Crystal Structure of Di-μ-pentafluorobenzenethiolato-*trans*-bis[(pentafluorobenzenethiolato)(triphenylphosphine)palladium(II)]: A Second Crystal Form

By **R. H. Fenn** * and **G. R. Segrott**, Physics Department, Portsmouth Polytechnic, Park Road, Portsmouth PO1 2DZ

The structure of a second crystal form of the title compound has been determined from three-dimensional *X*-ray data collected photographically. This form is monoclinic, space-group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions: $a = 1{\cdot}32$, $b = 1{\cdot}64$, $c = 1{\cdot}51$ nm, $\beta = 96°$ (all ±1%). The structure was solved by conventional Patterson and Fourier methods and refined by least-squares techniques to R 0·128 for 2230 independent reflections. The ligands are approximately square planar about each palladium atom and the dimer possesses a centre of symmetry so that the non-bridging pentafluorobenzenethiolato-ligands are in the *trans*-configuration. It is suggested that the crystal structure also includes molecules of ethanol.

THE preparation and properties of pentafluorobenzenethiolato-derivatives of palladium(II) have been described[1-3] and a crystal structure of $[Pd^{II}(Ph_3P)(SC_6F_5)_2]_2$ has been determined.[4] However a second crystal form was found, the structure of which is now reported.

EXPERIMENTAL

X-Ray diffraction data were collected photographically from an orange crystal, by use of a Nonius Weissenberg camera for layers 0—11*kl*. The intensities were measured visually and the usual corrections applied but no absorption corrections were made. Layer scale-factors to place all the data on the absolute scale were obtained by a procedure[5] based on Wilson's method.[6] 2230 independent non-zero reflections were observed; unobserved reflections were not included in the structure determination. Only approximate cell dimensions could be obtained as the crystal used for data collection was lost before accurate values were obtained, and no other crystal of this form could be grown. It is to be expected that the measured cell dimensions have errors up to 1%.

Crystal Data.—$C_{60}H_{30}F_{20}P_2Pd_2S_4$, $M = 1534$, Monoclinic, $a = 1{\cdot}32$, $b = 1{\cdot}64$, $c = 1{\cdot}51$ (all ±1%) nm, $\beta = 96°$, $U = 3{\cdot}262$ nm^3, $D_m = 1{\cdot}68(5) \times 10^3$ kg m^{-3} (by flotation), $Z = 2$, D_c (including two molecules of ethanol per dimer) $= 1{\cdot}65 \times 10^3$ kg m^{-3}, $F(000) = 1512$. Space-group $P2_1/c$ (No. 14)[7] from systematic absences: *hkl*, none; *h0l*, $l =$

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[1] R. S. Nyholm, J. F. Skinner, and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 38.

[2] W. Beck, K. H. Stetter, S. Tadros, and K. E. Schwarzhans, *Chem. Ber.*, 1967, **100**, 3944.

[3] W. Beck, W. P. Fehlhammer, K. H. Stetter, and S. Tadros, *Chem. Ber.*, 1967, **100**, 3955.

[4] R. H. Fenn and G. R. Segrott, *J. Chem. Soc.* (*A*), 1970, 3197.

[5] M. T. G. Powell, personal communication.

[6] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[7] 'International Tables for *X*-Ray Crystallography,' vol. I, Kynoch Press, Birmingham, 1952, p. 99.

$2n + 1$, $0k0$, $k = 2n + 1$. Cu-K_α radiation, $\lambda = 0{\cdot}15418$ nm; μ(Cu-K_α) = $76(2) \times 10^2$ m^{-1}.

Structure Determination.—With two dimer molecules per cell in space-group $P2_1/c$, the dimer itself must possess a centre of symmetry. The two terminal pentafluorobenzenethiolato-ligands are thus in the *trans*-position.

