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trans-Bis(diethylphenylthiophosphoryl)dichloropalladium(II)

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Abstract. $[PhEt_2P(S)]_2PdCl_2$, $PdCl_2P_2S_2C_{20}H_{30}$, monoclinic, $P2_1/c$, $a=9{\cdot}7783$ (10), $b=9{\cdot}4022$ (5), $c=13{\cdot}3605$ (20) Å, $\beta=91{\cdot}293$ (6)°, $Z=2$, $d_c=1{\cdot}55$ g cm^{-3} $V=1228{\cdot}0$ Å^3. The Pd atoms lie on the special positions in the unit cell with square-planar coordination and mutually *trans* Cl and S atoms. The Pd–S–P bond angle suggests sp^3 hybridization for the S atom.

Introduction. A dark-red crystal of the complex prepared as previously described (Satek, 1974), approximately $0{\cdot}4\times0{\cdot}15\times0{\cdot}15$ mm, was mounted along the needle parallel to **b**. Weissenberg photographs and diffractometry established the space group from systematic absences ($0k0$ absent for k odd; $h0l$ absent for l odd). A Picker FACS-I diffractometer with Mo radiation (graphite monochromator, $K\alpha$, $\lambda=0{\cdot}71069$ Å) was used for lattice parameter and intensity measurements. The final unit-cell parameters were obtained by a least-squares fit to the 2θ values of 12 reflections manually centered at $\pm2\theta$.

Intensities were measured by the θ–2θ scan method with a 2θ rate of $0{\cdot}5°$ min^{-1} and with 10 s background on each side of the scan. Three standard intensities were counted at 100 reflection intervals. 2494 reflections were collected to a 2θ maximum of 50°, giving 2254 unique data (excluding 152 systematically absent); 1807 of these were 3σ above background and classified observed. The structure was solved by the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The crystal system ($P2_1/c$) and two molecules per unit cell indicated the locations of the Pd atoms at the special positions 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. An electron density map phased with Pd revealed two sets of Cl, P and S positions; subsequent electron density maps phased with Pd and each of the probable Cl positions clearly indicated the proper Cl position and gave the correct positions for P and S. The C atoms were located from a difference map phased with the four heavy atoms. Three cycles of anisotropic least-squares refinement and a difference map located all H atoms. Further least-squares refinement was accomplished on all atoms simultaneously, using anisotropic temperature factors for Pd, P, S, Cl and C, isotropic terms for H. The final refinement was by full-matrix least-squares calculations minimizing the function $\sum\omega(F_o-F_c)^2$ where $\omega=1$ for $F_o\le20$ and $\omega=(20/F_o)^2$ for $F_o>20$ [Hughes (1941) scheme]. No absorption corrections were made. The $10\overline{2}$ reflection appeared to suffer from extinction and was thus eliminated from final refine-

