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μ-[1,9-Bis(diphenylphosphino)-3,7-dithianonane]-bis[dichloropalladium(II)]*

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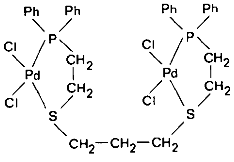
Abstract. $C_{31}H_{34}Cl_4P_2Pd_2S_2$,$[Pd_2(C_{31}H_{34}P_2S_2)Cl_4]$, $M_r = 887 \cdot 29$, triclinic, $P\bar{1}$, $a = 9 \cdot 914\,(1)$, $b = 12 \cdot 713\,(2)$, $c = 13 \cdot 905\,(2)$ Å, $\alpha = 84 \cdot 102\,(9)$, $\beta = 81 \cdot 041\,(9)$, $\gamma = 79 \cdot 675\,(9)°$, $V = 1698$ Å^3, $Z = 2$, $D_m = 1 \cdot 72$, $D_x = 1 \cdot 74$ Mg m^{-3}, final $R = 0 \cdot 036$ for 3045 observed reflexions. 1,9-Bis(diphenylphosphino)-3,7-dithianonane, $(C_6H_5)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2$-$P(C_6H_5)_2$, (pssp), acts as a bis(bidentate) ligand through the two P and two S atoms. The complex between the ligand and $PdCl_2$ is dinuclear. One P atom and the closest S atom are bonded to one Pd atom forming a five-membered ring ($PdPC_2S$). The two remaining places in the square plane around the Pd atom are occupied by two Cl atoms in *cis* positions. The other S and P atoms of the same ligand molecule are bonded to another Pd atom in the same way as above. The compound is diamagnetic.

Introduction. A yellow crystal of $Pd_2(pssp)Cl_4$ (*cf.* outline diagram *A*), of dimensions $0 \cdot 06 \times 0 \cdot 18 \times 0 \cdot 20$ mm, prepared according to Degischer (1968) and provided by the late Professor G. Schwarzenbach, Zürich, was used for the intensity measurements.



(*A*)

All data were collected on an Enraf–Nonius CAD-4 four-circle diffractometer at room temperature. The background was measured for one quarter of the scan time at each end of the interval. A least-squares refinement of 48 accurately measured θ values gave the cell parameters. Possible space groups are $P1$ and $P\bar{1}$. Details of the collection and reduction of the intensities are given in Table 1. The intensities and their standard deviations were corrected for Lorentz–polarization and absorption effects and for a decrease of about 4% in the three standard reflexions measured every second hour. The positions of the two Pd atoms were determined from a Patterson synthesis and the other non-H atoms were found in successive electron-density maps, $P\bar{1}$ being assumed. The least-squares refinement was performed with *SHELX* (Sheldrick, 1976), minimizing $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = k\sigma^2(F)$. The phenyl rings were treated as rigid groups (C—C $1 \cdot 395$ Å). The phenyl and methylene H atoms were geometrically generated at the end of each cycle of the refinement of the non-H atoms (C—H $1 \cdot 080$ Å). The atoms Pd, Cl, S and P were refined with anisotropic and the other atoms with isotropic temperature factors. A correction for anomalous dispersion was made (Cromer & Liberman, 1970). The intensities did not show any indication of extinction. The highest residual electron density was $0 \cdot 7$ e Å^{-3} and the deepest pit $0 \cdot 5$ e Å^{-3}. Scattering factors for neutral non-H atoms were from Doyle & Turner (1968) and for neutral H atoms from Stewart, Davidson & Simpson (1965). Final positional parameters are given in Table 2.†

An investigation of the structure in space group $P1$ was not made because of the then low quotient between the number of reflexions and parameters and as the

Table 1. *Details of the collection and reduction of the intensities and the least-squares refinement*

Radiation	Mo $K\alpha$ (Zr filtered)
θ internal (°)	3–25
Scan type/width $\Delta\omega$ (°)	ω–2θ/$0 \cdot 85 + 0 \cdot 40 \tan\theta$
Maximum recording time (min)	3
Control reflexions	$\bar{3}34$; $\bar{2}1\bar{1}$; $\bar{5}4\bar{1}$
μ (mm^{-1})	$1 \cdot 58$
Range of transmission factors	$0 \cdot 77$–$0 \cdot 91$
Number of reflexions measured	6215
Number of reflexions used in the final refinement $[I > 2\sigma(I)]$	3045
Number of parameters	183
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	$0 \cdot 036$
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w\lvert F_o\rvert^2]^{1/2}$	$0 \cdot 041$

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* Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands. XII.

