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The Trifluorophosphonium Ion, PF_3H^+, Preparation and Structure

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The PF_3H^+ion is prepared as $PF_3H^+\cdot SbF_6^-\cdot HF$ by protonation of PF_3 with HF/SbF_5 at low temperatures in anhydrous HF. Crystals are obtained directly from this solvent. A crystal structure determination shows the presence of a pseudo-tetrahedral PF_3H^+ ion with a mean P−F distance of 148.7(2) pm, a P−H distance of 122(4) pm, and a mean PF_2 angle of 106.1(1)°. Raman spectra were recorded of $PF_3H^+SbF_6^-\cdot HF$ and $PF_3D^+\cdot SbF_6^-\cdot DF$ and assigned with the help of ab initio calculations. AsF_3 does not react with HF/SbF_5, whereas SF_4 forms $SF_3^+SbF_6^-\cdot HF$, which is isostructural with $PF_3H^+SbF_6^-\cdot HF$.

Introduction

Phosphonium salts with the ion PR_4^+ have long been classic compounds. R can be, among others, hydrogen, alkyl groups, aromatic groups, halogens, and mixtures thereof. The knowledge about fluorinated phosphonium salts is fairly limited. From a first glance there is no reason that should be so. $PF_4^+Sb_3F_{16}^-$ has been obtained by reacting PF_5 or KPF_6 with SbF_5, and has been identified by vibrational and NMR spectroscopy.[1,2,3]

Similarly, PH_2F_3 has been reacted with AsF_5, forming $PH_2F_2^+AsF_6^-$, which was identified by vibrational spectroscopy,[4] and independently by NMR spectroscopy.[3] PH_3F^+ and PF_3H^+ have also been identified by NMR spectroscopy.[3]

The difficulty of preparing PF_3H^+ becomes more obvious if the simple reaction $PF_3 + H^+$ is considered. The gas-phase proton affinities decrease in the sequence $P(CH_3)_3$ (∼230), PH_3 (∼185), and PF_3 (160 kcal mol^{-1}).[5] This decrease, although in accord with expectations, already indicates that the protonation of PF_3 may be difficult to achieve in condensed phases. In two cases it is reported that PF_3 does not undergo protonation in "magic acids".[6] We have accidentally encountered the PF_3/H^+ reaction at low temperatures in our investigations of the AuF_3/AsF_3/SbF_5/HF and AuF_3/PF_3/SbF_5/HF systems.[7]

Experimental Section

Synthetic work and sample handling were performed using Teflon-PFA ((poly) perfluoroether-tetrafluoroethylene copolymerizate) tubes that are sealed at one end and equipped at the other end with a metal valve, and therefore connectable to a metal vacuum line. HF was dried by performing several trap-to-trap condensations and by discarding the less volatile fractions. SbF_5 (Merck) was purified similarly by discarding the highly volatile fractions. PF_3 was used as received (Apollo Scientific LTD, Whaley Bridge, U.K.).

Raman spectra were recorded on a Bruker RFS 100 S instrument with Nd:YAG laser excitation, $\lambda = 1064$ nm. Samples were kept in the Teflon-PFA tubes, and the Raman scattering from the tubes was digitally subtracted.

NMR spectra were recorded with a JEOL multinuclear instrument at 400 MHz for ^1H. Spectra were recorded relative to TMS, $CFCl_3$, and H_3PO_4 as external standards. Single crystals were handled in a special device, cut to appropriate size, and mounted on a Bruker SMART CCD 1000 TU diffractometer, using Mo Kα irradiation, a graphite monochromator, a scan width of $0-3\omega$, and a measuring time of 10 s per frame. After semiempirical absorption corrections (SADABS) were performed by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement.[8] Ab initio calculations were performed with the GAUSSIAN program, using a 611++ G(d,p) basis set and the implemented Møller−Plesset second-order perturbation theory for the correlation energy correction (MP2), or coupled cluster calculation, with double substitutions from the Hartree−Fock determinant CCD for the configuration interaction.[9]

