Preparation and Characterization of Perfluorophosphonium Hexadecafluorotriantimonate(V) $[PF_4]^+$ $[Sb_3F_{16}]^-$

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Summary Phosphorus pentafluoride forms a 1:3 adduct with SbF_5, shown to be $[PF_4]^+[Sb_3F_{16}]^-$ by vibrational spectroscopy; phosphorus trifluoride undergoes a redox reaction with AsF_5 and SbF_5.

We report that phosphorus pentafluoride reacts at room temperature with antimony pentafluoride to form the white solid $[PF_4]^+[Sb_3F_{16}]^-$. In a typical experiment PF_5 (28·7 mmol) was condensed on to SbF_5 (21·4 mmol). The maximum pressure in the vessel was estimated to be 11 atm. at room temperature. The mixture was repeatedly thermally cycled between room temperature and −196°. After two days the excess of PF_5 was removed at −78°. The weight of solid corresponded to the formation of 7·2 mmol $PF_5(SbF_5)_3$. At room temperature the pressure of PF_5 above the white solid was *ca.* 130 Torr. Phosphorus pentafluoride (6·7 mmol) was condensed out of the vessel containing the adduct, leaving 21·7 mmol liquid SbF_5 residue.

Table

Comparison of stretching frequencies[a] *of* SiF_4,[b] $[NF_4]^+$,[c] *and* $[PF_4]^+$

SiF_4 Raman	SiF_4 I.r.	$[NF_4]^+$ Raman	$[NF_4]^+$ I.r.	$[PF_4]^+$ Raman	$[PF_4]^+$ I.r.	Assignment
1010vw	1031vs	1185w 1153w	1162s	1170vw 1160vw	1160s	ν_3 (F_2) asymmetric stretch
800vs		849s		908s		ν_1 (A_1) symmetric stretch

[a] Frequencies in cm^{-1}. [b] Ref. 1. [c] Refs. 2 and 3.

The i.r. and Raman spectra of $PF_5(SbF_5)_3$ showed bands in the P–F stretching region that were similar in intensity, but at higher energy, than the corresponding bands of SiF_4,[1] and similar to those of NF_4^+ [2,3] (see Table). Bands at 700 cm^{-1} and below were similar but not identical to those of $[Sb_2F_{11}]^-$ [4,5] and are possibly due to the *trans*-bridged $Sb_3F_{16}^-$ isomer, previously found[6] in $[Br_2]^+[Sb_3F_{16}]^-$. The structure can therefore be formulated as $[PF_4]^+[Sb_3F_{16}]^-$. The P–F bending vibrations have not been unambiguously assigned. The P–F stretching frequency is the highest so far observed: it is possible that valence bond structures of the type $\overset{+}{F}=PF_3$ make a significant contribution to the bonding in the cation. The isoelectronic $[OSF_3]^+$ contains very strong S–O and S–F bonds,[7,8] and exists as a discrete, non-bridged ion in solid[8] $[OSF_3]^+[AsF_6]^-$.

$PF_3 \cdot AsF_5$ and $PF_3 \cdot SbF_5$ have been reported by Kemmitt *et al.*,[9] and, on the basis of their vibrational spectra it was suggested that these adducts were best formulated as $[PF_2]^+[AsF_6]^-$ and $[PF_2]^+[SbF_6]^-$. We have found that PF_3 reacts with AsF_5 to form AsF_3 and PF_5, at −78°, and at room temperature with all components in the gas phase. Antimony pentafluoride and phosphorus trifluoride also undergo a redox reaction at room temperature to form PF_5 and $SbF_3 \cdot (SbF_5)_x$. Phosphorus pentafluoride may itself react with SbF_5 to form $[PF_4]^+[Sb_3F_{16}]^-$. We were unable to prepare an adduct of definite composition $PF_3 \cdot SbF_5$.

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