

$S = 1.049$   
5964 reflections  
310 parameters  
Riding-model refinement of  
H-atom parameters

$\Delta\rho_{\max} = 0.426 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.358 \text{ e } \text{\AA}^{-3}$   
Atomic scattering factors  
from *International Tables*  
for *Crystallography* (1992,  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)

For both compounds: Data collection: Stoe *DIF4*, version 7.08. Cell refinement: Stoe *DIF4*, version 7.08. Data reduction: Stoe *REDU4*. Program(s) used to solve structure: *SHELXS92* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL92*.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (II)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{\text{eq}}$
In1	0.27762 (2)	0.59884 (2)	0.316886 (12)	0.02375 (14)
In2	0.22009 (2)	0.76616 (2)	0.193749 (13)	0.02486 (14)
O1	0.3550 (2)	0.7631 (2)	0.29591 (12)	0.0251 (12)
O2	0.1282 (2)	0.6125 (2)	0.22508 (12)	0.0247 (12)
Si1	0.49915 (9)	0.84184 (8)	0.33258 (5)	0.0280 (5)
Si2	0.01570 (9)	0.50427 (8)	0.17776 (5)	0.0277 (5)
Si3	0.41147 (11)	0.77613 (10)	0.03269 (6)	0.0376 (6)
Si4	0.01058 (11)	0.98014 (8)	0.17185 (6)	0.0343 (6)
Si5	0.48484 (10)	0.38086 (8)	0.31469 (6)	0.0333 (6)
Si6	0.08412 (11)	0.73994 (10)	0.46630 (6)	0.0385 (6)
C11	0.6383 (4)	0.7862 (4)	0.2709 (2)	0.049 (2)
C12	0.5421 (4)	0.8283 (3)	0.4343 (2)	0.040 (2)
C13	0.4805 (4)	0.9974 (3)	0.3342 (2)	0.048 (3)
C21	0.0808 (4)	0.4179 (3)	0.0865 (2)	0.047 (2)
C22	-0.1428 (4)	0.5631 (4)	0.1502 (3)	0.053 (2)
C23	-0.0204 (5)	0.4072 (4)	0.2446 (2)	0.053 (3)
C3	0.3310 (4)	0.6897 (3)	0.0952 (2)	0.040 (2)
C31	0.5375 (5)	0.6909 (5)	-0.0264 (3)	0.075 (3)
C32	0.5015 (5)	0.9180 (4)	0.0928 (3)	0.061 (3)
C33	0.2777 (4)	0.8084 (4)	-0.0360 (2)	0.049 (3)
C4	0.0925 (4)	0.9017 (3)	0.2383 (2)	0.039 (2)
C41	-0.0773 (5)	0.8743 (4)	0.0828 (2)	0.065 (3)
C42	0.1410 (5)	1.0794 (4)	0.1422 (3)	0.067 (4)
C43	-0.1194 (4)	1.0692 (3)	0.2233 (2)	0.052 (3)
C5	0.3986 (4)	0.4670 (3)	0.2558 (2)	0.035 (2)
C51	0.6119 (5)	0.4798 (4)	0.3885 (3)	0.075 (4)
C52	0.5745 (5)	0.2656 (4)	0.2496 (3)	0.059 (3)
C53	0.3590 (5)	0.3096 (4)	0.3674 (3)	0.062 (3)
C6	0.2016 (4)	0.6270 (3)	0.4313 (2)	0.038 (2)
C61	0.0257 (6)	0.7249 (5)	0.5625 (3)	0.085 (4)
C62	0.1707 (5)	0.8892 (4)	0.4792 (3)	0.072 (3)
C63	-0.0680 (4)	0.7225 (4)	0.3958 (3)	0.064 (3)

Table 4. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II)

