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cis-[1,4-Bis(diphenylphosphino)-butane](μ-tetrathiotungstato)-palladium(II) *N*,*N*′-dimethylform-amide hemisolvate hemihydrate

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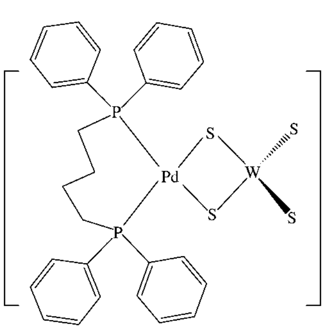
In the title compound, [1,4-bis(diphenylphosphino)butane-$2\kappa^2P,P'$]di-μ-thio-1:$2\kappa^4S$-dithio-$1\kappa^2S$-palladium(II)tungsten(VI) *N*,*N*′-dimethylformamide hemisolvate hemihydrate, [PdWS$_4$-(C$_{28}$H$_{28}$P$_2$)]·0.5C$_3$H$_7$NO·0.5H$_2$O, the Pd atom is coordinated by two S atoms from the distorted-tetrahedral [WS$_4$]$^{2-}$ anion and two P atoms from the dppb molecule [dppb is 1,4-bis(diphenylphosphino)butane] in an approximately square-planar configuration. A puckered seven-membered ring is formed by the Pd atom and the dppb ligand.

Comment

Over the past two decades, transition metal complexes with thiometalate anions, [$MO_{4-n}S_n$]$^{2-}$ (M = Mo and W, and n = 2–4), have been widely studied (Müller *et al.*, 1981; Sarkar & Mishra, 1984; Hou *et al.*, 1996). Many of these complexes play important roles in the fields of catalysis, new materials and medicinal chemistry (Holm & Berg, 1986; Howard *et al.*, 1986; Burgess, 1990; Munakata *et al.*, 1995). Heterobimetallic thiometalate complexes containing dithiolate ligands, namely (Et$_4$N)$_2$PdWS$_4$(S$_2$C$_4$N$_2$) (Long, Zheng *et al.*, 1997), (Et$_4$N)-[PdWS$_4$(S$_2$CNC$_4$H$_8$)] (Long, Wong *et al.*, 1997) and [(C$_2$H$_5$)$_4$N]-[NiWS$_4$(S$_2$CNC$_4$H$_8$)] (Long *et al.*, 1998), have been structurally characterized. Recently, bidentate phosphine ligands, R_2P(CH$_2$)$_n$PR_2 [R = Ph; n = 1 for 1,4-bis(diphenylphosphino)-methane (dppm), n = 2 for 1,4-bis(diphenylphosphino)ethane (dppe) and n = 3 for 1,4-bis(diphenylphosphino)propane (dppp)], which have versatile coordination modes with transition metals, have attracted some attention (Fenske & Langetepe, 2001; Lemaitre *et al.*, 2002; Saravanabharathi *et al.*, 2002). However, only a few examples containing thiometalate and bidentate phosphines have been reported, examples being (dppm)PtWS$_4$ (Potvin *et al.*, 1987) and (dppe)PdWS$_4$, (III) (Wu *et al.*, 1997). We sought to extend our investigations by using different diphosphine ligands to confirm whether the structures of the products were similar to those already reported, anticipating the formation of new cluster frameworks. For example, (dppm)$_2$Pd$_4$W$_2$S$_8$, (II) (Zheng, Leung *et al.*, 2000), has a windmill-shaped structure, whereas (dppp)PdWS$_4$, (IV) (Zheng, Tan *et al.*, 2000), has a so-called 'linear' (binuclear) structure.



$\cdot 0.5\mathrm{Me_2NC(O)H}\cdot 0.5\mathrm{H_2O}$

(I)

The present X-ray crystallographic study of the title compound, [PdWS$_4$(dppb)]·0.5DMF·0.5H$_2$O, (I) [dppb is 1,4-bis(diphenylphosphino)butane and DMF is dimethylformamide], shows that the bond lengths and angles (Table 1) all fall within normal ranges. The Pd atom has a *cis* quasi-square-planar coordination geometry, with two P-donors from the dppb ligand and two S-donors from the [WS$_4$]$^{2-}$ anion (Fig. 1). The average deviation from the least-squares plane through atoms Pd1, P1, P2, S1 and S2 is 0.0533 (11) Å. The W···Pd separation [2.9457 (6) Å] is shorter than that found in the

