Preparation and Properties of Difluoro(isoselenocyanato)phosphine: Low-frequency Vibrations of Difluorophosphine Pseudohalides

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Difluoro(isoselenocyanato)phosphine has been prepared by reaction of bromodifluorophosphine with silver(I) isoselenocyanate. Its n.m.r., photoelectron, and i.r. spectra are reported. The low-frequency vibrations of the related compounds $P(CN)F_2$, $PF_2(NCO)$, $PF_2(NCS)$, and $PF_2(NCSe)$ have been studied in the far i.r. with gas-phase samples. With B_2H_6, $PF_2(NCSe)$ forms a complex formulated as $PF_2(NCSe){\cdot}BH_3$; ^1H, ^{11}B, ^{19}F, and ^{31}P n.m.r. data are reported for this complex.

THE pseudohalides $P(CN)F_2$,[1] $PF_2(NCO)$,[2] and $PF_2(NCS)$[2] are known, and their structures have been investigated by electron diffraction.[3,4] In the course of these investigations it was found that low-frequency vibrations imposed limits on the precision with which the ground-state structures could be defined, and attempts were made to estimate the frequencies of the torsional and bending modes of $PF_2(NCO)$ and $PF_2(NCS)$. In continuation of these studies we have now prepared $PF_2(NCSe)$ and investigated the low-frequency i.r. spectra of all the four pseudohalide derivatives in order to obtain definitive values for the low-frequency vibrations.

EXPERIMENTAL

Characterisation.—Compounds were handled in vacuum systems of conventional design, fitted with either glass or Teflon Sovirel taps. Mass spectra were obtained by means of an A.E.I. MS 902 spectrometer, n.m.r. spectra using a Varian XL-100 instrument operating in the Fourier-transform mode, and photoelectron (p.e.) spectra with a Perkin-Elmer PS16 spectrometer (instrument resolution was between 30 and 40 meV).† Infrared spectra were obtained using a Perkin-Elmer 577 (200—4 000 cm^{-1}) and a Beckman RIIC IR 720 interferometer (20—400 cm^{-1}) which was equipped with a single-pass long-path (1.4 m) gas cell. Raman spectra were recorded using a Spex instrument with 4 880-Å argon-ion laser excitation.

Preparation of Difluoro(isoselenocyanato)phosphine, $PF_2(NCSe)$.—The compound $PBrF_2$ was prepared by reaction of HBr with $PF_2(NMe_2)$.[5] Silver(I) isoselenocyanate was prepared by mixing aqueous solutions of $Ag[NO_3]$ and K[NCSe]; it was filtered off, washed with acetone, and dried, finally by pumping. Bromodifluorophosphine (1.49 g, 10.0 mmol) was allowed to react with Ag[NCSe] (10 g, excess) in an evacuated tube at room temperature. The pure *product* was separated from more volatile impurities (HCN, PF_3, PF_2HO) by condensation at 209 K. The yield was not recorded as the sample was unstable in the liquid phase at room temperature, depositing red selenium. In solution in deuteriochloroform the compound appeared to be much more stable. In the vapour phase it was moderately stable in clean glassware, but the decomposition appeared to be catalysed by the Se deposited. Hydrogen cyanide and PF_3 were detected as volatile products of the decomposition. The vapour pressure at room temperature was recorded as 18 Torr, although this value may be incorrect in view of the ready decomposition.

Reaction of $PF_2(NCSe)$ *with* B_2H_6.—Diborane (0.20 mmol) and $PF_2(NCSe)$ (0.20 mmol) were allowed to react in an n.m.r. tube with $CDCl_3$ as solvent. After the initial reaction, the tube was kept at liquid-nitrogen temperature and warmed only to allow ^1H, ^{19}F, and ^{31}P n.m.r. spectra to be run at low temperature (−20 to −70 °C).

RESULTS AND DISCUSSION

Properties of $PF_2(NCSe)$.—*N.m.r. spectra.* The ^{19}F n.m.r. spectrum ($CDCl_3$ solvent) showed a simple doublet, with $\delta(^{19}F) = -56.0_5$ p.p.m. [^1J(PF) 1 334 Hz]. The ^{31}P spectrum consisted of a triplet, with $\delta(^{31}P) = +121.8_5$ p.p.m. [^1J(PF) 1 335 Hz]; the lines were broadened, and showed an incipient triplet pattern (J *ca.* 50 Hz) presumably because of coupling to ^{14}N. The intensity ratio within each group was rather far from 1 : 1 : 1, implying that the coupling was substantially affected by quadrupole relaxations of the ^{14}N nucleus.