In1—C6	2.147 (4)	In2—C4	2.149 (4)
In1—C5	2.158 (4)	In2—C3	2.154 (4)
In1—O1	2.163 (2)	In2—O2	2.180 (3)
In1—O2	2.168 (2)	In2—O1	2.182 (2)
C6—In1—C5	130.87 (13)	C4—In2—O1	104.21 (11)
C6—In1—O1	110.42 (12)	C3—In2—O1	103.61 (13)
C5—In1—O1	107.23 (12)	O2—In2—O1	78.93 (8)
C6—In1—O2	113.73 (12)	Si1—O1—In1	127.65 (12)
C5—In1—O2	103.02 (11)	Si1—O1—In2	130.18 (12)
O1—In1—O2	79.62 (8)	In1—O1—In2	100.37 (9)
C4—In2—C3	144.17 (14)	Si2—O2—In1	123.63 (12)
C4—In2—O2	104.96 (12)	Si2—O2—In2	132.62 (12)
C3—In2—O2	102.17 (12)	In1—O2—In2	100.29 (9)

This work was supported by the Deutsche Forschungsgemeinschaft. EP is grateful to the Stiftung Stipendienfonds des Verbands der chemischen Industrie for a fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55973 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1019]

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## Cu<sup>II</sup> and Pd<sup>II</sup> Complexes of 3-Hydroxy-1,3-bis(2-thienyl)prop-2-en-1-one

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## Abstract

The 1:2 complexes formed between Cu<sup>II</sup> or Pd<sup>II</sup> and the anion of 3-hydroxy-1,3-bis(2-thienyl)prop-2-en-1-one [LH: Baxter, Blake, Heath & Stephenson (1990). *Acta Cryst.* **C46**, 508–510], bis[(3-hydroxy- $\kappa\text{O}'$ )-1,3-bis(2-thienyl)prop-2-en-1-onato(1-)- $\kappa\text{O}$ ]copper(II) and bis[(3-hydroxy- $\kappa\text{O}'$ )-1,3-bis(2-thienyl)prop-2-en-1-onato(1-)- $\kappa\text{O}$ ]palladium(II), crystallize with the metal ions occupying crystallographic inversion centres and coordinated by approximately square planes of four O atoms. The similarities within the pairs of M—O, C—C and C—O bonds in the chelate rings indicate the latter are behaving as delocalized systems. The mean Cu—O and Pd—O distances are

1.910 (3) and 1.980 (3) Å, respectively. Both molecules, their thiophene substituents included, are essentially flat. In both  $ML_2$  structures the asymmetric unit contains one ordered and one disordered thiophene ring: in the Cu case the latter is equally disordered over two orientations such that each  $CuL_2$  molecule has, on average, three S atoms *endo* and one *exo*. In the Pd case the occupancy of the *exo* orientation is only 0.262 (5), or approximately one ring for every two  $PdL_2$  units. The *exo* S atoms [S(4A)] make axial  $M\cdots S$  contacts of 3.127 and 3.431 Å for  $M = Cu$  and Pd, respectively; the distances to the corresponding C atoms in a ring with the S atoms *endo* are 3.237 and 3.309 Å. An examination of  $S\cdots S$  intermolecular contacts strongly suggests an alternation of *endo* and *exo* S atoms such that the crystal contains only  $Cu^{II}$  centres with one close axial contact. These constraints on possible structures are not so obviously present in the  $Pd^{II}$  complex and it is therefore impossible to provide a unique interpretation of this structure.