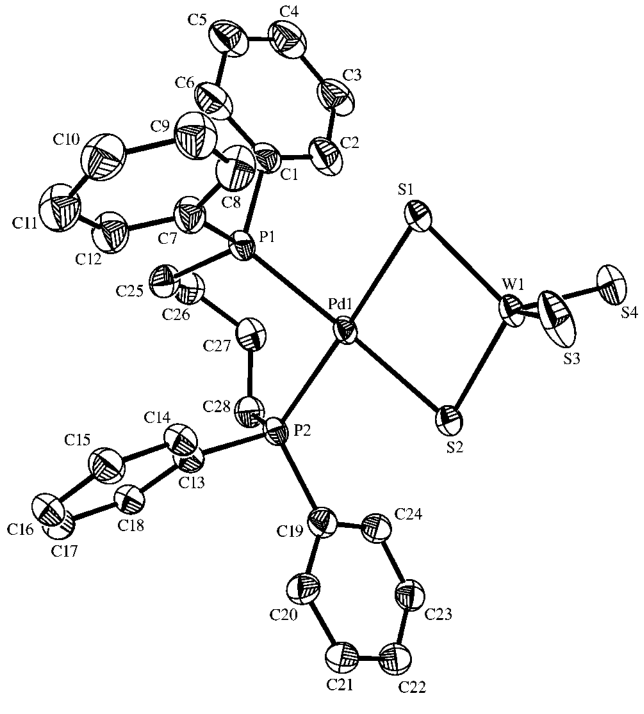


Figure 1
The structure of the title compound, with displacement ellipsoids shown at the 30% probability level. The DMF and water molecules have been omitted for clarity.

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heteroselenometallic compound (Zhang *et al.*, 2002) and is longer than that found in (III) [2.887 (2) Å] and (IV) [2.9259 (6) Å]. The corresponding increase in the W—S—Pd angles, *viz*. from a mean value of 78.0 (2)° for (III) to 79.19 (7)° for (IV) and to 80.27 (5)° for (I), is in accordance with this trend, suggesting that the metal–metal interactions weaken when the alkyl chain length of the diphosphine increases.

The terminal W—S bond distances in (I) [mean 2.12 (2) Å] are comparable to those reported in (III) (mean 2.14 Å) and (IV) (mean 2.15 Å). The bridging W—S [mean 2.21 (2) Å] bond distances are also similar to those found in (III) (mean 2.23 Å) and (IV) (mean 2.22 Å). The $S_{bridge}—W—S_{bridge}$ angles are 105.7 (3), 104.88 (7) and 103.87 (7)° for (III), (IV) and (I), respectively. These parameters suggest that the tetrathiotungstate anion structure is not perturbed significantly in any of these complexes.

As the alkyl chain length increases, the P—Pd—P angles increase from 86.1 (2) (for $n = 2$) to 92.00 (5) (for $n = 3$) and to 92.87 (7)° (for $n = 4$). Concomitant with the increasing P—Pd—P angle is a decrease in the S—Pd—S angle, and thus the S—Pd—S angles are 98.3 (3), 96.98 (5) and 95.57 (7)°. Some puckering of the chains occurs and an unusual seven-membered chelate ring is formed. The Pd—P [mean 2.31 (2) Å] and Pd—S [mean 2.35 (2) Å] bond distances in (I) are within the range reported for $[Pd(S_2CNEt_2)\{Ph_2P(CH_2)_nPPh_2\}]^+$ (Exarchos *et al.*, 2000) and $(PPh_3)Pd(S_2C_4N_2)$ (Long, Zheng *et al.*, 1997), and are similar to those found in (III) and (IV).