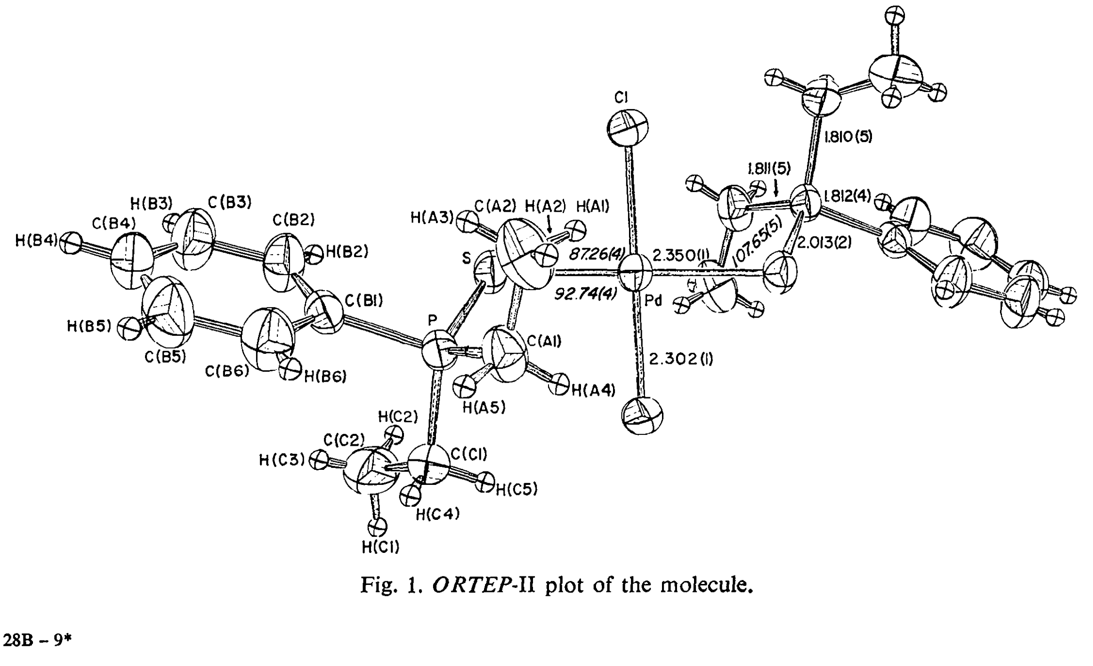

Fig. 1. *ORTEP*-II plot of the molecule.

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Table 1. *Fractional coordinates, temperature factors* (Å) *and e.s.d's* (*in parentheses*)

The form of the anisotropic temperature factors is exp $[-2\pi^2(u_{11}h^2a^{*2}+\ldots 2u_{23}klb^*c^*)]$.

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Pd	0	0	0	0·0350 (2)	0·0391 (2)	0·0477 (3)	0·0010 (2)	−0·0078 (2)	0·0031 (2)
Cl	0·0790 (1)	0·2291 (1)	0·0202 (1)	0·0494 (6)	0·0389 (6)	0·0930 (9)	−0·0028 (5)	−0·0213 (6)	−0·0012 (6)
S	−0·2281 (1)	0·0751 (1)	−0·02069 (8)	0·0323 (5)	0·0478 (6)	0·0565 (6)	0·0029 (4)	−0·0027 (4)	0·0152 (5)
P	−0·2334 (1)	0·2250 (1)	−0·12829 (8)	0·0322 (5)	0·0386 (6)	0·0496 (6)	0·0035 (4)	0·0010 (4)	0·0071 (5)
C(*A*1)	−0·1080 (5)	0·1972 (6)	−0·2241 (4)	0·048 (3)	0·063 (3)	0·060 (3)	0·011 (2)	0·012 (2)	0·013 (2)
C(*A*2)	−0·1115 (8)	0·0496 (8)	−0·2680 (5)	0·078 (4)	0·085 (4)	0·069 (4)	0·027 (4)	0·013 (3)	0·002 (3)
C(*B*1)	−0·4029 (4)	0·2211 (4)	−0·1860 (3)	0·041 (2)	0·039 (2)	0·044 (2)	0·008 (2)	−0·004 (2)	0·003 (2)
C(*B*2)	−0·5137 (5)	0·1672 (6)	−0·1365 (4)	0·044 (2)	0·081 (4)	0·060 (3)	0·002 (2)	−0·004 (2)	0·023 (3)
C(*B*3)	−0·6431 (5)	0·1755 (7)	−0·1783 (5)	0·039 (3)	0·090 (4)	0·083 (4)	0·002 (3)	−0·004 (3)	0·014 (3)
C(*B*4)	−0·6649 (6)	0·2336 (6)	−0·2701 (4)	0·050 (3)	0·065 (3)	0·079 (4)	0·010 (3)	−0·023 (3)	−0·003 (3)
C(*B*5)	−0·5567 (7)	0·2864 (7)	−0·3200 (5)	0·079 (4)	0·093 (5)	0·069 (4)	0·014 (3)	−0·023 (3)	0·024 (3)
C(*B*6)	−0·4267 (6)	0·2813 (7)	−0·2790 (4)	0·057 (3)	0·084 (4)	0·062 (3)	0·000 (3)	0·001 (3)	0·023 (3)
C(*C*1)	−0·2094 (5)	0·4055 (5)	−0·0842 (5)	0·045 (3)	0·040 (2)	0·079 (3)	−0·001 (2)	−0·003 (2)	0·007 (2)
C(*C*2)	−0·3199 (7)	0·4561 (7)	−0·0161 (6)	0·079 (4)	0·058 (4)	0·096 (5)	−0·002 (3)	0·003 (4)	−0·019 (3)