A three-dimensional Patterson synthesis was calculated and solved for the positions of the palladium, sulphur, and phosphorus atoms. A three-dimensional electron density distribution and then, after refinement, a difference Fourier synthesis revealed the remaining atoms in the molecules. The difference Fourier synthesis also indicated that the heavier atoms were vibrating anisotropically. The atomic positional parameters, temperature factors, and layer scale-factors were refined by block-diagonal least-squares, the quantity minimized being $\sum_{hkl} w\big||F_o| - |F_c|\big|^2 = \sum_{hkl} \omega\Delta^2$. The weighting scheme was chosen [8] so that the average value of $\Sigma\omega\Delta^2$ was constant for different ranges of $|F_o|$ and the final function used was $\omega = 1$ if $|F_o| < 60$ and $\omega = 60/|F_o|$ if $F_o > 60$. This refinement reduced R to 0·144 and the average $\Sigma\omega\Delta^2$ to 70·2.

TABLE 1

Fractional co-ordinates of non-hydrogen atoms with the estimated standard deviations ($\times 10^4$)

	x/a	y/b	z/c
Pd	109(1)	−47(1)	1214(1)
P	1421(5)	−130(4)	2290(4)
S(1)	−1003(6)	8(6)	2386(4)
S(2)	1146(5)	−209(4)	−16(4)
C(1)	1935(20)	952(17)	2330(18)
C(2)	2881(25)	1136(20)	2131(23)
C(3)	3213(29)	2030(24)	2174(27)
C(4)	2446(31)	2644(27)	2334(28)
C(5)	1564(31)	2418(27)	2679(29)
C(6)	1201(25)	1523(21)	2571(23)
C(7)	2383(19)	−864(16)	2037(18)
C(8)	3329(24)	−792(21)	2466(23)
C(9)	4082(31)	−1462(27)	2223(29)
C(10)	3805(29)	−2037(24)	1622(27)
C(11)	2911(27)	−2172(23)	1278(25)
C(12)	2135(23)	−1526(19)	1463(21)
C(13)	1182(23)	−408(19)	3449(21)
C(14)	1552(21)	77(19)	4186(19)
C(15)	1476(23)	−216(17)	5092(20)
C(16)	940(26)	−930(22)	5243(25)
C(17)	454(29)	−1354(25)	4517(27)
C(18)	583(23)	−1131(19)	3539(21)
C(19)	−1966(23)	670(19)	2036(21)
C(20)	−2918(28)	414(24)	2110(26)
C(21)	−3809(26)	918(22)	1863(24)
C(22)	−3689(25)	1654(21)	1500(23)
C(23)	−2760(27)	1932(22)	1387(25)
C(24)	−1928(25)	1440(22)	1619(23)
C(25)	1888(18)	664(15)	−41(16)
C(26)	2914(22)	528(18)	−92(20)
C(27)	3668(26)	1171(21)	−182(24)
C(28)	3232(27)	1973(22)	−220(24)
C(29)	2322(31)	2156(27)	−146(28)
C(30)	1600(24)	1469(20)	−82(22)
F(20)	3188(17)	4631(13)	2567(19)
F(21)	−4725(16)	597(15)	1950(19)
F(22)	−4469(16)	2148(14)	1234(16)
F(23)	−2569(17)	2726(11)	1010(15)
F(24)	−992(12)	1750(11)	1533(14)
F(26)	3400(11)	−222(10)	4(12)
F(27)	4648(13)	1022(17)	−210(16)
F(28)	3961(19)	2640(16)	−303(17)
F(29)	1952(17)	2940(14)	−155(18)
F(30)	655(15)	1667(10)	−16(14)
O	5401(30)	670(26)	4029(27)
C(31)	5894(40)	788(35)	4779(38)

A second difference Fourier synthesis showed a pair of peaks well removed from the suggested atomic positions. They were of low weight, the peak heights being 2880 and 2380 e nm^{-3} respectively. It was thought that this electron density might represent the oxygen and carbon atoms of a solvent molecule but the low weight indicates that the position of this molecule is slightly disordered or that every equivalent position in every unit cell is not occupied in the crystal. These positions were included in further cycles of refinement giving a final R of 0·128 and mean $\Sigma\omega\Delta^2$ of 58·2 on absolute scale. The differences in the parameters of all other atoms caused by the introduction of the two solvent atoms into the refinement were all $< 2\sigma$. Although caution must be exercised in applying Hamilton's test [9] to unweighted R factors,[10] it would seem that this reduction in R factor for the eight extra parameters included in the refinement is significant.