P.e. spectra. Broad peaks were observed, with vertical ionisation potentials at 9.8, 11.7, 13.6, 15.2, and 16.4 eV, assigned [by analogy with $PF_2(NCO)$ and $PF_2(NCS)$][6] to NCSe 2π, P $3p_z$, NCSe 1π, P–N σ-bonding, and F $2p_\pi$ levels respectively. A pair of distinct peaks on the 1π band, at 13.62 and 13.85 eV, are separated by 0.23_5 eV (1 900 ± 50 cm^{-1}) which is probably the CN stretching frequency in the ion, excited on removal of a π-bonding electron.

Mass spectrum. This showed groups of peaks at m/e (relative intensities and assignments in braces): 255 {12, $[PF_2(NCSe)Se]^+$}; 175 {22, $[PF_2(NCSe)]^+$}; 95 {0.6, $[P(CN)F_2]^+$}; 80 {4, Se^+}; 69 {100, $[PF_2]^+$}; 50 {6, $[PF]^+$}; 31 {2, P^+}; and 27 {85, $[HCN]^+$}. Where appropriate the characteristic isotope pattern of selenium was present.‡ The relatively low abundance of the parent ion is not surprising; it is interesting to observe that it apparently takes up selenium from its surroundings. No stable compound $PF_2(NCSe)Se$ appears to have been reported; the positive ion may be formed from PF_2-

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† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 Torr = (101 325/760) Pa.

‡ Weak peaks were also present in the mass spectrum due to $PBrF_2$ and F_2POPF_2 impurities; these may have been introduced while the sample was traversing the vacuum manifold of the spectrometer.

[1] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, 1966, **88**, 3729.

[2] H. H. Anderson, *J. Amer. Chem. Soc.*, 1947, **69**, 2495.

[3] G. C. Holywell and D. W. H. Rankin, *J. Mol. Structure*, 1971, **9**, 11.

[4] D. W. H. Rankin and S. J. Cyvin, *J.C.S. Dalton*, 1972, 1277.

[5] M. Lustig, J. K. Ruff, and C. B. Colburn, *J. Amer. Chem. Soc.*, 1966, **88**, 3875.

[6] S. Cradock and D. W. H. Rankin, *J.C.S. Faraday II*, 1972, 940.

(NCSe) and Se$^+$ or from [PF_2(NCSe)]$^+$ and Se or PF_2(NCSe) in the ionisation region of the spectrometer. No ' metastable peaks ' were observed in the mass spectrum, showing that none of the ions formed was prone to decompose in flight.

Vibrational spectra. The bands observed are listed in Table 1. By detailed comparison of the spectra of PF_2(NCSe) with the published[4] i.r. and Raman spectra and our new low-frequency data for PF_2(NCO) and PF_2(NCS), we arrive at the list of fundamentals shown in Table 2. The assignments given for PF_2(NCO) and PF_2(NCS) here are identical with those published earlier, except in the lowest-frequency regions. There we *observe* bands at 113 and 70 cm^{-1} (NCO), 86 and 55 cm^{-1} (NCS), and 75 and 54 cm^{-1} (NCSe) that must be assigned in each case to the bend at N (ν_8) and the torsion (ν_{12}) respectively. In each case the higher-frequency band is considerably stronger than the other. In the spectra of PF_2(NCO) and PF_2(NCS), bands at *ca.* 360 cm^{-1} have been assigned to the overtone of a skeletal bend (ν_{11}). We do not observe strong bands near 180 cm^{-1} for PF_2(NCO) and PF_2(NCS), as predicted, and therefore assign the bands at 367 cm^{-1} (NCO) and 362 cm^{-1} (NCS) to ν_{11}, the asymmetric FPN deformation. The corresponding band in PF_2(NCSe) appears at 347 cm^{-1}. The compounds PF_2(NCO) and PF_2(NCS) each give a single moderately strong band, at 324 and 312 cm^{-1} respectively, to low frequency of this, that is polarised in the Raman and is assigned to the symmetric FPN deformation. The compound PF_2(NCSe) shows *three* weak bands, at 323, 293, and 262 cm^{-1}, in the i.r. in this region: that at 323 cm^{-1} is probably the difference band $\nu_6 - \nu_8$ ($396 - 75 = 321$ cm^{-1}); the corresponding sum $\nu_6 + \nu_8$ would give a band close to the much stronger band at 490 cm^{-1} due to ν_{11}, and almost coincident with a weak band at 460 cm^{-1} due to a trace impurity ($PBrF_2$). The weakest of the three bands, at 293 cm^{-1}, may be the difference $\nu_{11} - \nu_{12}$ ($347 - 54 = 293$ cm^{-1}); the corresponding sum would coincide with ν_6 at 396 cm^{-1}. This leaves 262 cm^{-1} for the symmetric FPN deformation, ν_7. This value is considerably lower than expected by comparison with PF_2(NCO) and PF_2(NCS), but we can suggest no plausible alternative assignment for this band.