Table 1 (*cont.*)

	x	y	z	u
H(*A*1)	−0·0063 (7)	−0·010 (7)	−0·224 (5)	0·11 (2)
H(*A*2)	−0·066 (6)	0·047 (6)	−0·0326 (5)	0·09 (2)
H(*A*3)	−0·195 (6)	0·032 (6)	−0·296 (4)	0·07 (2)
H(*A*4)	−0·025 (5)	0·216 (5)	−0·194 (4)	0·06 (1)
H(*A*5)	−0·134 (5)	0·259 (6)	−0·275 (4)	0·07 (2)
H(*B*6)	−0·370 (6)	0·310 (6)	−0·305 (4)	0·07 (2)
H(*B*5)	−0·567 (6)	0·319 (7)	−0·375 (5)	0·10 (2)
H(*B*4)	−0·747 (5)	0·236 (5)	−0·294 (4)	0·06 (1)
H(*B*3)	−0·702 (6)	0·162 (6)	−0·148 (4)	0·07 (2)
H(*B*2)	−0·500 (5)	0·139 (6)	−0·079 (4)	0·08 (2)
H(*C*1)	−0·290 (5)	0·548 (7)	0·009 (4)	0·08 (2)
H(*C*2)	−0·322 (8)	0·396 (8)	0·041 (6)	0·13 (3)
H(*C*3)	−0·395 (6)	0·461 (6)	−0·055 (4)	0·09 (2)
H(*C*4)	−0·206 (5)	0·453 (6)	−0·138 (4)	0·07 (2)
H(*C*5)	−0·123 (5)	0·408 (5)	−0·054 (4)	0·07 (1)

ment cycles. Atomic scattering factors for Pd, C, P, S, and Cl were obtained from Cromer & Mann (1968), and for H from Stewart, Davidson & Simpson (1965). In the final least-squares cycles, the average and maximum shifts were 0·06 and 0·7 σ. The final $R(\sum|F_o-F_c|/\sum F_o)$ and weighted $R(\sum\omega(F_o-F_c)^2/\sum\omega F_o^2)$ values were 0·029 and 0·034. The final atomic parameters are listed in Table 1.*

Discussion. The structure was undertaken to unambiguously determine the stereochemistry of the Pd complexes with organophosphine sulfides. The only monodentate complex previously reported, $[Ph_3P(S)]_2PdCl_2$, Bannister & Cotton (1960); King & McQuillan (1967)] did not comment on the structure of the complex. Some ambiguity existed in the following experimental evidence. First, this complex is significantly less soluble than, for example, the corresponding *trans*-phosphine complex, indicating a possible *cis* structure. Second, two bands are observed in the $\nu_{\text{M-Cl}}$ region of the infrared spectrum (335, 325 cm^{-1}), indicative of a *cis*-compound. And third, the intense color of the complex is usually associated with a *trans* configuration. The only structural assignment of an organophosphine sulfide complex with a platinum group metal is *cis*-$[Ph_3P(S)]_2PtCl_2$ (King & McQuillan, 1967) on the basis of physical properties. The second band observed in the infrared spectrum may be attributed to a Pd–S stretch or to some coupling mode in the complex. Full details on the physical and chemical properties of *trans*-$[R_3P(S)]_2PdCl_2$ complexes will be reported shortly (Satek, 1975).

An *ORTEP*-II (Johnson, 1971) plot appears in Fig. 1 with the most significant bond lengths and angles. Other heavy-atom bond lengths and angles appear in Table 2; C–H bond lengths and angles have been deposited with the structure factor table.* Two important features should be noted. First, the P–S bond distance is one of the longest of the few reported to date. Second, the P–S–Pd bond angle is very close to the theoretical 109·5° for sp^3 hybridization. Thus the ligands should be described as coordinating by $R_3\overset{\oplus}{P}\text{–}S^{\ominus}$ rather than $R_3P{=}S$.

We wish to acknowledge the Computer Science Center of the University of Maryland for providing the computer time (to L. C. S.) for this project.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(*A*1)–C(*A*2)	1·507 (9)	C(*A*1)–P———C(*C*1)	106·3 (2)
C(*C*1)–C(*C*2)	1·505 (9)	C(*B*1)–P———C(*C*1)	105·6 (2)
C(*B*1)–C(*B*2)	1·378 (6)	P———C(*C*1)–C(*C*2)	113·8 (4)
C(*B*2)–C(*B*3)	1·374 (7)	P———C(*A*1)–C(*A*2)	113·4 (4)
C(*B*3)–C(*B*4)	1·355 (9)	P———C(*B*1)–C(*B*2)	121·7 (3)
C(*B*4)–C(*B*5)	1·357 (9)	P———C(*B*1)–C(*B*6)	120·5 (3)
C(*B*5)–C(*B*6)	1·373 (9)	C(*B*1)–C(*B*2)–C(*B*3)	120·7 (5)
C(*B*6)–C(*B*1)	1·381 (7)	C(*B*2)–C(*B*3)–C(*B*4)	121·0 (5)
S———P–C(*A*1)	113·4 (2)	C(*B*3)–C(*B*4)–C(*B*5)	118·9 (5)
S———P–C(*B*1)	107·3 (1)	C(*B*4)–C(*B*5)–C(*B*6)	121·1 (6)
S———P–C(*C*1)	115·0 (2)	C(*B*5)–C(*B*6)–C(*B*1)	120·6 (5)
C(*A*1)–P–C(*B*1)	108·9 (2)	C(*B*6)–C(*B*1)–C(*B*2)	117·6 (4)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31143 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* See previous footnote.

