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Structures of Difluorophosphine Sulfide at 98 K and Difluorophosphine Oxide at 158 K

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Abstract. PF_2HS, $M_r = 102{\cdot}04$, monoclinic, $P2_1/c$, $a = 9{\cdot}2034\,(27)$, $b = 4{\cdot}383\,(8)$, $c = 8{\cdot}5370\,(27)$ Å, $\beta = 98{\cdot}766\,(25)°$, $U = 340{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}992$ Mg m^{-3}, $T = 98$ K, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}120$ mm^{-1}, $F(000) = 200$, $R = 0{\cdot}0414$ for 934 unique observed reflections. The structure comprises discrete molecules in which the P=S bond length is 1·8782 (5) Å, the P—F bond lengths 1·5480 (10) and 1·5432 (10) Å. The environment at P is markedly distorted from tetrahedral, with SPF angles of 115·65 (4) and 115·92 (4)° and an FPF angle of 98·50 (5)°. The molecular structure in the crystal is very similar to that in the gas phase. PF_2HO, $M_r = 85{\cdot}98$, orthorhombic, $Pbca$, $a = 14{\cdot}363\,(9)$, $b = 5{\cdot}974\,(8)$, $c = 6{\cdot}464\,(3)$ Å, $U = 554{\cdot}6$ Å^3, $Z = 8$, $D_x = 2{\cdot}059$ Mg m^{-3}, $T = 158$ K, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}69$ mm^{-1}, $F(000) = 336$, $R = 0{\cdot}0802$ for 349 unique observed reflections. The structure of the oxide consists of molecules which participate in extensive O···P intermolecular contacts to form corrugated sheets, in marked contrast to that of the sulfide. Individual molecules have short P—F bonds of 1·528 (6) and 1·530 (6) Å and a P=O bond length of 1·435 (6) Å. Angles around P are again substantially distorted from tetrahedral, with OPF angles of 113·2 (3) and 114·5 (4)° and an FPF angle of 99·3 (3)°.

Introduction. As part of our established programme of work on low-melting inorganic compounds, we are interested in the crystal structures of species containing PF_2— substituents (Barrow, Ebsworth, Harding & Henderson, 1979; Blake, Cradock, Ebsworth, Rankin & Welch, 1984; Blake, Ebsworth & Welch, 1984). The lattice structures of PF_2HY (Y = O, S) are particularly interesting because of the range of possible intermolecular interactions, and especially of P=O···H—P hydrogen bonding which might be regarded as leading to incipient tautomerization to the $PF_2(OH)$ form. In addition, relatively few studies have investigated the structural consequences of varying the chalcogen atom in simple phosphine chalcogenides (*e.g.* Blake & McQuillan, 1984). We have therefore determined the crystal structures of difluorophosphine sulfide (m.p. 188 K) and difluorophosphine oxide (m.p. 248 K). Gas-phase structural data for these compounds have previously been obtained from electron diffraction and other data (Blair, Cradock & Rankin, 1985), and microwave spectroscopy (Centofanti & Kuczkowski, 1968) respectively.

Experimental. Colourless cylindrical crystal of PF_2HS, 0·4 × 0·4 × 0·5 mm, grown *in situ* from sample sealed in Pyrex capillary on Weissenberg camera equipped with low-temperature device. Space group identified by oscillation and Weissenberg photography, crystal transferred without melting to similarly equipped CAD-4 diffractometer, 98 K, 25 reflections ($17 < \theta < 18°$) for refinement of orientation matrix, graphite-monochromated Mo $K\alpha$ radiation. For data collection, $\theta_{\max} = 30°$, ω–2θ scans with ω-scan width $(0{\cdot}80 + 0{\cdot}35\tan\theta)°$, rapid prescan after which reflections with $I > 0{\cdot}5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 75 s. Data corrected for isotropic crystal decay (min. 0·837, max. 1·117). 1167 reflections, 985 unique in 11 X-ray hours. No absorption correction. For structure solution and refinement 934 reflections with $F > 2\sigma(F)$, automatic direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least squares (F) (Sheldrick, 1976), $w^{-1} = \sigma^2(F) + 0{\cdot}003937F^2$, anisotropic thermal parameters for S, P and F, isotropic for H; R, wR 0·0414, 0·0573, S 0·902, data:variable ratio 23:1, max. shift/e.s.d. in final cycle <0·01, max. peak and min. trough in final difference Fourier synthesis 0·64 and −0·90 e Å^{-3} respectively. No correction for secondary extinction.

