	110.9 (7)
C61—C6—S2	115.6 (7)	C61'—C6'—S2'	119.0 (7)
C12—C11—C1	132.5 (10)	C12'—C11'—C1'	128.2 (10)
C12—C11—S11	111.8 (7)	C12'—C11'—S11'	112.9 (7)
C1—C11—S11	115.6 (8)	C1'—C11'—S11'	119.0 (9)
C32—C31—C3	127.7 (8)	C32'—C31'—C3'	129.3 (10)
C3—C31—S31	120.3 (8)	C3'—C31'—S31'	118.2 (9)
C42—C41—C4	128.2 (10)	C42'—C41'—C4'	131.0 (10)
C4—C41—S41	118.5 (8)	C4'—C41'—S41'	116.1 (8)
C62—C61—C6	130.5 (5)	C62'—C61'—C6'	131.2 (4)
C6—C61—S61	117.7 (5)	C6'—C61'—S61'	114.4 (4)
C72—C71—C6	129.4 (5)	C72'—C71'—C6'	133.3 (4)
C6—C71—S71	118.1 (5)	C6'—C71'—S71'	117.5 (5)

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1989).

Software used to prepare material for publication: local programs.

We thank the SERC and the ERASMUS Programme of the EU for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Dichloro(1-trimethylsilyl-1,5-cyclooctadiene)-palladium(II)

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## Abstract

There are two independent molecules of [PdCl<sub>2</sub>(C<sub>11</sub>-H<sub>20</sub>Si)] in the asymmetric unit. The coordination geometry about Pd<sup>II</sup> is square planar. The structure exhibits positional disorder. The silyl substitution at the vinylic position is found to cause a lengthening of the metal–olefin bond.

## Comment

A substituent on a C=C double bond modifies the available  $\pi$ -electronic charge and affects olefin–