O7	−0.25629 (15)	−0.0360 (2)	0.10615 (8)	0.0344 (6)
C8	−0.2629 (2)	0.0368 (2)	0.09855 (13)	0.0388 (9)
C9	−0.3345 (3)	0.0285 (3)	0.12513 (13)	0.0429 (10)
O10	−0.3113 (2)	0.0412 (2)	0.17101 (9)	0.0463 (7)
C11	−0.3774 (3)	0.0283 (3)	0.19959 (15)	0.0492 (11)
C12	−0.3526 (3)	0.0325 (3)	0.24726 (14)	0.0489 (11)
O13	−0.2887 (2)	0.1141 (2)	0.25859 (9)	0.0466 (7)
C14	−0.2766 (3)	0.1267 (3)	0.30565 (13)	0.0454 (10)
C15	−0.2263 (3)	0.0931 (3)	0.32697 (14)	0.0441 (10)
O16	−0.1412 (2)	0.1448 (2)	0.31542 (9)	0.0410 (7)
C17	−0.0892 (3)	0.1173 (3)	0.33456 (14)	0.0450 (10)
C18	−0.0846 (3)	0.0502 (3)	0.30735 (12)	0.0373 (9)
P1	0	0	0	0.0292 (5)
F11	0.00286 (14)	0.07149 (13)	0.03095 (7)	0.0409 (5)
P2	0	1/2	0	0.0540 (5)
F21	0.0927 (2)	0.5565 (2)	0.01702 (12)	0.0826 (9)
F22	−0.0266 (2)	0.4535 (2)	0.04606 (11)	0.0844 (10)
F23	−0.0216 (2)	0.5671 (2)	0.01779 (13)	0.0868 (11)
O1*W*	1/3	2/3	0.0703 (4)	0.158 (4)
O2*W*†	0.5770 (13)	0.8251 (13)	0.1388 (7)	0.150 (7)
O1*M*†	0.4050 (12)	0.8616 (12)	0.1196 (6)	0.135 (6)
C2*M*†	0.4388 (15)	0.8224 (15)	0.1073 (8)	0.110 (7)

† Occupancy of 0.33.

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

Ru—S1	2.3859 (9)	C8—C9	1.492 (6)
Ru—S4	2.3620 (9)	C9—O10	1.421 (5)
S1—C18	1.820 (4)	O10—C11	1.416 (5)
S1—C2	1.827 (4)	C11—C12	1.487 (6)
C2—C3	1.500 (6)	C12—O13	1.426 (5)
C3—S4	1.824 (4)	O13—C14	1.424 (5)
S4—C5	1.827 (3)	C14—C15	1.503 (6)
C5—C6	1.520 (5)	C15—O16	1.425 (5)
C6—O7	1.424 (4)	O16—C17	1.423 (5)
O7—C8	1.440 (5)	C17—C18	1.528 (6)
S4^{i}—Ru—S4	94.55 (3)	O7—C8—C9	108.2 (3)
S4^{i}—Ru—S1	175.66 (3)	O10—C9—C8	108.3 (3)
S4—Ru—S1	87.24 (3)	C11—O10—C9	112.7 (3)
S4—Ru—S1^{i}	81.36 (3)	O10—C11—C12	110.3 (4)
S1—Ru—S1^{i}	96.94 (3)	O13—C12—C11	110.8 (3)
C18—S1—C2	100.0 (2)	C14—O13—C12	112.9 (3)
C3—C2—S1	111.9 (3)	O13—C14—C15	115.4 (3)
C2—C3—S4	110.9 (3)	O16—C15—C14	109.3 (3)
C3—S4—C5	100.8 (2)	C17—O16—C15	112.8 (3)
C6—C5—S4	111.5 (2)	O16—C17—C18	114.0 (3)
O7—C6—C5	113.6 (3)	C17—C18—S1	112.0 (3)
C6—O7—C8	112.8 (3)		
C18—S1—C2—C3	−80.6 (3)	C9—O10—C11—C12	173.2 (3)
S1—C2—C3—S4	−58.0 (3)	O10—C11—C12—O13	66.2 (5)
C2—C3—S4—C5	−72.4 (3)	C11—C12—O13—C14	165.8 (3)
C3—S4—C5—C6	−86.3 (3)	C12—O13—C14—C15	79.8 (4)
S4—C5—C6—O7	65.4 (4)	O13—C14—C15—O16	73.7 (5)
C5—C6—O7—C8	84.1 (4)	C14—C15—O16—C17	179.7 (3)
C6—O7—C8—C9	−169.9 (3)	C15—O16—C17—C18	84.3 (4)
O7—C8—C9—O10	73.6 (4)	O16—C17—C18—S1	65.4 (4)
C8—C9—O10—C11	−175.4 (3)	C2—S1—C18—C17	−82.4 (3)

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

A crystal suitable for single-crystal X-ray diffraction studies was mounted on a glass fibre and placed in the stream of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986).

