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Structure of *trans*-Dichlorobis[(triisobutylphosphine sulphide)-*S*]palladium(II), $[PdCl_2(C_{12}H_{27}PS)_2]$

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Abstract. $M_r = 646{\cdot}06$, monoclinic, $P2_1/c$, $a = 9{\cdot}735\,(1)$, $b = 14{\cdot}956\,(1)$, $c = 11{\cdot}614\,(1)$ Å, $\beta = 102{\cdot}97\,(1)°$, $V = 1647{\cdot}82$ Å^3, $Z = 2$, $D_x = 1{\cdot}302$, $D_m = 1{\cdot}298$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 9{\cdot}43$ cm^{-1}, $F(000) = 680$, $T = 295$ K, $R = 0{\cdot}037$ for 2496 observed reflections. The complex lies on a crystallographic centre of symmetry. The palladium atom is coordinated to two sulphur and two chlorine atoms at the corners of a slightly distorted square. The Pd—Cl, Pd—S, and P—S bond distances are 2·297 (1), 2·334 (1), and 2·014 Å, respectively, and the S—Pd—Cl bond angle is 95·52 (5)°.

Introduction. In a ^{31}P NMR study of palladium(II) chloride complexes of triorganophosphine sulphides, several peaks were observed, including one due to the free ligand (Jones, 1983), instead of the single peak expected. These peaks could be due to a mixture of *cis* and *trans* isomers, as well as to partial polymerization with loss of ligand. Dimeric, trimeric, and tetrameric complexes have been postulated for triphenylphosphine sulphide complexes of palladium(II) thiocyanate (King, McQuillan & Milne, 1973), where bridging is presumed to take place through the thiocyanate ligands, but a copper(I) complex is known where bridging occurs through the thiophosphoryl sulphur (Tiethof, Stalick & Meek, 1973). We are undertaking a study of the complexes which can be isolated from these systems, for a better understanding of their chemical and spectroscopic behaviour.

Experimental. Synthesis by shaking a mixture of triisobutylphosphine sulphide in Varsol with aqueous HCl solutions of Pd^{II} at 328 K, reddish-brown well formed crystals separating on cooling, data crystal $0{\cdot}22 \times 0{\cdot}31 \times 0{\cdot}46$ mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, lattice parameters from 25 reflections with $17 < \theta < 24°$, one standard reflection measured every hour, max. variation 3%, 3455 reflections (h $-11 \rightarrow 11$, k $0 \rightarrow 17$, l $0 \rightarrow 13$) with $\theta < 25°$, 2889 independent, 2496 with $I > 3\sigma(I)$, Lp correction, no absorption correction, heavy-atom method, refinement by full-matrix least squares on F's, H-atom positions calculated, methyl groups treated as rigid rotors with C—H 1·08 Å, H—C—H 109·5°, 163 parameters including the overall scale factor, an extinction correction, 45 positional parameters and 96 anisotropic thermal parameters for the non-H atoms, 18 parameters for the methyl groups, an isotropic temperature factor for the methyl H atoms, and an isotropic temperature factor for the remaining H atoms, $R = 0{\cdot}037$, $R_w = 0{\cdot}042$, max. shift/$\sigma = 0{\cdot}4$ on final cycle, $w = [\sigma^2(F) + 0{\cdot}0002\,F^2]^{-1}$, final difference map with no features greater than $0{\cdot}6$ e Å^{-3} or less than $-0{\cdot}7$ e Å^{-3}, scattering factors including anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974), computer programs *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1976).