TABLE 2

(*a*) Isotropic temperature factors ($\times 10^2$ nm^2)

C(1)	3·6	C(12)	4·8	C(23)	6·3
C(2)	5·4	C(13)	4·5	C(24)	5·8
C(3)	7·2	C(14)	4·8	C(25)	2·9
C(4)	8·0	C(15)	4·6	C(26)	4·4
C(5)	7·9	C(16)	6·4	C(27)	6·0
C(6)	5·4	C(17)	7·2	C(28)	6·4
C(7)	3·4	C(18)	4·8	C(29)	7·9
C(8)	5·5	C(19)	4·7	C(30)	5·1
C(9)	8·0	C(20)	6·7		
C(10)	7·2	C(21)	6·2	O	14·5
C(11)	6·7	C(22)	5·7	C(31)	12·0

(*b*) Anisotropic temperature factors given by $\exp[-10^{-5}(\sum_{ij}\Sigma b_{ij}h_ih_j)]$ where $i, j = 1, 2, 3$ ($j \geq i$) and h_i is the ith reflection index

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Pd	416	45	280	366	−37	301
P	441	138	89	310	−7	326
S(1)	647	313	258	577	123	389
S(2)	280	−87	85	365	−30	412
F(20)	1155	1	1318	529	−420	1655
F(21)	883	−409	666	797	122	1641
F(22)	928	445	791	786	−118	1233
F(23)	1568	550	668	368	136	1058
F(24)	544	−249	642	595	242	994
F(26)	374	−50	429	603	−252	828
F(27)	367	−234	977	1283	−53	1263
F(28)	1413	−1333	734	1046	314	1134
F(29)	1186	−154	494	676	280	1317
F(30)	1118	309	840	343	−16	948

The final positions with their estimated standard deviations obtained from the inverse least-squares matrix are given in Table 1 and the temperature factors are given in Table 2.

A final difference Fourier synthesis was calculated and this showed some features around the positions of the heavy atoms. Around the palladium there were values of up to ±3500 e nm^{-3} which were bond-orientated. Elsewhere the mean background was 500 e nm^{-3}.

The calculations were performed on the Polytechnic's ICL 4130 computer using a suite of programmes called 'Crystal '69' written by J. H. Cross, A. Griffiths, and M. T. G. Powell.

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[8] 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon Press, Oxford, 1965, p. 114.

[9] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[10] G. C. Ford and J. S. Rollett, *Acta Cryst.*, 1970, *A*, **26**, 162.

RESULTS

The intramolecular bond lengths and angles are given in Tables 3 and 4 and a projection of the dimer on to the plane of the heavy atom network (S, Pd, P, S) is shown in the Figure. Both the molecule whose structure has been determined here and that previously determined [4] in the other crystal form are *trans*-isomers. However, the solvent in the original preparation of the complex [1] was ethanol and it is suggested that this crystal structure includes ethanol with a disordered methyl group position, since the methyl carbon has not been located.

TABLE 3

Intramolecular bond lengths ($\times 10^3$ nm) with estimated standard deviations in the least significant figure