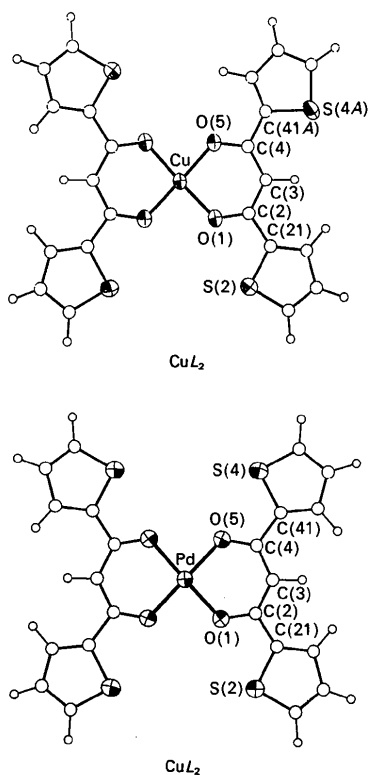


Fig. 1. Views of  $CuL_2$  and  $PdL_2$  showing the labelling of the non-H atoms. In  $CuL_2$  one thiophene ring has its S atom *exo*. For each molecule of  $PdL_2$  with all S atoms *endo* as shown, there is another with one S atom *exo* as shown for  $CuL_2$ . Thermal ellipsoids are drawn at the 30% probability level and C and H atoms have been assigned arbitrary radii of 0.15 and 0.10 Å, respectively.

### Comment

The refinement model for the Cu complex does not distinguish between a structure in which all the molecules are equivalent with the metal having one close  $Cu\cdots S$  axial contact and one in which there are equal numbers with two and none. However, several pieces of evidence favour the former:

(i) The first arises from a consideration of  $S\cdots S$  intermolecular contacts involving the *exo* S atoms [S(4A)]. If the S atoms of two thiophene rings related by the inversion centre at  $(\frac{1}{2}, 1, 0)$  are both *exo*, this results in an unfavourable  $S\cdots S$  contact of 3.478 Å (the van der Waals sum is 3.70 Å), suggesting that rings with *exo* and *endo* S atoms must alternate and therefore that all the Cu centres are equivalent.

(ii) Both the absence of supercell reflections and the observation of sharp diffraction maxima even at high angles suggest that, apart from the orientational disorder of one thiophene ring, the structure is essentially ordered and does not represent an average of two different metal environments.

The Pd structure shows some similar features, such as an unfavourable  $S\cdots S$  contact of 3.444 Å, which suggests that adjacent thiophenes do not have *exo* S

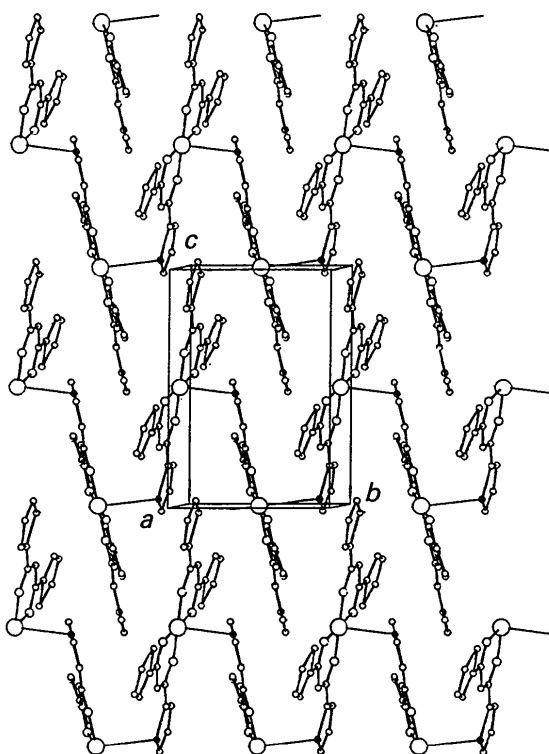


Fig. 2. Packing diagram for  $CuL_2$  showing the relationship between each molecule and a thiophene ring in a neighbouring molecule at  $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$  bearing an *exo* S(4A) atom (shaded circle).

atoms. The lower proportion of *exo* S atoms (possibly fortuitously close to 0.25) renders it impossible to make inferences as clearly as for the Cu structure. Our tentative conclusion is that the thiophene disorder in the Pd structure is random.