TABLE 1

Gas-phase i.r. and liquid-phase Raman spectra of PF_2(NCSe)

I.r.	Assignment	Raman
3 918w	$2\nu_1$	
2 536m	$\nu_1 + \nu_4$	
2 390vw	$\nu_1 + \nu_5$	
2 370vw	$\nu_1 + \nu_6$	
2 231m	$\nu_1 + \nu_7$	
2 118w	$\nu_1 + 2\nu_8$	
2 040s	$\nu_1 + \nu_8$	
1 972vvs	ν_1	1 977w
1 900 (sh)	$\nu_1 - \nu_8$	
1 762w	$\nu_3 + \nu_2$	
1 710w	$2\nu_3$? $\nu_3 + \nu_9$?	
1 382w	?	
1 020 (sh)	?	
985m	$2\nu_{10}$, $\nu_4 + \nu_5$, $O(PF_2)_2$ impurity?	
920m	ν_2	
851vs	ν_3, ν_9	850w, br (60 cm^{-1})
769vw	$\nu_3 - \nu_8$?	
630mw	$\nu_4 + \nu_8$	
569s	ν_4	562m (30 cm^{-1})
490m	ν_{10}	
429w	ν_5	
396m	ν_6	405ms, sp (12 cm^{-1})
347w	ν_{11}	
323w	$\nu_6 - \nu_8$	
293vw	$\nu_{11} - \nu_{12}$	
262vw	ν_7	270s, sp (12 cm^{-1})
77w	ν_8	84vs, sp (12 cm^{-1})
54vw	ν_{12}	

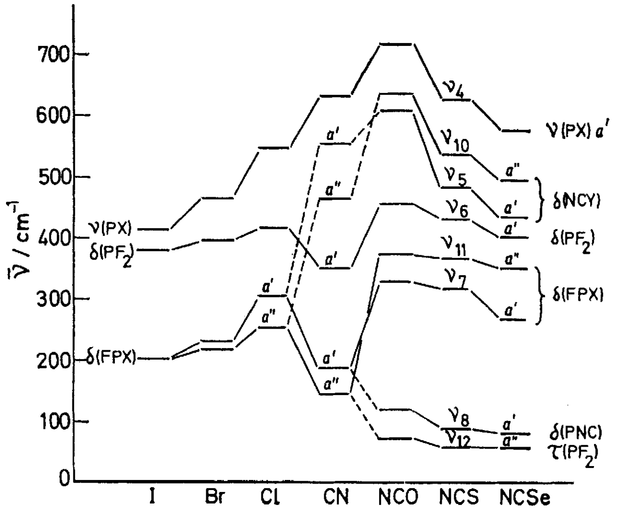
s = Strong, w = weak, m = medium, v = very, sp = sharp, sh = shoulder.

TABLE 2

Fundamental vibration frequencies of PF_2(NCO), PF_2(NCS), and PF_2(NCSe)

ν/cm^{-1}				
PF_2(NCO)	PF_2(NCS)	PF_2(NCSe)	Assignment *	
2 283	1 883	1 972	ν_1	ν(NC)
1 422	1 028	920	ν_2	ν(CY)
853	859	851	ν_3	$\nu_{sym}(PF_2)$
714	622	569	ν_4	ν(PN)
604	476	429	ν_5	(NCY)
451	426	396	ν_6	$\delta(PF_2)$
324	312	262	ν_7	δ_{sym}(FPN)
113	86	75	ν_8	δ(PNC)
839	845	851	ν_9	$\nu_{asym}(PF_2)$
630	531	490	ν_{10}	δ(NCY)
367	362	347	ν_{11}	δ_{asym}(FPN)
70	55	54	ν_{12}	torsion

*As shown in ref. 4, the descriptions are at best approximate, as extensive mixing occurs.