Pd–P	224·9(7)	S(1)–C(19)	171(3)
Pd–S(1)	241·4(7)	S(2)–C(25)	174(3)
Pd–S(2′)	235·8(7)		
Pd–S(2)	243·2(7)	C(19)–C(20)	134(5)
P–C(1)	190(3)	C(20)–C(21)	145(5)
P–C(7)	182(3)	C(21)–C(22)	134(5)
P–C(13)	187(3)	C(22)–C(23)	133(5)
Mean P–C	186	C(23)–C(24)	138(5)
		C(24)–C(19)	141(5)
C(1)–C(2)	135(4)	C(25)–C(26)	138(4)
C(2)–C(3)	153(5)	C(26)–C(27)	146(5)
C(3)–C(4)	146(6)	C(27)–C(28)	143(5)
C(4)–C(5)	137(6)	C(28)–C(29)	125(6)
C(5)–C(6)	155(6)	C(29)–C(30)	148(5)
C(6)–C(1)	142(4)	C(30)–C(25)	137(4)
C(7)–C(8)	135(4)	Mean C–C(C_6F_5)	139
C(8)–C(9)	155(5)		
C(9)–C(10)	133(6)	C(20)–F(20)	143(5)
C(10)–C(11)	126(5)	C(21)–F(21)	134(4)
C(11)–C(12)	152(5)	C(22)–F(22)	134(4)
C(12)–C(7)	140(4)	C(23)–F(23)	145(4)
C(13)–C(14)	141(4)	C(24)–F(24)	135(4)
C(14)–C(15)	146(4)	C(26)–F(26)	139(3)
C(15)–C(16)	140(5)	C(27)–F(27)	132(4)
C(16)–C(17)	140(5)	C(28)–F(28)	147(4)
C(17)–C(18)	155(5)	C(29)–F(29)	137(5)
C(18)–C(13)	144(4)	C(30)–F(30)	130(4)
Mean C–C(Ph)	143	Mean C–F	138
Solvent molecule O–C(31)	126(7)		

The mean bond lengths in the dimer are, in the phenyl rings, C–C 0·143 nm, and in the pentafluorobenzene rings, C–C 0·139 and C–F 0·138 nm. These last two values agree closely with those found in other pentafluorobenzene complexes; a comparison between crystal structures including this group is given in Table 5. In addition this complex follows the trend previously noted [11–14] that in C_6F_5X complexes, the ring angle at the carbon bonded to X is less than 120° with other angles (X–C–C) greater than 120° to maintain the planarity of the group.

TABLE 4

Intramolecular bond angles (°) with estimated standard deviations in the least significant figure

P–Pd–S(1)	87·2(2)	P–Pd–S(2)	95·5(2)
S(2)–Pd–S(2)′	80·6(2)	S(1)–Pd–S(2)	174·9(3)
		P–Pd–S(2)′	171·8(3)
Pd–P–C(1)	102·2(9)	Pd–S(1)–C(19)	106·5(11)
Pd–P–C(7)	112·8(9)	Pd–S(2)–C(25)	106·8(9)
Pd–P–C(13)	120·0(10)	Pd–S(2)′–C(25)′	100·8(9)
P–C(1)–C(2)	122(2)	P–C(7)–C(8)	118(2)
P–C(1)–C(6)	112(2)	P–C(7)–C(12)	121(2)
C(1)–C(2)–C(3)	118(3)	C(7)–C(8)–C(9)	114(3)
C(2)–C(3)–C(4)	118(3)	C(8)–C(9)–C(10)	122(4)
C(3)–C(4)–C(5)	120(4)	C(9)–C(10)–C(11)	126(4)
C(4)–C(5)–C(6)	119(4)	C(10)–C(11)–C(12)	115(3)
C(5)–C(6)–C(1)	116(3)	C(11)–C(12)–C(7)	122(3)
C(6)–C(1)–C(2)	125(3)	C(12)–C(7)–C(8)	121(3)
P–C(13)–C(14)	122(2)	P–C(13)–C(18)	116(2)
C(13)–C(14)–C(15)	120(3)	C(16)–C(17)–C(18)	123(3)
C(14)–C(15)–C(16)	121(3)	C(17)–C(18)–C(13)	114(3)
C(15)–C(16)–C(17)	119(3)	C(18)–C(13)–C(14)	122(3)
		Mean P–C–C	118
		C–C–C(Ph)	120
S(1)–C(19)–C(20)	117(3)	S(2)–C(25)–C(26)	115(2)
S(1)–C(19)–C(24)	130(2)	S(2)–C(25)–C(30)	130(2)
C(19)–C(20)–C(21)	123(3)	C(25)–C(26)–C(27)	125(3)
C(20)–C(21)–C(22)	119(3)	C(26)–C(27)–C(28)	113(3)
C(21)–C(22)–C(23)	121(3)	C(27)–C(28)–C(29)	127(4)
C(22)–C(23)–C(24)	119(3)	C(28)–C(29)–C(30)	117(4)
C(23)–C(24)–C(19)	125(3)	C(29)–C(30)–C(25)	124(3)
C(24)–C(19)–C(20)	113(3)	C(30)–C(25)–C(26)	115(3)
		Mean C–C–C(C_6F_5)	120
C(19)–C(20)–F(20)	93(3)	C(25)–C(26)–F(26)	126(2)
C(20)–C(21)–F(21)	118(3)	C(26)–C(27)–F(27)	123(3)
C(21)–C(22)–F(22)	123(3)	C(27)–C(28)–F(28)	115(3)
C(22)–C(23)–F(23)	124(3)	C(28)–C(29)–F(29)	124(4)
C(23)–C(24)–F(24)	118(3)	C(29)–C(30)–F(30)	116(3)
		Mean C–C–F(C_6F_5)	118