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1354). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Stoe & Cie (1990*a*). *DIF4. Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1990*b*). *REDU4. Data Reduction Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.

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Bis[1-hydroxy-2(1*H*)-pyridinethionato-*O*,*S*]-palladium(II)

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Abstract

In the structure of the title compound, $[Pd(C_5H_4NOS)_2]$, the Pd atom is coordinated by a slightly distorted planar array of two S and two O atoms; the two 1-hydroxy-

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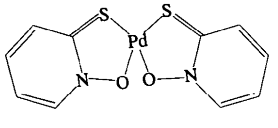
2(1*H*)-pyridinethione ligands adopt a *cis* configuration. Intermolecular Pd···Pd and Pd···S interactions of 4.05 and 3.80 Å, respectively, are observed in the structure.

Comment

Owing to their useful bactericidal and antifungal activities, transition metal complexes of 1-hydroxy-2(1*H*)-pyridinethione (HPT) have been investigated widely. Moreover, HPT exhibits unusual versatility in coordinating to metals (Barnett, Kretschmar & Hartman, 1977; West, Hines, Bunting, Symons & Malik, 1988). On the other hand, the simulation of many metallo-enzymes involving the thiolato group has also received considerable attention, particularly the assessment of the antitumor activity of some Pd complexes with chelating ligands (Alice & Prabhakaran, 1990; Wimmer *et al.*, 1989). As part of our studies of metal complexes of HPT (Chen, Hu, Wu, Wang & Kang, 1991; Xiong, Song, You, Mak & Zhou, 1996; Xiong, Zuo, You & Huang, 1996), we now report the crystal structure of bis[1-hydroxy-2(1*H*)-pyridinethionato-*O*,*S*]palladium(II), (I).



(I)

A displacement ellipsoid plot and atom-numbering scheme of (I) are shown in Fig. 1. The complex is formed with *cis*-oriented HPT ligands and shows nearly planar geometry. The Pd atom is coordinated by the S and O atoms of the two ligands and has a distorted square-planar geometry. The Pd—S distances are significantly shorter than those found in both bis(3-aminopyridinium) bis(dithiooxalato)palladium(II) and dithiooxalatobis(trimethylphosphine)palladium(II), in agreement with a lower degree of strain within the five-membered ring (Roman, Luque, Beitia & Guzman-Miralles, 1992; Bonamico, Dessy & Fares, 1977). Similarly, the Pd—O bond lengths are also shorter than those observed in related structures (Balavoine, Client, Zerbib & Boubekeur, 1990; Izatt, Wu, Jiang & Dalley, 1990). The dihedral angle between the planes of the two ligands around the Pd atom is 5.84 (9)°, which may be consistent with better conjugation effects leading to the shortness of the Pd—S and Pd—O bonds.

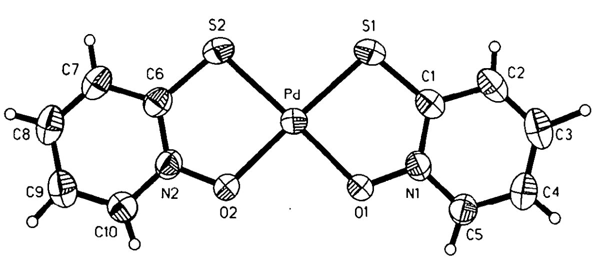


Fig. 1. A displacement ellipsoid plot (50% probability) of the title molecule showing the atom-numbering scheme.

In the crystal lattice, the complex molecules are connected by short Pd···Pd^{i} and Pd···S^{i} contacts [4.0513 (4) and 3.8000 (8) Å, respectively], and by intermolecular C—H···O hydrogen bonds: C5···O1^{ii} 3.220 (3) Å and C5—H5···O1^{ii} 151 (2)° [symmetry codes: (i) $-x$, $2-y$, $2-z$; (ii) $1-x$, $2-y$, $2-z$].