FIGURE

Fundamental vibrations of PF_2X (X = halide or pseudohalide)

To complete our analysis of the low-frequency motions in PF_2 pseudohalides we studied the far-i.r. spectrum of $P(CN)F_2$, which is expected to have two low-frequency deformations related to the FPX deformations of the PF_2 halides, and of the halides themselves, which have been reported only partially.[7] The results obtained are summarised in the Figure, which shows the correlations between corresponding modes of the same symmetry for

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[7] A. Muller, E. Niecke, B. Kregs, and O. Glemser, *Z. Naturforsch.*, 1968, **B23**, 588.

the various species. The band contours we observe for the lowest-frequency bands of $PClF_2$, $PBrF_2$, and $P(CN)F_2$ confirm that the lowest-frequency mode of all is of a'' symmetry in each case. For PF_2I we observe only a single very weak band at 201 cm^{-1}, that we assign to both FPI deformations. The bands of $P(CN)F_2$ occur at 185 and 145 cm^{-1}, with A- and B-type contours respectively.

The Figure shows that the band positions shift as expected as the mass of the halogen or pseudohalogen changes, and also the effects of the addition of two extra deformation modes in the cyanide compared to the halides, and the addition of a further two modes in the pseudohalides $PF_2(NCY)$. It may be noted that, despite the reversals in the a' and a'' ordering of the deformation frequencies between $P(CN)F_2$ and the other pseudohalides, in each case the lowest-frequency mode of all is of a'' symmetry.

Like $PF_2(NCO)$ and $PF_2(NCS)$, $PF_2(NCSe)$ shows a number of weak bands near the 'asymmetric NCY stretching' band (ν_1). As we now know all the fundamental vibration frequencies it is easy to assign these as combinations of ν_1 with *all* the a' (symmetric) vibrations except ν_3, the PF stretch, and ν_2 the 'symmetric NCY stretch.' The assignment of ν_7 at 262 cm^{-1} suggested above is confirmed by the appearance of a band at 2 231 cm^{-1}, 1 972 + 259 cm^{-1}.

The lowest-frequency a' band, ν_8 at 75 cm^{-1}, gives rise to both sum and difference bands, at 2 045 and 1 900 cm^{-1} respectively. We are also able to confirm the earlier suggestion[4] that the corresponding weak 'satellite' bands to ν_1 for $PF_2(NCS)$ are due to the same sum and difference combinations with the band ν_8. We remeasured $\nu_1 - \nu_8$ for $PF_2(NCO)$, and find its position to be 2 171 cm^{-1}, not 2 178 cm^{-1}; the difference 2 283 − 113 cm^{-1} is therefore exact within experimental uncertainty, as expected.

The torsion frequencies for $PF_2(NCO)$, $PF_2(NCS)$, and $PF_2(NCSe)$ can be used to calculate the barrier to internal rotation, if sufficient structural information is available. For $PF_2(NCO)$ and $PF_2(NCS)$ the effective rotation constant F for rotation about the PN bond can be calculated from the electron-diffraction structures[4] to be 0.53 and 0.37 cm^{-1} respectively. Reasonable assumptions about the structure of $PF_2(NCSe)$ lead to an estimate of 0.28 cm^{-1} in this case. Using these values of F and the observed torsional fundamentals of 70, 55, and 54 cm^{-1} respectively, one calculates V_2, the two-fold barrier height, as follows.

For a two-fold barrier, a dimensionless parameter S is defined as $S = V/F$. The fundamental vibration frequency ν is given, for large S, by the approximate relation[8] $\nu/F = 2S^{\frac{1}{2}} - 1$. Values of S and V thus derived are listed in Table 3. From the barrier height the root-mean-square (r.m.s.) amplitude of the torsional oscillation, δ, can also be calculated if we assume that the potential well may be approximated by a parabola (the harmonic-oscillator approximation[9]). The values of δ, calculated at 300 K, which depend only on V_2, are given in Table 3. The values for $PF_2(NCO)$ and $PF_2(NCS)$ agree well with the mean dihedral angles (14° in each case) found in the electron-diffraction study,[4] confirming the suggestion that these angles represent the mean deviation from the stable C_s form rather than the true dihedral angle of the ground-state structure.