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Structure Cristalline du Tétraaquo Bis(méthanesulfonato) Cuivre(II)

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Abstract. $[Cu(CH_3SO_3)_2\ (H_2O)_4]$, monoclinic, $P2_1/c$, $a=9\cdot32\pm0\cdot02$, $b=9\cdot636\pm0\cdot005$, $c=7\cdot31\pm0\cdot01$ Å, $\beta=122\cdot2\pm0\cdot1°$, $Z=2$, $V=555$ Å^3, $M=325\cdot79$, $D_m=1\cdot93$, $D_x=1\cdot95$ g cm^{-3}, $F(000)=334$, $\mu(\text{Mo } K\bar{\alpha})=24\cdot2$ cm^{-1}. $R=0\cdot104$. The molecule is symmetrical with respect to the copper atom, which is octahedrally surrounded by four water molecules in a square-planar arrangement [average Cu–O = 1·971 (6) Å] and two oxygen atoms in axial positions [Cu–O = 2·381 (8) Å], each belonging to one of the symmetrically related methanesulphonato groups. The methanesulphonato groups consist of distorted tetrahedra around the sulphur atom with two equal S–O bonds [1·463 (8) Å] and one of 1·433 (8) Å involving the copper-bonded oxygen, with a longer S–C bond of 1·754 (14) Å.

Introduction. Le tétraaquo bis(méthanesulfonato) cuivre(II) a été obtenu par action d'une solution d'acide méthanesulfonique (Merck) en léger excès sur de l'hydroxyde de cuivre fraîchement préparé selon la méthode de Weiser, Milligan & Cook (1942), améliorée par Gauthier (1958). Après concentration de la solution à 50 °C, le composé cristallisé à 3 °C a été redissous de façon à obtenir des solutions environ 2×10^{-3} M. L'évaporation lente à l'air à temperature ambiante permet d'isoler des aiguilles bleues allongées suivant l'axe [001].

Les paramètres cristallins ont été affinés en minimisant la somme $\sum(\sin^2\theta_o-\sin^2\theta_c)^2$ pour 51 raies d'un cliché de poudre obtenu en radiation Cu $K\alpha_1$ à l'aide d'une chambre de Guinier. Les incertitudes ont été calculées pour une probabilité de 0,1 % de la distribution de Student.

L'enregistrement des niveaux hkn pour $n=0,1,\cdots9$ a été effectué en équi-inclinaison sur chambre de Weissenberg sous rayonnement Mo $K\bar{\alpha}$. Les intensités mesurées au moyen d'un microdensitomètre Nonius ont été corrigées des facteurs de Lorentz et de polarisation, l'absorption étant négligée. Nous avons recueilli ainsi 1211 intensités non nulles.

Comme la maille ne renferme que deux atomes de cuivre, ceux-ci sont nécessairement situés sur les centres de symétrie (positions spéciales du groupe). La fonction de Patterson et la synthèse de Fourier calculée avec les phases dues aux atomes de cuivre ont permis de localiser immédiatement les atomes de soufre, d'oxygène et de carbone. L'affinement des coordonnées et des facteurs d'agitation thermique isotrope des huit atomes du motif asymétrique pratiqué en minimisant la quantité $\sum w(F_o-F_c)^2$ conduit en quatre itérations à un indice $R=\sum||F_o|-|F_c||/\sum|F_o|$ égal à 0,133. La pondération utilisée était $w=(2|F_o|\text{min}+|F_o|+2F_o^2/|F_o|\text{max})^{-1}$. Les atomes de cuivre et de soufre ont seuls été traités ensuite en anisotropie et en trois itérations l'indice a pris une valeur finale égale à 0,104, la pondération étant du type $w=(aF_o^2+bF_o+c)^{-2}$ avec $a=0{,}0022$, $b=-0{,}035$ et $c=1{,}4$.* Nous n'avons pu affiner en anisotropie les atomes d'oxygène et de carbone, certains facteurs d'agitation thermique β_{ij} prenant des valeurs sans signification physique. De même les posi-

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* La liste des facteurs de structure a été déposée au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 31181: 7 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.