Structure and Fluxionality in the $PF_{6-n}(CN)_n^-$ and $PF_3Cl_{3-n}(CN)_n^-$ Series

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Several new ions in the series $PF_{6-n}(CN)_n^-$ and $PF_3Cl_{3-n}(CN)_n^-$ have been prepared, and identified by n.m.r. spectroscopy; some species with three or more fluorine atoms present are fluxional at 307.2 K.

The only reported six-co-ordinate phosphorus(v) anion containing both fluoride and cyanide ligands is $PF_5(CN)^-$, formed by reaction of PF_5 with cyanide ions.[1] ^{19}F N.m.r. parameters were measured for this species in CH_2Cl_2 solution at 178 K, at which temperature it was stereochemically rigid.[1] We have prepared six-co-ordinate anions of the types $PF_{6-n}(CN)_n^-$ ($1 \leqslant n \leqslant 4$) and $PF_3Cl_{3-n}(CN)_n^-$ ($1 \leqslant n \leqslant 3$) by a variety of routes. Reaction of PF_5 with Et_4NCN in CH_2Cl_2 gave $PF_5(CN)^-$ and PF_6^-, while PF_3Cl_2 under similar conditions yielded an isomeric mixture of $PF_3Cl_2(CN)^-$ ions. Treatment of a *cis/trans* mixture of $PCl_4(CN)_2^-$ (ref. 2) with AgF produced *cis-/trans*-$PF_4(CN)_2^-$ and some PF_6^-, while a *fac/mer* mixture of $PF_3Cl_3^-$ ions[3] reacted with an excess of LiCN[4] to yield a single isomer of $PF_3Cl(CN)_2^-$. *mer*-$PF_3(CN)_3^-$ was formed as the major phosphorus(v) product from the exchange reaction between $P(CN)_3$ and $PF_3Cl_3^-$ (ref. 3) in CH_2Cl_2, together with PCl_3 and smaller quantities of $PF_4(CN)_2^-$ and $PF_2(CN)_4^-$. A *fac*-$PF_3(CN)_3^-/PF_6^-$ mixture was produced by oxidation of $Pr_4N^+PBr(CN)_3^-$ (refs. 5 and 6) with SF_4. All the cyanofluorophosphate ions gave intensely red solutions in CH_2Cl_2. The ions $PF_3Cl_2(CN)^-$ and $PF_3Cl(CN)_2^-$ were isolated as their Et_4N^+ salts, which gave satisfactory elemental analyses.

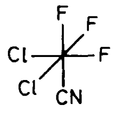
Table 1. ^{31}P N.m.r. data for PF_{6-n} $(CN)_n^-$ ions in CH_2Cl_2.

Ion *n*	 Isomer	^{31}P, δ/p.p.m.[a] Observed	 Calculated[c]	 Multiplicity	 $^1J_{PF}$/Hz
0		−145.1	−144.6	Septet	714
1		−157.7	−158.4	Sextet[b]	744
2	*cis*	−183.8	−184.3	Quintet[b]	753
	trans	−172.6	−172.1	Quintet	741
3	*fac*	−225.5	−222.4	Quartet	744
	mer	−210.5	−210.2	Doublet of triplets	780(d),684(t)
4	*cis*		−260.5		
	trans	−250.7	−248.4	Triplet	853
5			−310.8		
6			−373.3		

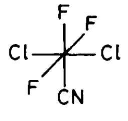
[a] Downfield from external H_3PO_4. [b] Fluxional at this temperature (307.2 K). [c] F: F −12·05, F : CN −15·49, CN : CN −31·11 p.p.m.