Colourless cylindrical crystal of PF_2HO, 0·2 × 0·1 × 0·2 mm, grown as above. Space group identified as above. Crystal transferred to CAD-4 diffractometer, 158 K, 25 reflections ($8 < \theta < 10°$) for refinement of orientation matrix, graphite-monochromated Mo $K\alpha$ radiation. For data collection, $\theta_{\max} = 30°$, ω–2θ scans with ω-scan width $(1{\cdot}2 + 0{\cdot}5\tan\theta)°$. Rapid prescan after which reflections with $I > 0{\cdot}5\sigma(I)$ remeasured such that final net intensity had $I > 50\sigma(I)$ subject to maximum measuring time of 90 s. Crystal orientation checked every 30 reflections and reset if necessary. No significant crystal decay or movement, 803 reflections over 24 X-ray hours, no absorption correction. For structure solution and refinement 347 reflections with $F > 2\sigma(F)$, Patterson and successive difference Fourier

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syntheses (Sheldrick, 1976), full-matrix least squares (F), $w^{-1} = \sigma^2(F) + 0{\cdot}00106F^2$, anisotropic thermal parameters for P, F and O, isotropic for H; R, wR 0·0802, 0·0692, S 1·123, data:variable ratio 8:1, max. shift/e.s.d. in final cycle <0·01. Max. peak and min. trough in final difference Fourier synthesis 0·88 and −0·92 e Å^{-3} respectively. No correction for secondary extinction.

Neutral-atom scattering factors for S, P, F, O and H (Sheldrick, 1976), computer programs *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), *SHELX*76 (Sheldrick, 1976), *ORTEP*II (Mallinson & Muir, 1985), *PLUTO* (Motherwell, 1976) and *CALC* (Gould & Taylor, 1986).

Discussion. PF_2HS. Table 1 lists derived fractional coordinates and thermal parameters* and Fig. 1 shows a perspective view of the molecule. Table 2 lists interatomic distances and interbond angles.

Table 1. *Positional (fractional coordinates) and thermal parameters* (Å^2) *with e.s.d.'s for* PF_2HS

	x	y	z
P	0·27149 (3)	0·46268 (8)	0·08370 (3)
F(1)	0·38511 (10)	0·26566 (21)	0·01296 (11)
F(2)	0·37916 (10)	0·64426 (20)	0·20544 (11)
S	0·12384 (4)	0·24584 (8)	0·16557 (4)
H	0·2393 (21)	0·662 (6)	−0·036 (3)

	U or U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0·0231 (3)	0·0132 (3)	0·0214 (3)	0·0004 (1)	0·0068 (2)	0·0002 (1)
F(1)	0·0297 (5)	0·0256 (5)	0·0356 (5)	−0·0050 (3)	0·0165 (4)	0·0007 (3)
F(2)	0·0338 (5)	0·0232 (5)	0·0316 (4)	−0·0062 (3)	0·0037 (3)	−0·0064 (4)
S	0·0234 (3)	0·0242 (3)	0·0318 (3)	0·0062 (1)	0·0108 (2)	0·0008 (1)
H	0·035 (5)					

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *for* PF_2HS

P—F(1)	1·5480 (10)	P—S	1·8782 (5)
P—F(2)	1·5432 (10)	P—H	1·345 (23)
F(1)—P—F(2)	98·50 (5)	F(2)—P—S	115·92 (4)
F(1)—P—S	115·65 (4)	F(2)—P—H	102·9 (10)
F(1)—P—H	98·5 (10)	S—P—H	121·6 (10)