## Experimental

### CuL<sub>2</sub>

#### Crystal data

[Cu(C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 534.13

Monoclinic

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

*a* = 11.841 (6) Å

*b* = 7.850 (6) Å

*c* = 11.586 (6) Å

β = 96.028 (19)°

*V* = 1071 Å<sup>3</sup>

*Z* = 2

#### Data collection

Stoe Stadi-2 two-circle diffractometer

ω scans

Absorption correction: none

2180 measured reflections

1434 observed reflections

[*F* ≥ 6.0σ(*F*)]

*R*<sub>int</sub> = 0.003

#### Refinement

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

Final *R* = 0.0398

*wR* = 0.0668

*S* = 0.659

1434 reflections

169 parameters

H atoms in calculated positions. Rigid groups: disordered thiophene orientations

*D<sub>x</sub>* = 1.656 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 12 reflections

θ = 3.5–22°

μ = 1.423 mm<sup>-1</sup>

*T* = 298 K

Rhomboid

0.52 × 0.36 × 0.20 mm

Reddish brown

θ<sub>max</sub> = 25°

*h* = -14 → 14

*k* = 0 → 9

*l* = 0 → 14

2 standard reflections

frequency: every second layer

intensity variation: insignificant

*w* = 1/[σ<sup>2</sup>(*F*) + 0.010055*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.17

Δρ<sub>max</sub> = 0.33 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.78 e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors in-laid (SHELX76; Sheldrick, 1976) except for Cu (Cromer & Mann, 1968)

C(24)	0.9754 (3)	0.8398 (5)	0.3325 (3)	0.0599 (7)
C(41)	0.36666 (13)	0.8862 (3)	0.15951 (18)	0.0275 (8)
S(4)	0.22477 (13)	0.9054 (3)	0.18013 (18)	0.0524 (6)
C(42)	0.37890 (13)	0.8603 (3)	0.04446 (18)	0.0848 (8)
C(43)	0.27406 (13)	0.8536 (3)	-0.02476 (18)	0.0555 (8)
C(44)	0.18447 (13)	0.8773 (3)	0.03658 (18)	0.0487 (8)
C(41A)	0.36080 (18)	0.9138 (3)	0.16450 (16)	0.0554 (8)
S(4A)	0.39363 (18)	0.8603 (3)	0.02720 (16)	0.0572 (6)
C(42A)	0.18598 (18)	0.9018 (3)	0.05574 (16)	0.0691 (8)
C(43A)	0.24564 (18)	0.9299 (3)	0.16558 (16)	0.0390 (8)
C(44A)	0.25470 (18)	0.8620 (3)	-0.02620 (16)	0.0713 (8)