^{31}P N.m.r. data (307.2 K) for $PF_{6-n}(CN)_n^-$ ions in CH_2Cl_2 are given in Table 1, while ^{31}P and ^{19}F n.m.r. results for $PF_3Cl_{3-n}(CN)_n^-$ ions are presented in Table 2. Isomeric configurations in the cyanofluorophosphate series were readily assigned by the method of pairwise interactions;[2,3,7-9] the calculated chemical shifts are included in Table 1. Of particular interest in this series is the sharp division between stereochemical rigidity and fluxionality on increasing the number of F atoms in the complex from 3 to 4. Similar trends have been observed for the N_3^- and NCS^- substituted chlorofluorophosphates.[3]

All three isomers of $PF_3Cl_2(CN)^-$ were present in the solid



(1)



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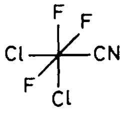

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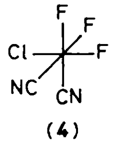

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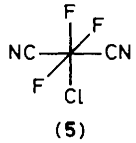

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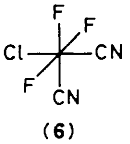

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Table 2. ^{31}P and ^{19}F N.m.r. data for $PF_3Cl_{3-n}(CN)_n^-$ in CH_2Cl_2.

Ion	^{31}P, δ/p.p.m.		Abundance/%[a]	^{19}F, δ/p.p.m.[b]	$^1J_{PF}$/Hz	^{19}F, δ/p.p.m.[b]	$^1J_{PF}$/Hz	$^2J_{FF}$/Hz
	Observed	Calculated		(unique F)				
(1)[c]	−180.0	−180.4	70	12.2	1010	−17.6	810	91
(2)	−167.2	−164.0	15	−6.8	835	27.3	925	65
(3)	−168.5[d]	−159.5	15	16.2[d]	940			
(4)		−201.5						
(5)		−189.1						
(6)[c]	−190.4	−185.1	100	1.8	905	−9.3	791	73
mer-$PF_3(CN)_3^-$	−210.5	−210.2		−9.6	780	−40.8	684	34

[a] Estimated from ^{19}F n.m.r. spectra. [b] Downfield from $CFCl_3$. [c] ^{19}F N.m.r. spectra analysed as AB_2 part of an AB_2X system. For other spectra first order analysis sufficed. [d] Fluxional.

isolated from the PF_3Cl_2–Et_4NCN reaction. The most striking feature of these complexes was the observation that two are stereochemically rigid while the third is fluxional at or just above ambient temperature, lines in the ^{19}F and ^{31}P n.m.r. spectra being sharp for all species. Clearly the energy barriers to non-rigidity depend critically on subtle variations in structure. The most abundant isomer (non-fluxional) was assigned structure (**1**) on the basis of the pairwise method (Table 2), but an unequivocal assignment of resonances to structures (**2**) and (**3**) cannot be made, and we are unable to say which of these isomers is fluxional.

The single isomer found for $PF_3Cl(CN)_2^-$ appears from the calculated shifts to have a meridional arrangement of the fluorines, *i.e.* structure (**5**) or (**6**) rather than (**4**) (Table 2). Since two CN stretching bands were observed in its i.r. spectrum, structure (**6**) seems probable, even though numerical agreement with the experimental shift is better for (**5**). We have found previously that the pairwise treatment does not hold too well for chlorocyanophosphates(V),[2] possibly because of distortions from regular octahedral geometry.

An interesting parallel exists between these complexes and the chlorocyano- and thiocyanato-phosphates,[2] in as much as certain types of reaction tend to yield products with a specific stereochemistry. Thus oxidation of a phosphorus(III) species leads to a predominantly facial distribution of ligands in $PF_3(CN)_3^-$, analogous to Cl_2 oxidation of $PCl(CN)_3^-$ (ref. 10) which gave mainly *fac*-$PCl_3(CN)_3^-$,[2] as well as the $PF_3/Cl^-/Cl_2$ reaction which produced *ca.* 75% *fac*-$PF_3Cl_3^-$.[3] On the other hand, ligand exchange reactions between phosphorus-(V) and -(III) compounds appear to favour meridional isomers, as exemplified by reaction of $PF_3Cl_3^-$ with $P(CN)_3$, and of PCl_6^- with $P(NCS)_3$.[2] Substitution of Cl in a phosphorus(V) species by metal cyanides also seems to lead preferentially to *mer*-isomers, since a single isomer of $PF_3Cl(CN)_2^-$ is formed with a meridional arrangement of F atoms even though they are mainly *fac* in the starting material, and *mer*-$PCl_3(CN)_3^-$ is the main product formed by substitution into hexachlorophosphates.[2]

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