† Lists of structure factors, anisotropic thermal parameters, fractional coordinates and isotropic temperature factors for the H atoms have been deposited with the British Library Lending Division as Supplementay Publication No. SUP 36155 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Fractional coordinates and isotropic temperature factors for the non-*H *atoms*

The values for H are deposited. E.s.d.'s are in parentheses. For Pd, Cl, P and S the isotropic mean values of U_{ij} are given, calculated according to Willis & Pryor (1975).

	x	y	z	U (Å^2)
Pd(1)	0·10868 (7)	−0·17344 (5)	0·17565 (4)	0·0382 (3)
Pd(2)	−0·37793 (8)	0·25996 (6)	0·32346 (5)	0·0488 (3)
Cl(1)	0·0676 (3)	−0·3101 (2)	0·0922 (2)	0·058 (1)
Cl(2)	0·2630 (3)	−0·1062 (2)	0·0460 (2)	0·066 (1)
Cl(3)	−0·2753 (3)	0·1463 (2)	0·4481 (2)	0·080 (1)
Cl(4)	−0·6037 (3)	0·2497 (2)	0·3906 (2)	0·073 (1)
S(1)	0·1569 (2)	−0·0513 (2)	0·2681 (2)	0·044 (1)
S(2)	−0·1591 (3)	0·2707 (3)	0·2489 (2)	0·075 (1)
P(1)	−0·0455 (2)	−0·2158 (2)	0·3003 (2)	0·037 (1)
P(2)	−0·4567 (2)	0·3790 (2)	0·2090 (2)	0·041 (1)
C(1)	0·0037 (9)	−0·1652 (7)	0·4064 (6)	0·043 (3)
C(2)	0·0354 (9)	−0·0536 (7)	0·3808 (6)	0·051 (3)
C(3)	0·1160 (11)	0·0835 (8)	0·2124 (8)	0·071 (3)
C(4)	0·0011 (17)	0·1068 (13)	0·1506 (12)	0·129 (5)
C(5)	−0·1207 (15)	0·1424 (11)	0·1843 (11)	0·113 (5)
C(6)	−0·1794 (11)	0·3832 (8)	0·1582 (8)	0·076 (4)
C(7)	−0·3113 (10)	0·3896 (8)	0·1135 (7)	0·060 (3)
C(8)	−0·0551 (5)	−0·3544 (4)	0·3347 (5)	0·039 (3)
C(9)	0·0692 (5)	−0·4255 (4)	0·3378 (5)	0·054 (3)
C(10)	0·0677 (5)	−0·5330 (4)	0·3698 (5)	0·063 (3)
C(11)	−0·0582 (5)	−0·5694 (4)	0·3986 (5)	0·057 (3)
C(12)	−0·1826 (5)	−0·4984 (4)	0·3955 (5)	0·068 (3)
C(13)	−0·1810 (5)	−0·3909 (4)	0·3636 (5)	0·054 (3)
C(14)	−0·2165 (6)	−0·1431 (4)	0·2855 (3)	0·038 (3)
C(15)	−0·2469 (6)	−0·1102 (4)	0·1913 (3)	0·047 (3)
C(16)	−0·3735 (6)	−0·0463 (4)	0·1778 (3)	0·054 (3)
C(17)	−0·4697 (6)	−0·0153 (4)	0·2585 (3)	0·057 (3)
C(18)	−0·4392 (6)	−0·0482 (4)	0·3527 (3)	0·053 (3)
C(19)	−0·3127 (6)	−0·1122 (4)	0·3662 (3)	0·049 (3)
C(20)	−0·5122 (6)	0·5112 (4)	0·2533 (4)	0·042 (3)
C(21)	−0·5128 (6)	0·6029 (4)	0·1888 (4)	0·058 (3)
C(22)	−0·5476 (6)	0·7043 (4)	0·2245 (4)	0·065 (3)
C(23)	−0·5818 (6)	0·7140 (4)	0·3248 (4)	0·057 (3)
C(24)	−0·5812 (6)	0·6224 (4)	0·3893 (4)	0·051 (3)
C(25)	−0·5464 (6)	0·5210 (4)	0·3536 (4)	0·043 (3)
C(26)	−0·5871 (6)	0·3503 (4)	0·1438 (4)	0·043 (3)
C(27)	−0·5565 (6)	0·2553 (4)	0·0969 (4)	0·061 (3)
C(28)	−0·6458 (6)	0·2329 (4)	0·0364 (4)	0·072 (3)
C(29)	−0·7659 (6)	0·3056 (4)	0·0228 (4)	0·066 (3)
C(30)	−0·7966 (6)	0·4006 (4)	0·0696 (4)	0·062 (3)
C(31)	−0·7072 (6)	0·4230 (4)	0·1302 (4)	0·052 (3)

refinement in $P\bar{1}$ was satisfactory. Magnetic-susceptibility measurements in the temperature interval 80–290 K with a Faraday balance (Blom & Hörlin, 1977) showed the compound to be diamagnetic. The computer work was performed on the Univac 1100 computer in Lund.