Experimental

A solution of PdCl$_2$ (1 mmol) in concentrated HCl was added slowly to a solution of HPT (2 mmol) in hot ethanol. The mixed solution was stirred for 1 h at 313 K and then cooled to room temperature and filtered. It was then evaporated slowly over a period of a few weeks, after which red–brown thick plate-like crystals suitable for X-ray analysis were obtained.

Crystal data

[Pd(C$_5$H$_4$NOS)$_2$]
M_r = 358.70
Monoclinic
$P2_1/n$
a = 8.682 (1) Å
b = 13.983 (1) Å
c = 9.956 (1) Å
β = 96.66 (1)°
V = 1200.5 (2) Å^3
Z = 4
D_x = 1.985 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–25°
μ = 1.882 mm^{-1}
T = 293 (2) K
Thick plate
0.56 × 0.30 × 0.10 mm
Red–brown

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (*XSCANS*; Siemens, 1994)
$T_{\min}$ = 0.740, $T_{\max}$ = 0.920
3553 measured reflections
2756 independent reflections
2465 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int}$ = 0.0244
$\theta_{\max}$ = 27.49°
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 18$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R(F)$ = 0.0257
$wR(F^2)$ = 0.0702
S = 1.024
2756 reflections
187 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002

$\Delta\rho_{\max}$ = 1.10 e Å^{-3}
$\Delta\rho_{\min}$ = −0.58 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0029 (4)
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 (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	0.10212 (2)	0.935504 (12)	0.85106 (2)	0.03686 (9)
S1	0.02076 (8)	1.08333 (5)	0.79578 (7)	0.0499 (2)
S2	−0.10097 (7)	0.86091 (5)	0.73816 (6)	0.0467 (2)
O1	0.2907 (2)	0.99930 (11)	0.9532 (2)	0.0455 (4)
O2	0.1817 (2)	0.80262 (12)	0.9065 (2)	0.0473 (4)
N1	0.2881 (2)	1.09602 (14)	0.9554 (2)	0.0380 (4)
N2	0.0898 (2)	0.7295 (2)	0.8590 (2)	0.0394 (4)
C1	0.1679 (3)	1.1449 (2)	0.8897 (2)	0.0407 (5)
C2	0.1732 (4)	1.2454 (2)	0.8995 (3)	0.0523 (7)
C3	0.2948 (4)	1.2902 (2)	0.9717 (3)	0.0557 (7)
C4	0.4158 (4)	1.2371 (2)	1.0344 (3)	0.0507 (6)
C5	0.4119 (3)	1.1399 (2)	1.0258 (2)	0.0449 (5)
C6	−0.0433 (3)	0.7449 (2)	0.7773 (2)	0.0392 (5)
C7	−0.1299 (3)	0.6649 (2)	0.7294 (3)	0.0494 (6)
C8	−0.0830 (4)	0.5752 (2)	0.7662 (3)	0.0556 (7)
C9	0.0534 (4)	0.5622 (2)	0.8519 (3)	0.0551 (7)
C10	0.1383 (4)	0.6402 (2)	0.8964 (3)	0.0494 (6)

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

Pd—O1	2.031 (2)	S1—C1	1.724 (3)
Pd—O2	2.036 (2)	S2—C6	1.729 (3)
Pd—S1	2.2325 (7)	O1—N1	1.353 (2)
Pd—S2	2.2362 (7)	O2—N2	1.349 (3)
O1—Pd—O2	92.09 (6)	S1—Pd—S2	95.71 (3)
O1—Pd—S1	86.01 (5)	C1—S1—Pd	97.78 (8)
O2—Pd—S1	178.03 (5)	C6—S2—Pd	97.67 (8)
O1—Pd—S2	178.13 (5)	N1—O1—Pd	115.67 (13)
O2—Pd—S2	86.20 (5)	N2—O2—Pd	115.39 (13)

The H atoms were located from difference maps and refined isotropically. In the final difference map, there were two spurious peaks of 1 e Å^{-3} close to the Pd atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*. Geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram viewed down the *b* axis, have been deposited with the IUCr (Reference: MU1242). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dibromo[*N*-(2-pyridylmethylidene)-2-pyridylmethylamine-*N*,*N*′,*N*″]copper(II) Complex

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Abstract

The title complex, $[CuBr_2(C_{12}H_{11}N_3)]$, is a monomer and the environment around the Cu^{2+} ion is that of a square pyramid, with one Br^- ion occupying the apical site and the other Br^- ion at a basal position.