Discussion. The atomic coordinates are listed in Table 1, and bond distances and angles are presented in Table 2. A view of the molecule and the numbering scheme are shown in Fig. 1.*

The structure of $[PdCl_2(Bu^i_3PS)_2]$ is similar to that of $[PdCl_2(PhEt_2PS)_2]$ (Satek, Ammon & Stewart, 1975). The Pd—S and Pd—Cl distances are 2·334 (1) and 2·297 (1) Å, respectively, in the present structure and 2·350 (1) and 2·302 (1) Å, respectively, in the latter. The shorter Pd—S length in $[PdCl_2(Bu^i_3PS)_2]$ may be due to the fact that alkylphosphine sulphides are expected to be better σ donors than arylphosphine sulphides. However, the P—S bond lengths in the two structures are essentially identical [2·014 (1) and 2·013 (2) Å]. The Cl—Pd—S and Pd—S—P angles are somewhat greater in $[PdCl_2(Bu^i_3PS)_2]$ than those in $[PdCl_2(PhEt_2PS)_2]$, probably because of the greater spatial requirements of the isobutyl groups.

A search of the Cambridge Structural Database (1984) shows that the P—S bond distance in uncomplexed triorganophosphine sulphide ligands ranges between approximately 1·92 and 1·97 Å. The shortest value was observed by Orama, Karhu & Uggla (1979) for bis(diphenylphosphinothioyl)acetylene, and the longest by Kerr, Boorman, Misener & van Roode (1977) for tricyclohexylphosphine sulphide. Complexing to a

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39718 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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metal ion results in a lengthening of about 0·05 Å; *e.g.* the P—S distances in uncomplexed Me_3PS, $[Cu(Me_3PS)_3]ClO_4$, and $[Cr(CO)_5(Me_3PS)]$ are 1·959 (2), 1·994 (17), and 1·991 Å, respectively (Eller & Corfield, 1971; Baker & Reay, 1973). This lengthening upon coordination is apparently not due to π-bonding effects since Cu^I is a much poorer π donor than Cr^0.

There are no unusual contacts, but the large number of H···H contacts of the order of 2·3–2·4 Å indicates a fairly tight packing arrangement (see Fig. 2). This may be responsible for the relatively low solubility of $[PdCl_2(Bu^i_3PS)_2]$, and may also be the cause of the compression in the C(1)—P—C(9) and S—P—C(5) angles, which are smaller than those usually observed for trialkylphosphine sulphide derivatives. The compression takes place in two mutually perpendicular directions.

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters for* $[PdCl_2(Bu^i_3PS)_2]$

E.s.d's are in parentheses.

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_ia^*_j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Pd	0·00000	0·50000	0·50000	0·0419
Cl	0·06518 (18)	0·51759 (9)	0·32315 (12)	0·0911
S	0·14235 (12)	0·37546 (7)	0·56051 (8)	0·0564
P	0·16441 (10)	0·29914 (6)	0·42292 (8)	0·0446
C(1)	0·2857 (4)	0·3423 (3)	0·3381 (3)	0·052
C(2)	0·4086 (5)	0·3996 (3)	0·4024 (4)	0·064
C(3)	0·4758 (6)	0·4462 (5)	0·3119 (5)	0·098
C(4)	0·5170 (5)	0·3494 (4)	0·4937 (5)	0·087
C(5)	0·2294 (4)	0·1932 (2)	0·4923 (2)	0·052
C(6)	0·2502 (5)	0·1149 (3)	0·4112 (4)	0·071
C(7)	0·2113 (8)	0·0274 (4)	0·4644 (7)	0·110
C(8)	0·3961 (8)	0·1094 (4)	0·3919 (7)	0·120
C(9)	0·0024 (4)	0·2793 (3)	0·3116 (3)	0·054
C(10)	−0·1364 (5)	0·2665 (4)	0·3499 (4)	0·076
C(11)	−0·2543 (6)	0·2595 (6)	0·2384 (5)	0·109
C(12)	−0·1419 (7)	0·1911 (5)	0·4289 (7)	0·122

Table 2. *Bond distances* (Å) *and angles* (°) *in* $[PdCl_2(Bu^i_3PS)_2]$

E.s.d.'s are in parentheses.