Table 2. Geometric parameters (Å, °) for CuL<sub>2</sub>

Cu—O(1)	1.9085 (24)	C(4)—C(41)	1.467 (4)
Cu—O(5)	1.9122 (25)	C(4)—C(41A)	1.450 (4)
O(1)—C(2)	1.273 (4)	C(21)—S(2)	1.720 (3)
C(2)—C(3)	1.392 (4)	C(21)—C(22)	1.366 (5)
C(2)—C(21)	1.473 (4)	S(2)—C(24)	1.710 (4)
C(3)—C(4)	1.389 (4)	C(22)—C(23)	1.425 (5)
C(4)—O(5)	1.277 (4)	C(23)—C(24)	1.339 (5)
O(1)—Cu—O(5)	93.35 (10)	O(5)—C(4)—C(41A)	111.3 (3)
Cu—O(1)—C(2)	125.44 (21)	Cu—O(5)—C(4)	125.92 (21)
O(1)—C(2)—C(3)	125.9 (3)	C(2)—C(21)—S(2)	118.04 (23)
O(1)—C(2)—C(21)	115.6 (3)	C(2)—C(21)—C(22)	130.3 (3)
C(3)—C(2)—C(21)	118.5 (3)	S(2)—C(21)—C(22)	111.70 (24)
C(2)—C(3)—C(4)	123.5 (3)	C(21)—S(2)—C(24)	91.43 (16)
C(3)—C(4)—O(5)	125.4 (3)	C(21)—C(22)—C(23)	111.4 (3)
C(3)—C(4)—C(41)	117.4 (3)	C(22)—C(23)—C(24)	113.4 (3)
C(3)—C(4)—C(41A)	123.2 (3)	S(2)—C(24)—C(23)	112.1 (3)
O(5)—C(4)—C(41)	117.1 (3)		
O(1)—C(2)—C(3)—C(4)		2.4 (5)	
C(21)—C(2)—C(3)—C(4)		-177.6 (3)	
O(1)—C(2)—C(21)—S(2)		-8.0 (4)	
O(1)—C(2)—C(21)—C(22)		171.1 (3)	
C(3)—C(2)—C(21)—S(2)		172.02 (24)	
C(3)—C(2)—C(21)—C(22)		-8.9 (5)	
C(2)—C(3)—C(4)—O(5)		0.9 (5)	
C(2)—C(3)—C(4)—C(41)		-174.7 (3)	
C(2)—C(3)—C(4)—C(41A)		176.9 (3)	
C(3)—C(4)—C(41)—S(4)		173.40 (23)	
C(3)—C(4)—C(41)—C(42)		-14.2 (4)	
O(5)—C(4)—C(41)—S(4)		-2.6 (3)	
O(5)—C(4)—C(41)—C(42)		169.80 (24)	
C(3)—C(4)—C(41A)—S(4A)		2.3 (4)	
O(5)—C(4)—C(41A)—S(4A)		178.80 (21)	
C(2)—C(21)—S(2)—C(24)		179.5 (3)	
C(22)—C(21)—S(2)—C(24)		0.2 (3)	
C(2)—C(21)—C(22)—C(23)		-179.1 (3)	
S(2)—C(21)—C(22)—C(23)		0.1 (4)	
C(21)—S(2)—C(24)—C(23)		-0.5 (3)	
C(21)—C(22)—C(23)—C(24)		-0.4 (4)	
C(22)—C(23)—C(24)—S(2)		0.6 (4)	
C(4)—C(41)—S(4)—C(44)		174.40 (19)	
C(4)—C(41)—C(42)—C(43)		-173.75 (23)	

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for CuL<sub>2</sub>

*U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu	0.5	1.0	0.5	0.0454 (3)
O(1)	0.63792 (20)	0.9284 (4)	0.44317 (19)	0.0545 (7)
C(2)	0.6500 (3)	0.8941 (4)	0.3378 (3)	0.0435 (7)
C(3)	0.5633 (3)	0.8839 (4)	0.2472 (3)	0.0485 (7)
C(4)	0.4500 (3)	0.9166 (4)	0.2602 (3)	0.0428 (7)
O(5)	0.41161 (20)	0.9615 (3)	0.35454 (21)	0.0518 (7)
C(21)	0.76751 (25)	0.8632 (4)	0.3122 (3)	0.0418 (7)
S(2)	0.87552 (8)	0.90202 (14)	0.42023 (8)	0.0578 (4)
C(22)	0.8080 (3)	0.8042 (4)	0.2135 (3)	0.0521 (7)
C(23)	0.9287 (3)	0.7911 (4)	0.2275 (3)	0.0593 (7)

### PdL<sub>2</sub>

#### Crystal data

[Pd(C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 577.01

Monoclinic

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

*a* = 11.892 (4) Å

*b* = 7.943 (4) Å

*c* = 11.582 (3) Å

β = 98.016 (25)°

*V* = 1083 Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.769 Mg m<sup>-3</sup>