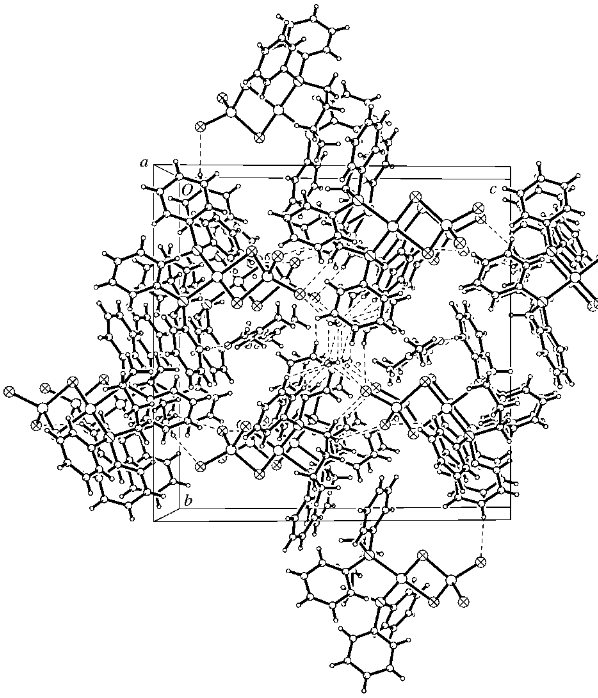

Figure 2
The packing of (I), viewed down the *a* axis. The dashed lines indicate the hydrogen bonds and weak interactions in the crystal structure.

There are weak intermolecular hydrogen bonds between the neutral complex and both the (partially occupied) water and dimethylformamide molecules, namely C24—H24···O1 (H···O = 2.48 Å) and O2—H2*B*···S4 (H···S = 2.32 Å) interactions (Table 2). There are also C3—H3···S3 (H···S = 2.71 Å), C25—H25*B*···S4 (H···S = 2.86 Å), C5—H5···O2 (H···O = 2.47 Å) and C6—H6···O2 (H···O = 2.50 Å) intermolecular close contacts, and one intramolecular C8—H8···S1 (H···S = 2.59 Å) close contact.

Experimental

The title compound was obtained when $PdCl_2(dppb)$ (Steffen & Palenik, 1976) and $(NH_4)_2WS_4$ (McDonald *et al.*, 1983) were added to a solution (20 ml) of CH_2Cl_2 and CH_3CN (1:1, *v*/*v*) and the mixture was stirred for 20 h. After filtration, the solid product was washed with CH_2Cl_2, distilled water, anhydrous ethanol and ether. Single yellow crystals were obtained by diffusing ethyl ether into a DMF solution. Analysis calculated for $C_{29.5}H_{32.5}N_{0.5}OP_2PdS_4W$: C 39.79, H 3.68, N 0.79%; found: C 39.75, H 3.65, N 0.76%.

Crystal data

$[PdWS_4(C_{28}H_{28}P_2)]\cdot 0.5C_3H_7NO\cdot 0.5H_2O$
$M_r = 890.49$
Monoclinic, $P2_1/n$
$a = 9.178$ (1) Å
$b = 19.566$ (2) Å
$c = 19.705$ (2) Å
$\beta = 98.44$ (1)°
$V = 3500.2$ (6) Å^3
$Z = 4$
$D_x = 1.690$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 878 reflections
$\theta = 2.3$–18.5°
$\mu = 4.15$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.3 × 0.2 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.385$, $T_{max} = 0.436$
17 162 measured reflections
6153 independent reflections
4371 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 1.05$
6153 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 1.99P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

W1—S1	2.212 (2)	Pd1—P1	2.301 (2)
W1—S2	2.2170 (18)	Pd1—P2	2.3126 (18)
W1—S3	2.109 (2)	Pd1—S2	2.344 (2)
W1—S4	2.136 (2)	Pd1—S1	2.3637 (19)
S3—W1—S4	108.09 (9)	S3—W1—Pd1	123.27 (7)
S3—W1—S1	110.46 (11)	S4—W1—Pd1	128.63 (6)
S4—W1—S1	110.67 (9)	S1—W1—Pd1	52.22 (5)
S3—W1—S2	111.23 (9)	S2—W1—Pd1	51.70 (5)
S4—W1—S2	112.53 (9)	W1—S1—Pd1	80.07 (7)
S1—W1—S2	103.87 (7)	W1—S2—Pd1	80.40 (6)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$B\cdots$S4$^{\rm i}$	0.85	2.32	2.737 (16)	111
C24—H24$\cdots$O1	0.93	2.48	3.410 (17)	179

Symmetry code: (i) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$.

H atoms were fixed geometrically and refined as riding, with C—H distances of 0.85–0.97 Å and $U_{\rm iso}$ values of $1.2U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1018). Services for accessing these data are described at the back of the journal.

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