TABLE 3

Torsional parameters for $PF_2(NCY)$ (Y = O, S, or Se)

Compound	$\frac{\nu}{\text{cm}^{-1}}$	$\frac{F}{\text{cm}^{-1}}$	S	$\frac{V_2}{\text{cm}^{-1}}$	$\frac{V_2}{\text{kJ mol}^{-1}}$	$\frac{\delta}{°}$
$PF_2(NCO)$	70	0.53	4 350	2 300	27.5 ± 3.6	12.2 ± 0.5
$PF_2(NCS)$	55	0.37	5 610	2 080	25.0 ± 3.2	12.8 ± 0.5
$PF_2(NCSe)$	54	0.28	9 400	2 640	31.6 ± 5.7	11.4 ± 1.0

Taking estimated errors in ν of ±5% and in F of ±3%, the estimated error in V is of the order of ±13% for $PF_2(NCS)$; the apparent difference between $PF_2(NCO)$ and $PF_2(NCS)$ on the one hand and $PF_2(NCSe)$ on the other may well not be significant. The estimated value of F for $PF_2(NCSe)$ has been given an uncertainty of ±0.02 (±8%), corresponding to PNC bond angles between 150 and 140°. Taking the lower end of the range of barriers as more probable implies that the bond angle is nearer 150 than 140°, as seems likely by comparison[4] with $PF_2(NCO)$ (138°) and $PF_2(NCS)$ (144°).

Reaction with B_2H_6. A slow reaction occurred at low temperature; the ^{31}P n.m.r. spectrum after reaction showed a triplet of (1 : 1 : 1 : 1) quartets that did not collapse with ^{1}H decoupling, indicating that the coupling was to ^{11}B ($I = \frac{3}{2}$), ^1J(PB) ≈ 52 Hz; the ^{31}P chemical shift had decreased from 121.8 to 106.4 p.p.m., and ^1J(PF) from 1 335 to *ca.* 1 270 Hz, both changes consistent with the formation of a simple adduct with phosphorus being four-co-ordinate. The ^{19}F spectrum showed a doublet of 1 : 3 : 3 : 1 quartets, with ^1J(PF) 1 278 Hz and $\delta(^{19}F) = -62.2$ p.p.m. The quartet splitting was shown to be due to $^1H-^{19}F$ coupling by ^{1}H noise decoupling, which left a simple ^{19}F doublet, ^3J(HF) 17.3 Hz. No coupling attributable to ^2J(BF) was observed. Phosphorus is thus coupled to one boron atom, fluorine to three equivalent protons; the most likely formulation for the product is the adduct $PF_2(NCSe)\cdot BH_3$.

TABLE 4

N.m.r. parameters of $PF_2(NCSe)\cdot BH_3$

	δ/p.p.m.		J/Hz
^{1}H	+1.0	^1J(BH)	*ca.* +85
^{11}B	−62.8	^2J(PH)	*ca.* −17
^{19}F	−62.2	^3J(FH)	17.3
^{31}P	+106.4	^1J(BP)	*ca.* +52
		^1J(PF)	−1 278
		^2J(BF)	*ca.* 0

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[8] A. V. Cunliffe, in 'Internal Rotation in Molecules,' ed. W. J. Orville-Thomas, Wiley, 1974, ch. 7, p. 228.

[9] W. G. Kately, R. K. Harris, F. A. Miller, and R. E. Witanowski, *Spectrochim. Acta*, 1965, **21**, 231; K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, 1973, **95**, 1003.

The proton spectrum was complicated by $^{1}H-^{11}B$ coupling and by the presence of uncomplexed B_2H_6. The coupling to boron gives rise to a broadened *1 : 1 : 1 : 1* quartet, with $\delta(^{1}H) \sim 1.0$ [$^{1}J(BH) \sim 85$ Hz]. Irradiation of the ^{11}B resonance collapsed this coupling and gave a quartet pattern that must arise from coupling to two fluorine atoms and one phosphorus with almost equal coupling constants. The exact magnitude of $^{2}J(PH)$ was not established. 'Tickling' experiments showed that $^{2}J(PH)$ and $^{1}J(BP)$ had opposite signs.* The ^{11}B frequency found corresponded to a chemical shift $\delta(^{11}B) = -62.8$ p.p.m. The coupling constants and chemical shifts found for the adduct are collected in Table 4.

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* Taking $^{1}J(BP)$ as positive[10] as in $PF_2H\cdot BH_3$ (+49) and $PF_2(NMe_2)\cdot BH_3$ (+79) implies that $^{2}J(PH)$ is negative.

[10] R. W. Rudolph and C. W. Schultz, *J. Amer. Chem. Soc.*, 1971, **93**, 6821.