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 13 reflections

θ = 16.5–17.5°

μ = 1.242 mm<sup>-1</sup>

*T* = 298 K

Plate

0.45 × 0.42 × 0.08 mm

Reddish brown

## Data collection

Stoe Stadi-4 four-circle diffractometer

 $\omega$ -2 $\theta$  scans

Absorption correction: none

1546 measured reflections

1153 observed reflections

 $[F \geq 6.0\sigma(F)]$  $\theta_{\max} = 22.5^\circ$  $h = -12 \rightarrow 12$  $k = 0 \rightarrow 8$  $l = 0 \rightarrow 12$ 

3 standard reflections

frequency: 120 min

intensity variation: insignificant

## Refinement

Refinement on  $F$ Final  $R = 0.0300$  $wR = 0.0434$  $S = 1.207$ 

1153 reflections

105 parameters

H atoms in calculated positions. Rigid groups: disordered thiophene orientations

 $w = 1/[\sigma^2(F) + 0.00011F^2]$  $(\Delta/\sigma)_{\max} = 0.007$  $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$ 

Extinction correction: none

Atomic scattering factors in-  
laid (SHELX76; Sheldrick,  
1976) except for Pd  
(Cromer & Mann, 1968)

O(1)—C(2)—C(3)—C(4)	2.1 (8)
C(21)—C(2)—C(3)—C(4)	-178.2 (4)
O(1)—C(2)—C(21)—S(2)	-11.2 (5)
O(1)—C(2)—C(21)—C(22)	170.2 (5)
C(3)—C(2)—C(21)—S(2)	169.1 (3)
C(3)—C(2)—C(21)—C(22)	-9.5 (7)
C(2)—C(3)—C(4)—O(5)	-0.7 (8)
C(2)—C(3)—C(4)—C(41)	-178.0 (4)
C(2)—C(3)—C(4)—C(41A)	176.0 (5)
C(3)—C(4)—C(41)—S(4)	174.1 (3)
C(3)—C(4)—C(41)—C(42)	-10.5 (6)
O(5)—C(4)—C(41)—S(4)	-3.5 (5)
O(5)—C(4)—C(41)—C(42)	171.9 (4)
C(3)—C(4)—C(41A)—S(4A)	-7.0 (9)
C(3)—C(4)—C(41A)—C(42A)	167.2 (7)
O(5)—C(4)—C(41A)—S(4A)	170.2 (5)
O(5)—C(4)—C(41A)—C(42A)	-15.6 (9)
C(24)—S(2)—C(21)—C(2)	-178.6 (4)
C(24)—S(2)—C(21)—C(22)	0.3 (4)
C(21)—S(2)—C(24)—C(23)	-0.6 (4)
C(2)—C(21)—C(22)—C(23)	178.7 (4)
S(2)—C(21)—C(22)—C(23)	0.1 (5)
C(21)—C(22)—C(23)—C(24)	-0.5 (6)
C(22)—C(23)—C(24)—S(2)	0.7 (6)
C(44)—S(4)—C(41)—C(4)	176.8 (3)
C(4)—C(41)—C(42)—C(43)	-176.5 (3)

Molecular graphics were produced using an interactive version of ORTEPII (Johnson, 1971), included in the GX crystallographic program package (Mallinson & Muir, 1985), and PLUTO (Motherwell, 1976). Molecular geometry calculations utilized CALC (Gould & Taylor, 1985). Crystals of  $\text{CuL}_2$  were assessed by oscillation and Weissenberg photography prior to data collection. The structure of  $\text{CuL}_2$  was solved by inferring the location of the metal atom from cell contents and space-group symmetry and by input of this information to DIRDIF (Beurskens *et al.*, 1983); iterative cycles of least-squares refinement and difference Fourier synthesis (SHELX76; Sheldrick, 1976) identified the positions of both ordered and disordered non-H atoms. The structure of  $\text{PdL}_2$  was solved by using the coordinates for the ordered region (the metal and its chelate ring) of the first structure. The structures were refined by full-matrix least squares using SHELX76.