Preparation of $PF_3H^+SbF_6$−·HF. −1 g (4.6 mol) SbF_5 was loaded into an 8-mm outer diameter Teflon-PFA tube in a drybox. About 5 mL of anhydrous HF was condensed onto it at −196 °C on the vacuum line. Warming to room temperature afforded complete dissolution of the SbF_5. Next, 100 mg PF_3 (1.1 mmol) was condensed into the tube in several portions at −196 °C, and the mixture was intermittently warmed to room temperature. The clear and colorless solution was cooled slowly from room temperature to −60 °C, and a colorless, crystalline solid formed. Raman spectrum (cm^{-1}, cryst., −70 °C): 2934 br, 2545(5), 1090(1), 989(5), 972(6), 948(28), 688(2), 665(20), 651(100), 550(9), 565(7), 480(1), 467(3), 380(7), 281(30).

$PF_3D^+SbF_6\cdot DF$ was prepared completely analogous from PF_3, DF, and SbF_5. Raman spectrum (cm^{-1}, cryst., −70 °C): 2314 br, 1868-

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Table 1. Crystal Data and Structure Refinement for $PF_3H^+SbF_6^-\cdot HF$ and $SF_3^+SbF_6^-\cdot HF$

	$PF_3H^+SbF_6^-\cdot HF$	$SF_3^+SbF_6^-\cdot HF$
empirical formula	$H_2F_{10}PSb$	$HF_{10}SSb$
fw	344.74	344.82
temp, K	153	153
space group	$P2_1/c$	$P2_1/c$
a, pm	564.3(1)	560.01(1)
b, pm	1029.5(4)	1028.26(3)
c, pm	1296.2(4)	1281.16(4)
β, deg	101.05(2)	100.291(2)
vol, $10^6 pm^3$	739.4(4)	725.87(3)
Z	4	4
d (calcd) Mg/m³	3.098	3.155
abs coeff, mm^{-1}	4.084	4.225
cryst size	0.3 × 0.1 × 0.1	0.3 × 0.1 × 0.1
final *R* indices($I > 2\sigma(I)$)	R1 = 0.018	0.019
	wR2 = 0.0514	0.046
all data	R1[a] = 0.021	0.023
	wR2[b] = 0.0534	0.047

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[(wF_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

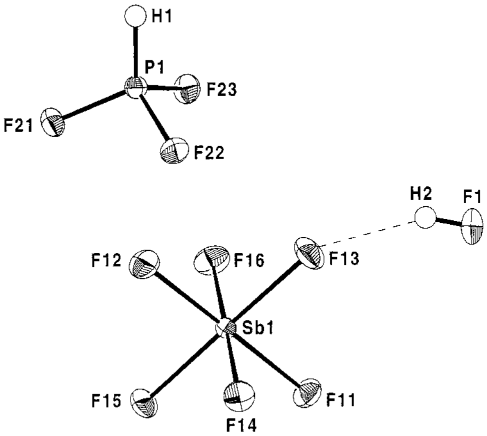

Figure 1. One molecular unit of $PF_3H\cdot SbF_6^-\cdot HF$, Ortep. Thermal ellipsoids are drawn at the 50% probability level. The $SbF_6^-\cdot HF$ contact of 194.1 pm length is indicated by dashed lines.

Table 2. Bond Lengths (pm) and Selected Angles (deg) for $PF_3H^+\cdot SbF_6^-\cdot HF$, by X-Ray Structure Determination and ab Initio Calculations

	X-ray	MP2	CCD
P−F	148.4(2), 148.8(2), 148.9(2)	150.9	150.2
P−H	122(4)	138.1	138.0
F−P−F	106.3(1), 106.0(1), 106.1(1)	108.5	108.4
F−P−H	111(2), 115(2), 112(2)	110.4	110.5
total energy, calcd (au)		−640.219289	−640.215803

Table 3. Mean Bond Lengths and Angles in PF_3H^+ in Comparison to PF_3, PF_4H, and PF_5H^-

	PF_3H^+	PF_3[a]a	PF_4H^-	PF_5H^- [d]
P−F	148.7	156.1(1)	153.7[b], 153.9[c](eq), 159.1[b], 159.6[c](ax)	159.5(eq);159.4(ax)
P−H	122		132.4[b], 138.0[c]	1.5
F−P−F	106.1	97.7(2)		
H−P−F	112.5			

[a] Data from ref 10. [b] Ref 12. [c] Ref 13. [d] Ref 11.