Pd—Cl	2·297 (1)	C(5)—C(6)	1·544 (5)
Pd—S	2·334 (1)	C(6)—C(7)	1·531 (7)
S—P	2·014 (1)	C(6)—C(8)	1·489 (7)
P—C(1)	1·818 (4)	P—C(9)	1·826 (3)
C(1)—C(2)	1·523 (5)	C(9)—C(10)	1·526 (6)
C(2)—C(3)	1·526 (6)	C(10)—C(11)	1·529 (6)
C(2)—C(4)	1·517 (6)	C(10)—C(12)	1·462 (7)
P—C(5)	1·825 (3)		
Cl—Pd—S	95·52 (5)	C(1)—C(2)—C(4)	114·3 (4)
Pd—S—P	112·03 (6)	C(3)—C(2)—C(4)	111·7 (4)
S—P—C(1)	115·3 (1)	P—C(5)—C(6)	118·0 (3)
S—P—C(5)	103·3 (1)	C(5)—C(6)—C(7)	108·9 (4)
S—P—C(9)	115·2 (1)	C(5)—C(6)—C(8)	113·2 (4)
C(1)—P—C(5)	110·1 (2)	C(7)—C(6)—C(8)	110·1 (4)
C(1)—P—C(9)	103·7 (2)	P—C(9)—C(10)	119·7 (3)
C(5)—P—C(9)	109·3 (2)	C(9)—C(10)—C(11)	107·9 (4)
P—C(1)—C(2)	117·9 (3)	C(9)—C(10)—C(12)	116·0 (4)
C(1)—C(2)—C(3)	109·3 (4)	C(11)—C(10)—C(12)	110·6 (5)

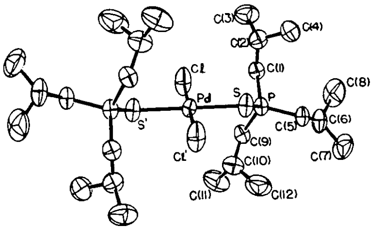

Fig. 1. *ORTEP* drawing (Johnson, 1976) of the $[PdCl_2(Bu^i_3PS)_2]$ molecule. The hydrogen atoms are not shown. The thermal ellipsoids are plotted at the 50% probability level.

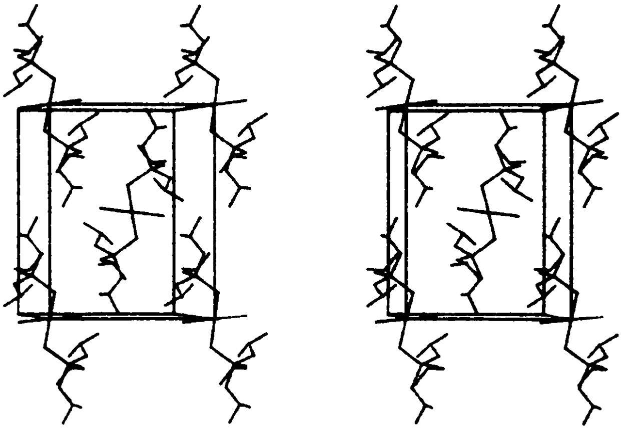

Fig. 2. Packing diagram for $[PdCl_2(Bu^i_3PS)_2]$. The c axis is horizontal, b is vertical.

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References

Baker, E. N. & Reay, B. R. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2205–2208.

Cambridge Structural Database (1984). Univ. Chemical Laboratory, Lensfield Road, Cambridge, England.

Eller, P. G. & Corfield, P. W. R. (1971). *J. Chem. Soc. Chem. Commun.* pp. 105–106.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Jones, T. R. B. (1983). Private communication.

Kerr, K. A., Boorman, P. M., Misener, B. S. & van Roode, J. H. G. (1977). *Can. J. Chem.* **55**, 3081–3085.

King, M. G., McQuillan, G. P. & Milne, R. (1973). *J. Inorg. Nucl. Chem.* **35**, 3039–3041.

Orama, O., Karhu, M. & Uggla, R. (1979). *Cryst. Struct. Commun.* **8**, 905–908.

Satek, L. C., Ammon, H. L. & Stewart, J. M. (1975). *Acta Cryst.* B**31**, 2691–2693.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Tiethof, J. A., Stalick, J. K. & Meek, D. W. (1973). *Inorg. Chem.* **12**, 1170–1174.