As shown in Fig. 2, the solid-state structure of PF_2HS contains essentially isolated molecules, with no close S···H contacts which would suggest incipient formation of the P^{iii} species $PF_2(SH)$. The only significant contacts are between the S atoms of molecules related by the c-glide. The S···S distance of 3·6160 (6) Å lies just within the sum of the van der Waals radii (3·70 Å); this fairly close approach suggests there is no significant charge on the S atoms and that the P=S bond is essentially non-polar. The S atoms may be envisaged as forming very loosely bound, zigzag (S···S···S = 74·62°) infinite chains. The molecular parameters (Table 2) are essentially identical to those obtained from vapour-phase electron diffraction and other data (Blair, Cradock & Rankin, 1985); this is consistent with the absence of strong intermolecular forces. The P=S bond length of 1·8782 (5) Å is comparable to those found in similar P=S species containing electronegative substituents at P, such as PF_3S, $PClF_2S$ and PCl_3S (Acha, Cromie & Rankin, 1981) and considerably shorter than those found in trialkylphosphine sulfides which fall in the range 1·94–1·96 Å. The SPF and SPH angles are considerably greater than tetrahedral.

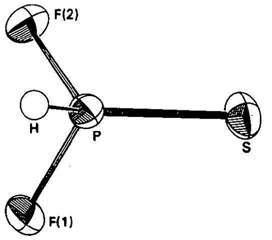

Fig. 1. View of a single molecule of PF_2HS.

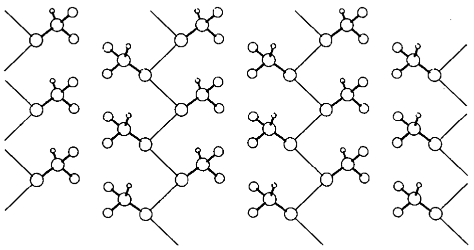

Fig. 2. Packing of PF_2HS molecules viewed along the b axis.

PF_2HO. Table 3 lists derived fractional coordinates and thermal parameters and Fig. 3 shows a perspective view of the molecule. Table 4 lists interatomic distances and interbond angles. As shown in Fig. 4 and detailed in Table 5, the crystalline structure of PF_2HO contains extensive intermolecular contacts. In addition to the primary bonding illustrated in Fig. 3, each P is also involved in secondary contacts to two O atoms, giving the P (4 + 2) coordination and an O···P···O angle of 107·79 (18)°: the O···P···O plane is essentially normal to the P=O bond. Moreover, it also appears that each O may be involved in hydrogen bonding to H, which also participates in an F···H contact; the large uncertainty in the H-atom position precludes any definitive conclusion as to the significance of hydrogen bonding in this structure (but see below). It may be indicative of weaker interaction that the involvement of only one F does not give inequivalent P—F distances as seen in PF_2NH_2 (Blake, Cradock, Ebsworth, Rankin & Welch, 1984) and PF_2NHMe (Blake, Ebsworth & Welch, 1984). The intermolecular interactions result in

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44722 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional (fractional coordinates) and thermal parameters* (Å²) *with e.s.d.'s for* PF_2HO

	x	*y*	*z*
P	0·14699 (15)	0·5540 (4)	0·1841 (3)
F(1)	0·1043 (3)	0·3798 (9)	0·0393 (9)
F(2)	0·0577 (3)	0·6512 (10)	0·2769 (9)
O	0·2044 (4)	0·7143 (11)	0·0787 (9)
H	0·168 (5)	0·392 (18)	0·363 (14)

	U or U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	0·0182 (8)	0·0170 (9)	0·0150 (8)	−0·0016 (12)	0·0017 (12)	−0·0002 (12)
F(1)	0·0234 (23)	0·027 (3)	0·039 (4)	−0·0137 (28)	−0·0037 (24)	−0·0039 (22)
F(2)	0·0204 (25)	0·040 (3)	0·044 (4)	−0·010 (3)	0·0069 (24)	0·0093 (27)
O	0·0298 (27)	0·027 (4)	0·020 (3)	0·005 (3)	−0·0014 (29)	−0·0067 (28)
H	0·05 (3)					

Table 4. *Interatomic distances* (Å) *and interbond angles* (°) *for* PF_2HO

P–F(1)	1·528 (6)	P–O	1·435 (6)
P–F(2)	1·530 (6)	P–H	1·54 (9)
F(1)–P–F(2)	99·3 (3)	F(2)–P–O	114·5 (4)
F(1)–P–O	113·2 (3)	F(2)–P–H	96 (3)
F(1)–P–H	96 (3)	O–P–H	132 (3)