TABLE 5

Comparison between mean bond lengths (nm) and angles (°) in crystal structures including the group C_6F_5X

Compound	C–C	C–F	C–C–C (all)	X–C–C	C–C–C (at X)
$Hg(C_6F_5)_2$ [a]	0·138	0·139	119·9	121·8	116·4
(π-C_7H_7)$Mo(C_6F_5)(CO)_2$ [b]	0·1381(12)	0·1344(12)	120·0(9)	122·8(5)	114·0(8)
(π-C_5H_5)$Ni(C_6F_5)(PPh_3)$ [c]	0·1384(23)	0·1342(18)	120·0(14)	122·9(11)	144·2(13)
$(PC_6F_5)_4$ [d]	0·1376(6)	0·1337(5)	120·0(3)	122·3(2)	115·2(3)
$(C_6F_5)_2Tl(OH)$ [e]	0·141(5)	0·137(4)	120(3)	122	116(3)
$Pt(Bu_3P)_2(SC_6F_5)_2$ [f]	0·137(5)	0·134(5)	120(4)	121(2)	118(3)
$[Pd(Ph_3P)(SC_6F_5)_2]_2$ [g]	0·137(7)	0·138(6)	120(4)	124(2)	111(4)
$[Pd(Ph_3P)(SC_6F_5)_2]_2$ [h]	0·139(5)	0·138(4)	120(3)	123(2)	114(3)

[a] N. R. Kunchur and M. Mathew, *Chem. Comm.*, 1966, 71. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13. [e] H. Luth and M. R. Truter, *J. Chem. Soc.* (*A*), 1970, 1287. [f] Ref. 14. [g] Ref. 4. [h] This work.

Several best least-squares planes were calculated and their equations and distances of atoms from them are given in Table 6; a comparison between the angles between the planes and the molecules (A) and (B) in the other crystal

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[11] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1969, 1110.

[12] M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1968, 2970.

[13] F. Sanz and J. J. Daly, *J. Chem. Soc.* (*A*), 1971, 1083.

[14] R. H. Fenn and G. R. Segrott, *J. Chem. Soc.* (*A*), 1970, 2781.

form is given in Table 7. From these angles it can be seen that the pentafluorobenzene rings are similarly positioned whereas there is much more variation in the position of the phenyl rings. Thus it seems that the triphenylphosphine ligand is more easily distorted by crystal packing than the pentafluorobenzene ligands.