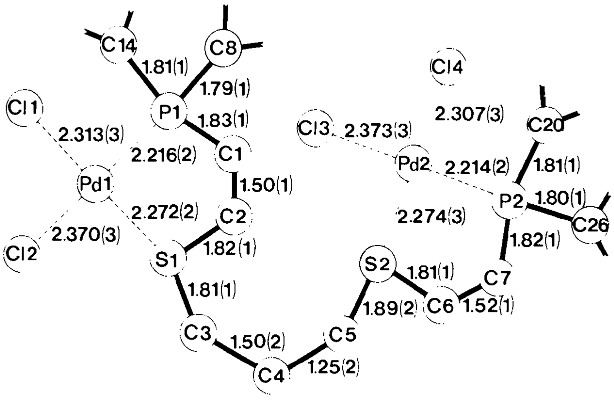

Fig. 1. A schematic drawing of the complex molecule $Pd_2(pssp)Cl_4$ showing interatomic distances (Å). The C–C distances in the phenyl rings (omitted in the drawing) are assumed to be 1·395 Å. The bonds of the ligand chain are drawn with heavy lines, those in the coordination polyhedra of Pd with dashed lines.

Table 3. *Angles* (°) *in the coordination polyhedra of* Pd(1), Pd(2), P(1), P(2), S(1) *and* S(2)

E.s.d.'s are given in parentheses. For labelling, see Fig. 1 and Table 2.

Cl(1)–Pd(1)–Cl(2)	95·2 (1)	Cl(3)–Pd(2)–Cl(4)	95·6 (1)
Cl(1)–Pd(1)–S(1)	174·6 (1)	Cl(3)–Pd(2)–P(2)	173·2 (1)
Cl(1)–Pd(1)–P(1)	90·2 (1)	Cl(3)–Pd(2)–S(2)	87·1 (1)
Cl(2)–Pd(1)–S(1)	87·5 (1)	Cl(4)–Pd(2)–P(2)	89·1 (1)
Cl(2)–Pd(1)–P(1)	173·1 (1)	Cl(4)–Pd(2)–S(2)	176·8 (1)
S(1)–Pd(1)–P(1)	87·5 (1)	S(2)–Pd(2)–P(2)	88·4 (1)
Pd(1)–P(1)–C(1)	105·1 (3)	Pd(2)–P(2)–C(7)	106·5 (3)
Pd(1)–P(1)–C(8)	119·1 (2)	Pd(2)–P(2)–C(20)	111·8 (2)
Pd(1)–P(1)–C(14)	110·6 (2)	Pd(2)–P(2)–C(26)	119·4 (2)
C(1)–P(1)–C(8)	105·2 (3)	C(7)–P(2)–C(20)	106·5 (4)
C(1)–P(1)–C(14)	106·3 (3)	C(7)–P(2)–C(26)	103·0 (4)
C(8)–P(1)–C(14)	109·5 (3)	C(20)–P(2)–C(26)	108·6 (3)
Pd(1)–S(1)–C(2)	106·5 (3)	Pd(2)–S(2)–C(5)	99·4 (5)
Pd(1)–S(1)–C(3)	110·9 (4)	Pd(2)–S(2)–C(6)	104·8 (4)
C(2)–S(1)–C(3)	104·4 (5)	C(5)–S(2)–C(6)	108·5 (6)

Discussion. Selected interatomic distances and angles are given in Fig. 1 and Table 3. A view of the atomic arrangement of $Pd_2(pssp)Cl_4$ and a stereoview of the contents of the unit cell are given in Figs. 2 and 3. In the structures of $[NiI(pssp)][B(C_6H_5)_4]$ (Aurivillius & Bertinsson, 1980) and $[Ni(pssp)][ClO_4]_2$ (Aurivillius & Bertinsson, 1981), fundamental building elements are the ions $[NiI(pssp)]^+$ and $[Ni(pssp)]^{2+}$ respectively. The complexes are thus mononuclear consisting of one ligand molecule, $(C_6H_5)_2P(CH_2)_2S(CH_2)_3S(CH_2)_2$-$P(C_6H_5)_2$ (pssp), coordinating one Ni atom by the two P and the two S atoms. The P and S atoms form the basal plane in a square pyramid with an I atom in the apical position in $[NiI(pssp)]^+$ and the corners in a square plane in $[Ni(pssp)]^{2+}$ respectively. In the complex between pssp and palladium(II) chloride the coordination figure around Pd is also a square plane. The complex is, however, not mononuclear, as in the case of the Ni compounds, but dinuclear (Figs. 1 and 2) and also uncharged. P(1) and S(1) are bonded to Pd(1) forming a five-membered ring ($PdPC_2S$). Cl(1) and Cl(2) are *trans* to S(1) and P(1). The coordination of Pd(2) is similar to that of Pd(1) with Cl(3) and Cl(4) *trans* to P(2) and S(2). C(3), C(4) and C(5) (Fig. 1) act as a connecting bridge between the two square planes of