Table 5. *Selected intermolecular contacts A—B···C—D* (Å, °)

A B C D	Symmetry *A B*	*B···C* (Å)	*A—B···C* (°)	*B···C—D* (°)
P O P O	$\frac{1}{2}-x, -\frac{1}{2}+y, z$	3·023 (7)	138·3 (4)	86·28 (29)
F(1)	$\frac{1}{2}-x, -\frac{1}{2}+y, z$			71·83 (24)
F(2)	$\frac{1}{2}-x, -\frac{1}{2}+y, z$			159·17 (27)
H	$\frac{1}{2}-x, -\frac{1}{2}+y, z$			67 (3)
P O P O	$x, \frac{3}{2}+y, \frac{1}{2}+z$	3·017 (7)	124·6 (3)	86·45 (29)
F(1)	$x, \frac{3}{2}+y, \frac{1}{2}+z$			160·04 (26)
F(2)	$x, \frac{3}{2}+y, \frac{1}{2}+z$			73·95 (25)
H	$x, \frac{3}{2}+y, \frac{1}{2}+z$			66 (3)
P H O P	$\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$	2·39 (9)	99·3 (26)	123 (2)
P H F P	$x, \frac{1}{2}-y, -\frac{1}{2}+z$	2·18 (9)	141 (5)	131 (2)

corrugated layers of molecules with no close contacts between the layers, reminiscent of the structure of PF_2NH_2; they also provide an explanation for both the higher melting point and the higher density of PF_2HO relative to PF_2HS.*

The heavy-atom (PF_2O) skeleton of the molecule in the crystal is similar to that found in the vapour by microwave spectroscopy (Centofanti & Kuczkowski, 1968). In both phases short P=O and P—F bonds are observed, the former characteristic of species with electronegative substituents on P such as $POCl_3$ (Olie, 1971), which has a P=O bond of 1·456 (10) Å. The invariance of the P=O bond distance from gas to solid suggests that the electron density on O involved in intermolecular bonding is essentially non-bonding with respect to this bond.

For gaseous species, the length of the P—F bond decreases from 1·582 (2) Å in PF_2H (Kuczkowski, 1968) to 1·546 (2) Å in PF_2HS (Blair, Cradock & Rankin, 1985) and 1·539 (3) Å in PF_2HO (Centofanti & Kuczkowski, 1968); there is a similar trend in the crystalline state from PF_2HS to PF_2HO. This implies a shortening of the P—F bonds as electronegative S or more electronegative O is added to PF_2H; the shortening may arise through increased π donation from F to P, though polar effects may also be important. The FPF angles do not appear to be sensitive to this addition. The SPF angles in PF_2HS are wider than the OPF angles in PF_2HO.

The molecular parameters which show the greatest *apparent* differences between PF_2HO in the crystal and in the vapour (and between the oxide and sulfide in the crystal) are those involving the H atom. At 1·54 Å, the P—H distance is long even before allowance is made for the underestimation of the lengths of bonds to H by X-ray methods, but the estimated standard deviation of 0·10 Å is so large that the difference from the gas-phase value of 1·387 (10) Å is not significant and no conclusions as to the presence of hydrogen bonding can be drawn from these values.

Examination of the published gas-phase and solid IR spectra of the compound (Centofanti & Parry, 1970) is useful here, since significant hydrogen bonding is expected to result in a lower P—H stretching frequency in the solid. However, the respective frequencies for gas and solid are 2570 and 2503 cm^{-1}, and we interpret this as indicating the absence of substantial hydrogen bonding. It appears therefore that there is no representation of the P^{III} form, $PF_2(OH)$, in the crystal.

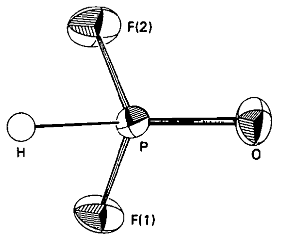

Fig. 3. View of a single molecule of PF_2HO.