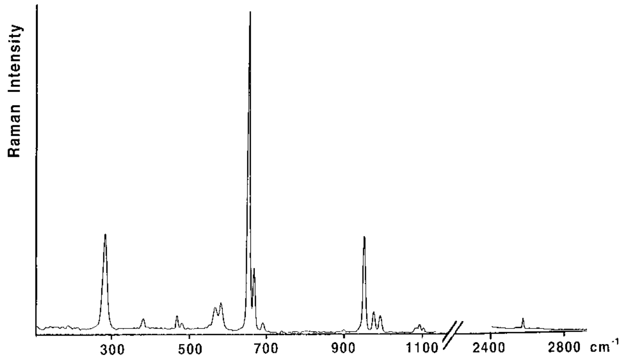

Figure 2. Raman spectrum of $PF_3H^+\cdot SbF_6^-\cdot HF$.

(18), 1089(1), 942(35), 725(3), 715(4), 687(3), 665(22), 651(100), 578(18), 561(15), 478(2), 464(3), 378(2), 280(34), 183(4).

Results and Discussion

PF_3, HF, and SbF_5 combine spontaneously at low temperature, forming colorless crystals of $PF_3H^+SbF_6^-\cdot HF$, as evidenced by a single-crystal structure determination and by Raman and NMR spectroscopy.

$$PF_3 + 2HF + SbF_5 \rightarrow PF_3H^+SbF_6^-\cdot HF$$

Experimental details of the crystal structure determination are presented in Table 1, and the result is shown in Figure 1; numerical values, see Table 2. The overall tetrahedral geometry of the cation is obvious. It is also noteworthy that the cation has neither shorter intermolecular contacts to the SbF_6^- nor to the solvate HF molecule. This comes as a surprise considering the exchange processes observed in the NMR spectra (see below). Contrary to this observation the atom F13 of the SbF_6^- anion forms a F···H bridge of 194.1 pm length with the HF molecule.

Protonation of PF_3 changes the structure of the PF_3 moiety. PF_3H^+ has considerably shorter P−F bond distances than PF_3.[10] In fact, PF_3H^+ obviously has the shortest known P−F bond length of all phosphorus fluorides (see Table 3). This length is in accord with conventional bond models and theories, and is predicted also by the ab initio results (see Table 3). Furthermore, the angles within the ion are very close to the ideal internal tetrahedral angle of 109.42°. In the view of the valence shell electron pair repulsion (VSEPR) model, it seems that the hydrogen atom appears here as a slightly larger ligand than the fluorine atom, given that the H−P−F angles are about 4° larger than the F−P−F angles.

A similar effect is found in PF_5H^-.[11] In PF_4H the effect of the hydrogen atom is such that the equatorial fluorine atoms are bent away from the hydrogen atom, but the axial fluorine atoms are bent toward the hydrogen atom.[12,13]

The Raman spectra of $PF_3H^+SbF_6^-\cdot HF$ and $PF_3D^+SbF_6^-\cdot DF$ are readily assigned with help of the ab initio calculations under the assumption of vibrationally independent cations and anions; see Figure 2 and Table 4. Bands at 651−665 (A_g), 555−580 (E_g), and 280−281 (T_2g) are easily assigned to the SbF_6^- vibrations.[14] The broad Raman bands at 2934 and 2314 cm^{-1} certainly are due to HF and DF. The effect of the deuteration as well as the analysis of the calculated vibrations indicate that all bands are rather characteristic with respect to the assignment.