We thank the SERC for support.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55901 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1005]

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for  $\text{PdL}_2$

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
Pd	0.5	1.0	0.5	0.0448 (3)
O(1)	0.64232 (25)	0.9344 (5)	0.44171 (25)	0.0526 (19)
C(2)	0.6467 (4)	0.8965 (6)	0.3337 (4)	0.045 (3)
C(3)	0.5548 (4)	0.8848 (6)	0.2459 (4)	0.051 (3)
C(4)	0.4422 (4)	0.9157 (6)	0.2554 (4)	0.044 (3)
O(5)	0.4023 (3)	0.9600 (4)	0.3492 (3)	0.0511 (19)
S(2)	0.87547 (10)	0.91398 (21)	0.41130 (11)	0.0612 (8)
S(4)	0.2155 (3)	0.9104 (4)	0.16978 (19)	0.0629 (18)
C(21)	0.7614 (4)	0.8638 (5)	0.3076 (4)	0.0442 (10)
C(22)	0.7969 (4)	0.7994 (6)	0.2088 (4)	0.0539 (12)
C(23)	0.9179 (4)	0.7916 (6)	0.2193 (4)	0.0574 (12)
C(24)	0.9692 (4)	0.8495 (6)	0.3218 (4)	0.0615 (13)
C(41)	0.3573 (3)	0.8892 (4)	0.14929 (19)	0.051 (3)
C(42)	0.3694 (3)	0.8606 (4)	0.03450 (19)	0.047 (3)
C(43)	0.2645 (3)	0.8535 (4)	-0.03458 (19)	0.0631 (25)
C(44)	0.1751 (3)	0.8794 (4)	0.02655 (19)	0.0549 (22)
S(4A)	0.3796 (5)	0.8895 (10)	0.0200 (6)	0.067 (3)
C(41A)	0.3476 (5)	0.9130 (10)	0.1613 (6)	0.019 (5)
C(42A)	0.2324 (5)	0.9128 (10)	0.1654 (6)	0.052 (15)
C(43A)	0.1719 (5)	0.8967 (10)	0.0547 (6)	0.094 (10)
C(44A)	0.2402 (5)	0.8817 (10)	-0.0310 (6)	0.040 (5)

Table 4. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for  $\text{PdL}_2$

Pd—O(1)	1.977 (3)	C(4)—C(41)	1.492 (5)
Pd—O(5)	1.983 (3)	C(4)—C(41A)	1.453 (8)
O(1)—C(2)	1.295 (5)	S(2)—C(21)	1.729 (5)
C(2)—C(3)	1.388 (6)	S(2)—C(24)	1.704 (5)
C(2)—C(21)	1.460 (6)	C(21)—C(22)	1.374 (6)
C(3)—C(4)	1.381 (6)	C(22)—C(23)	1.428 (7)
C(4)—O(5)	1.293 (5)	C(23)—C(24)	1.338 (7)
O(1)—Pd—O(5)	94.66 (13)	O(5)—C(4)—C(41A)	107.3 (5)
Pd—O(1)—C(2)	122.9 (3)	Pd—O(5)—C(4)	123.0 (3)
O(1)—C(2)—C(3)	126.1 (4)	C(21)—S(2)—C(24)	91.43 (24)
O(1)—C(2)—C(21)	113.9 (4)	C(2)—C(21)—S(2)	118.7 (3)
C(3)—C(2)—C(21)	120.0 (4)	C(2)—C(21)—C(22)	130.1 (4)
C(2)—C(3)—C(4)	127.1 (4)	S(2)—C(21)—C(22)	111.2 (3)
C(3)—C(4)—O(5)	126.0 (4)	C(21)—C(22)—C(23)	111.6 (4)
C(3)—C(4)—C(41)	117.5 (4)	C(22)—C(23)—C(24)	113.0 (4)
C(3)—C(4)—C(41A)	126.5 (5)	S(2)—C(24)—C(23)	112.7 (4)
O(5)—C(4)—C(41)	116.4 (4)		