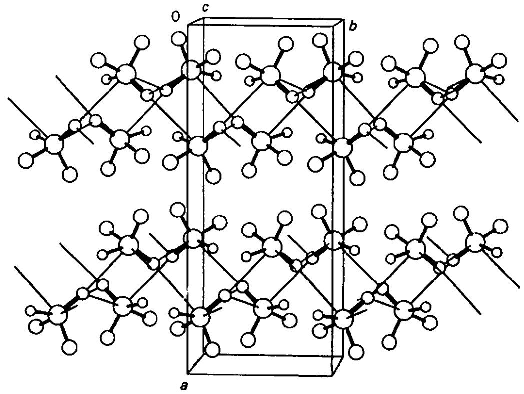

Fig. 4. Corrugated layers of PF_2HO molecules viewed along the *c* axis.

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* At 98 K, D_x values are 2·082 and 1·992 Mg m^{-3} respectively.

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Structural Characterization of Two Oxotungsten(IV) Complexes, [WOCl(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$]ClO$_4$ and [WOCl{Me$_2$PCH$_2$P(S)Me$_2$}$_2$]PF$_6$

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Abstract. (1) Chlorobis[ethylenebis(dimethylphosphine-*P,P'*)oxotungsten(IV) perchlorate, [WClO(C$_6$H$_{16}$P$_2$)$_2$]ClO$_4$, $M_r = 635{\cdot}04$, monoclinic, $P2_1/n$, $a = 11{\cdot}823\ (3)$, $b = 14{\cdot}980\ (3)$, $c = 13{\cdot}794\ (3)$ Å, $\beta = 96{\cdot}04\ (2)°$, $V = 2429\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}74$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 53{\cdot}56$ cm^{-1}, $F(000) = 1248$, $T = 284$ K, $R = 0{\cdot}056$ for 1691 observed reflections. (2) Chloro[dimethyl(dimethylphosphinomethyl)thiophosphoric acid-*P,S*]oxotungsten(IV) hexafluorophosphate, [WClO(C$_5$H$_{14}$P$_2$S)$_2$]PF$_6$, $M_r = 716{\cdot}63$, monoclinic, $P2_1/c$, $a = 12{\cdot}4463\ (9)$, $b = 8{\cdot}6000\ (9)$, $c = 23{\cdot}260\ (2)$ Å, $\beta = 98{\cdot}214\ (6)°$, $V = 2464\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}932$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 54{\cdot}26$ cm^{-1}, $F(000) = 1392$, $T = 284$ K, $R = 0{\cdot}0336$ for 3241 observed reflections. In each case the coordination of W is distorted octahedral with Cl *trans* to O and the two ligands forming roughly coplanar five-membered chelate rings. For (1) and (2) the W=O distances are 1·68 (1) and 1·711 (5) Å, respectively. In (1) the mean O—W—P angle is 97·6 (15)°. In (2) the two chelate rings are arranged to give *cis*-S$_2$ and *cis*-P$_2$ coordination. The mean O—W—P and O—W—S angles are 91·6° and 101·5°, respectively. The W—Cl bonds are relatively long, being 2·539 (5) and 2·554 (2) Å in (1) and (2), respectively.

Introduction. We have unintentionally prepared and structurally characterized two oxotungsten(IV) complexes in the course of a synthetic program directed towards the preparation of sulfur-capped tritungsten cluster compounds. Because of the dearth of structural data on oxotungsten(IV) species, we report this work here, even though the methods of preparation are quite unsatisfactory. No doubt they can be improved, but we have no plans to undertake such work.

Experimental. The two compounds described here were obtained as follows. A suspension of WCl$_4$ (684 mg, 2·1 mmol) in 20 mL of THF was reduced with sodium amalgam (2·1 mmol). The resulting green solution was filtered under argon over NaHS (112 mg, 2 mmol) and methanol (10 mL) was added in order to dissolve the sulfide. Dmpe (330 μL, 2 mmol) or dmpm (300 μL, 2 mmol) was introduced and the reaction mixture was refluxed for 2 h. After the reaction mixture had cooled to room temperature, a brown precipitate formed which was separated from the brown solution by filtration. This solution was absorbed on a silica gel column. After

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