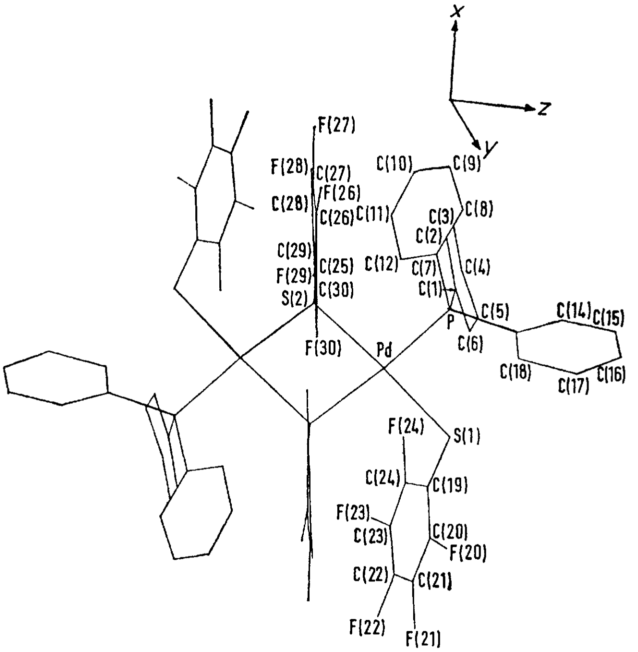
TABLE 6

Best fit planes with equations of the form $AX' + BY' + CZ' + 1 = 0$,* and, in square brackets, distances (nm) of relevant atoms from the planes

Plane	Atoms	A	B	C	Distances
Plane (1):	C(1)—(6)	−0·714	0·252	−2·507	[C(1) 0·0023, C(2) −0·0010, C(3) −0·0048, C(4) 0·0100, C(5) −0·0099, C(6) 0·0040]
Plane (2):	C(7)—(12)	1·428	2·488	−3·388	[C(7) 0·0029, C(8) −0·0017, C(9) −0·0024, C(10) 0·0051, C(11) −0·0039, C(12) 0·0003]
Plane (3):	C(13)—(18)	−6·519	4·174	−0·167	[C(13) −0·0033, C(14) 0·0060, C(15) −0·0023, C(16) −0·0045, C(17) 0·0046, C(18) 0·0002]
Plane (4):	C(19)—(24), F(20)—(24)	0·097	−1·207	−2·780	[C(19) −0·0037, C(20) −0·0013, C(21) −0·0039, C(22) −0·0011, C(23) 0·0002, C(24) 0·0038, F(20) 0·0039, F(21) 0·0012, F(22) 0·0001, F(23) 0·0014, F(24) −0·0005]
Plane (5):	C(25)—(30), F(26)—(30)	−2·847	−2·717	−35·737	[C(25) 0·0059, C(26) 0·0045, C(27) 0·0020, C(28) 0·0023, C(29) −0·0015, C(30) 0·0051, F(26) −0·0054, F(27) −0·0002, F(28) −0·0013, F(29) −0·0060, F(30) 0·0028]
Plane (6):	S(1), S(2), P	2·896	42·005	−1·575	

* X', Y', and Z' are orthogonal axes related to the crystal axes by $X' = X + Z \cos \beta$, $Y' = Y$, and $Z' = Z \sin \beta$.

The closest intermolecular contacts between dimers are F(27) and F(22) displaced (1, 0, 0) 0·300 nm and F(27) and F(26) related by a centre of symmetry at ($\frac{1}{2}$, 0, 0) 0·287 nm. All other intermolecular contacts are >0·3 nm. The shortest intermolecular contact involving the suggested solvent atoms is 0·313 nm between F(21) and the oxygen displaced (1, 0, 0). All other contacts are >0·35 nm. Thus the ethanol is situated in a large hole in the crystal structure.



Dimer projected on to plane of Pd, S(1), S(2), and P

TABLE 7

Comparison of angles (°) between planes in this structure and molecules (A) and (B) in the previous crystal form *

Planes	Present work	Molecule (A)	Molecule (B)
(1)–(2)	45·8	68·3	77·2
(1)–(3)	72·4	59·1	65·7
(2)–(3)	87·3	76·2	78·2
(1)–(6)	83·5	80·7	85·3
(2)–(6)	52·5	88·2	69·8
(3)–(6)	61·3	51·9	49·7
(4)–(5)	20·1	9·0	20·0
(4)–(6)	68·9	72·8	66·8
(5)–(6)	87·5	78·8	84·4

* Ref. 4.

[1/1422 *Received, August* 11*th*, 1971]