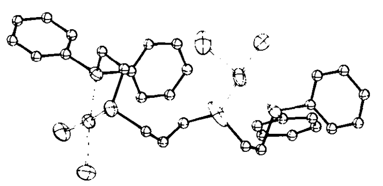

Fig. 2. A drawing of the complex $Pd_2(pssp)Cl_4$. The bonds in the ligand molecule, pssp, are drawn with heavy lines, those in the coordination polyhedra of Pd with double lines. The H atoms are omitted. The ellipsoids of Pd, Cl, P and S are drawn to enclose 50% probability. The C atoms are drawn with a fixed radius of the spheres.

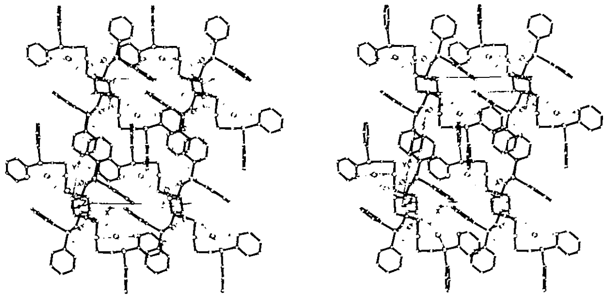

Fig. 3. A stereoview of the contents of one unit cell of $Pd_2(C_{31}H_{34}P_2S_2)Cl_4$. The H atoms are omitted.

Table 4. *The coordination of* Pd: *deviations* (Å) *from the least-squares planes with e.s.d.'s in parentheses*

P, S and Cl were used for the calculation of the planes.

Pd(1)	−0·005 (1)	Pd(2)	−0·040 (1)
P(1)	−0·074 (2)	P(2)	0·045 (2)
S(1)	0·099 (2)	S(2)	−0·096 (3)
Cl(1)	0·082 (3)	Cl(3)	0·074 (3)
Cl(2)	−0·121 (3)	Cl(4)	−0·058 (3)

Pd(1) and Pd(2). The two Pd atoms are situated 0·005 (1) and 0·040 (1) Å outside the least-squares planes formed by the P, S and Cl atoms (Table 4). The distances Pd—P [2·215 (2) Å, mean] are in good agreement with Pd—P [2·22 (1) Å, mean] (P *trans* to Cl) in [bis(diphenylphosphino)ethylamine]dichloropalladium(II) (Mokuolu, Payne & Speakman, 1973) but somewhat shorter than 2·260 (2) Å (P *trans* to Cl) found in *cis*-dichlorobis[dimethyl(phenyl)phosphine]-palladium(II) (Martin & Jacobson, 1971).

The Pd—S distances [2·273 (2) Å, mean] are in good agreement with 2·28 Å (S *trans* to Cl) reported by Stephenson, McConnell & Warren (1967) in (±)-methioninepalladium(II) chloride.

The distances in a square-planar arrangement around a Pd^{2+} ion are dependent on the *trans* influence of the coordinating atoms.

In $Pd_2(pssp)Cl_4$ the distances Pd—Cl (Cl *trans* to P) [2·372 (3) Å, mean] are significantly longer than Pd—Cl (Cl *trans* to S) [2·310 (3) Å, mean] indicating, as expected, a stronger *trans* influence for P. The following values are reported for corresponding distances. Pd—Cl (Cl *trans* to P) 2·37 Å (Mokuolu *et al.*, 1973) and 2·362 (2) Å (Martin & Jacobson, 1971) and for Pd—Cl (Cl *trans* to S) 2·35 Å (Stephenson *et al.*, 1967).

The angles between neighbouring atoms in the square-planar arrangements vary for Pd(1) from 87·5 to 95·2° and for Pd(2) from 87·1 to 95·6° (Table 3). The Cl—Pd—Cl angles are the largest.