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## (1,1-Cyclobutanedicarboxylato-*O,O'*)-bis(trimethylphosphine-*P*)platinum(II) Monohydrate

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### Abstract

The coordination around platinum is conventional square planar. The cyclobutane ring and the platinum coordination sphere are almost perpendicular to each other. The lattice contains water molecules though the crystals were grown from a cyclohexanol solution. Atom O(5) of the water molecule forms hydrogen bonds with the carboxylato O atoms O(4) and O(3<sup>i</sup>), respectively; the structure of the compound consists of one-dimensional polymeric chains.

### Comment

The structure determination of the title compound (I) was undertaken in order to compare the structure with those of diammine analogues. Both the platinum coordination sphere and the cyclobutane ring are almost planar, with maximum displacements out of the least-squares plane of 0.111 Å for O(1) and 0.09 Å for C(5). The dihedral angle between the platinum coordination sphere and the cyclobutane ring is 88.66°. The mean distance of Pt—P(1) and Pt—P(2) is 2.222 (2) Å. The P(1)—Pt—P(2) angle is 95.13 (6)°. The mean distance of Pt—O(1) and Pt—O(2) is 2.056 (5) Å. The O(1)—Pt—O(2) angle is 86.3 (2)°. The C(4)—C(3)—C(6) and C(1)—C(3)—C(2) angles in the 1,1-cyclobutanedicarboxylate group are 88.5 (5) and 110.4 (5)°, respectively. The observed O(1)—Pt—O(2) angle of the title compound is smaller than those found in the diammine analogues [Pt(NH<sub>3</sub>)<sub>2</sub>(cbdca)] [89.9 (4)°; Neidle, Ismail & Sadler (1980)], where H<sub>2</sub>cbdca is 1,1-cyclobutanedicarboxylic acid, and [Pt(*R,R*-dach)(cbdca)].H<sub>2</sub>O [89.2 (4)°; Bitha *et*

*al.* (1990)], where *R,R*-dach is (1*R*,2*R*)-1,2-diaminocyclohexane. The mean Pt—O distances in these molecules are 2.029 (9) Å {[Pt(NH<sub>3</sub>)<sub>2</sub>(cbdca)]} and 2.006 (10) Å {[Pt(*R,R*-dach)(cbdca)].H<sub>2</sub>O}. The corresponding C(4)—C(3)—C(6) and C(1)—C(3)—C(2) angles in the 1,1-cyclobutanedicarboxylate ligands are 89.2 (12) and 107.4 (8)° in [Pt(NH<sub>3</sub>)<sub>2</sub>(cbdca)] and 86.3 (11) and 115.9 (12)° in [Pt(*R,R*-dach)(cbdca)].H<sub>2</sub>O, respectively.

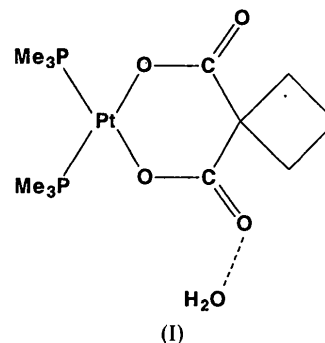


Fig. 1. A view of the unit cell. Hydrogen-bonding interactions between the water of crystallization and the carboxylato O atoms are shown as broken lines. Symmetry code: (ii)  $x, y, z-1$ .

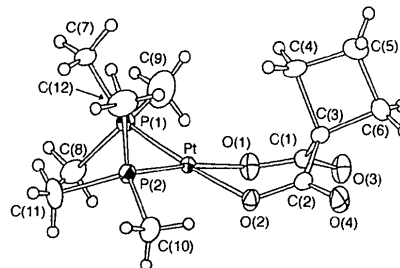


Fig. 2. ORTEP (Johnson, 1976) view of the molecule with atomic labeling except for H atoms. The water of crystallization has been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level for non-H atoms.