The P and the S atoms are, as expected, sp^3 hybridized although in a distorted way (Table 3). For the P atoms the angles vary from 103·0 to 119·4° and for the S atoms from 99·4 to 110·9°. These are in good agreement with the values found in $[Ni(pssp)][ClO_4]_2$.

The mean values of the distances P—C(phenyl) and P—C(methylene) are 1·80 (1) and 1·83 (1) Å respectively, compared to 1·80 (1) and 1·83 (1) Å for $[Ni(pssp)][ClO_4]_2$. The mean S—C distances are 1·81 (1) Å [C(5)—S(2) 1·89 (2) Å excluded] in agreement with 1·84 (1) Å for $[Ni(pssp)][ClO_4]_2$.

The C—C distances and angles are all normal except the C(4)—C(5) distance [1·25 (2) Å] in the connecting bridge. An IR investigation shows no significant indication of a double bond in the structure. The anisotropic thermal ellipsoids of C(4) and C(5) indicate as expected a large motion in the chain C(3), C(4) and C(5). The highest residual electron density in the region is 0·7 e $Å^{-3}$. No alternatives for the positions of C(4) and C(5) could be detected in the difference map. Possibly disorder occurs but alternative positions of these atoms could not be found because of the low resolution of data, about 0·8 Å (*cf.* Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980). Thus our opinion is that the structural formula *A* is the correct one.

The packing of the molecules is shown in Fig. 3. The shortest intermolecular distance is Cl(1)—H(29) (2·58 Å).

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The Structure of *N*-(γ-Hydroxypropyl)granatanine-3-spiro-5′-hydantoin Monohydrate[*][†]

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Abstract. $C_{13}H_{21}N_3O_3.H_2O$, monoclinic, $P2_1/n$, a = 12·389 (1), b = 12·108 (1), c = 9·213 (1) Å, β = 93·80 (3)°, Z = 4, V = 1378·96 (6) Å^3, D_x = 1·374, D_m = 1·38 Mg m^{-3}, μ(Cu $K\alpha$) = 0·80625 mm^{-1}, λ = 1·5418 Å. The structure was solved by direct methods and refined to R = 0·052 for 2195 reflections. The bicyclo[3.3.1]nonane system adopts a boat–chair conformation. The resolution of the structure confirms the interpretation of IR spectra which showed the quaternary character of the piperidine N atom.

Introduction. Crystals of the title compound were supplied by Drs C. Avendaño and P. Ballesteros of the Departamento de Química Orgánica y Farmacéutica de la Facultad de Farmacia de la Universidad Complutense de Madrid. A crystal of dimensions 0·25 × 0·30 × 0·20 mm was used to measure the unit-cell parameters and the intensity data on a Philips PW 1100 automatic diffractometer fitted with a graphite-crystal monochromator. An ω–2θ scanning mode with Cu $K\alpha$ radiation was used to measure 2638 independent reflections with θ values below 65°; 2195 of these were considered as observed [$I > 2\sigma(I)$ where $\sigma(I)$ was determined from counting statistics]. The intensity data were reduced to structure factors and no absorption correction was applied.

The structure was solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1977). 18 out of 20 atoms appeared on the E map calculated with 150 reflections. The two remaining atoms were located in a difference Fourier map. The structure was refined by full-matrix least squares with isotropic and anisotropic thermal factors. All the H atoms, with the exception of the two water H atoms, were located in a difference map, and included only in one cycle of refinement with isotropic temperature factors. In successive cycles these temperature factors were kept fixed. The H atoms of the water were included at ideal positions in the first refinement and, in subsequent refinements, were kept fixed.

The refinement continued to a stage at which no parameter shift was significant. The final R value was 0·052 and R_w = 0·066 where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. A weighting scheme was applied so as to give no trends in $\langle w\Delta^2\rangle$ *vs* $|F_o|$ and sin θ/λ. The expression for the function of the weighting scheme is given in Table 1 (Martinez-Ripoll & Cano, 1975). No trend in sin θ/λ was observed.

The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974).

Computations were carried out with programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970).

Table 1. *Function and coefficients for the weighting scheme*

$w_T = K/|f(|F_o|)|^2,\ 1/f(\sin\theta/\lambda);\ K = 0{\cdot}673;\ f(|F_o|) = a + b|F_o|.$

	a	b
$|F_o| <$ 0·12	–	–
0·12 $< |F_o| <$ 9·53	0·506	0·006
9·53 $< |F_o| <$ 24·38	0·268	0·036
24·38 $< |F_o|$	–0·647	0·065

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[*] The Conformation of Heterocyclic Spiro Compounds. X.

[†] Granatanine is 9-azabicyclo[3.3.1]nonane and hydantoin is 2,4-imidazolidinedione.

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