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Table 4. Vibrational Spectra of the PF_3H^+ and PF_3D^+ Cations [cm^{-1}], by Raman Spectroscopy in Comparison to ab Initio Calculations, Including Assignment under the Assumption of C_{3v} Symmetry

PF_3H^+	PF_3D^+	PF_3H^+, MP2	PF_3D^+, MP2	PF_3H^+, CCD	assignment
2544	1868	2688.7	1939.1	2680.9	νPH, PD(A_1)
1090	1089	1120.5	1115.8	1137.7	$\nu PF_3(E)$
989, 972	725, 715	977.6	720.0	981.8	δPH, PD(E)
948	942	954.4	948.5	954.4	$\nu PF_3(A_1)$
480, 467	478, 464	480.5	476.9	488.7	$\delta PF_3(A_1)$
380	378	360.7	375.5	367.0	$\delta PF_3(E)$

NMR spectroscopy has only limited value in identification of the PF_3H^+ cation, although ^1H, ^{19}F, and ^{31}P are the most sensitive NMR probes known. At first, neither a ^{19}F signal nor $^{19}F-^{31}P$ coupling could be recorded for it. We therefore conclude that rapid exchange occurs between PF_3H^+ and HF fluorine atoms, whereas the ^{19}F lines of SbF_6^- can be separately assigned as the usual broadened multiplett at $\delta = -127.5$ ppm, due to coupling to ^{121}Sb ($I = 5/2$, 57%) and ^{123}Sb ($I = 7/2$, 43%) isotopes. Most informative is the ^{31}P NMR spectrum. At -20 to -85 °C it shows a doublet due to $^{31}P-^{1}H$ coupling ($\delta = 28.41$ ppm, $J^1H^{31}P = 1128$ Hz). The doublet collapses to a singlet in the $\{^1H\}-^{31}P$ spectrum, and similarly upon deuteration. The ^{1} H NMR spectrum is dominated by the solvent HF, and one line of the expected doublet is visible at $\delta = 6.3$ ppm, while the other line is partially obscured by the HF resonance. It could, however, be located by a $^{31}P-^{1}H$ double-resonance COSY experiment. In the first identification of the PF_3H^+ ion, highly resolved ^1H, ^{19}F, and ^{31}P spectra have been obtained. This is certainly a result of the solvent SO_2 chosen there.[3]

The fact that in HF the fluorine atoms, but not the hydrogen atoms, exchange (on the time scale of the NMR experiment) comes as a surprise, especially if compared with the solid-state structure, where the PF_3H ion is found rather undisturbed by the HF solvate molecule.

The NMR spectra do not change upon cooling to the melting point of the solvent. However, if all HF, SbF_5, and $PF_3H^+SbF_6^-$ are frozen out, there remains the isotropic ^{31}P and ^{19}F spectrum of excess PF_3. Furthermore, a new isotropic spectrum appears, which is clearly identified as that of PF_4H by comparison with literature data.[15] Upon warming, the latter spectrum disappears reversibly. From this we conclude that in HF there is equilibrium.

$$PF_3H^+SbF_6^- \rightleftharpoons PF_4H + SbF_5$$

In solution, excess SbF_5 is needed for the formation of $PF_3H^+SbF_6^-$. It should be noted that there is no reaction between neat PF_3 and HF in the range -20 to -90 °C. Solid $PF_3H^+SbF_6^-\cdot HF$ is thermally unstable also. If warmed above $-20°$, PF_3 can be pumped off, leaving behind a colorless solid, which is certainly some kind of $xHF\cdot ySbF_5$.[16]

The protonation of PF_3 cannot be extended to its chemically closest neighbors. AsF_3 is recrystallized unchanged at $-78°$ from HF/SbF_5 solutions. SF_4 reacts with HF/SbF_5, forming $SF_3^+SbF_6^-\cdot HF$, containing the otherwise well described SF_3^+ cation.[17] The crystal structures of $SF_3^+SbF_6^-\cdot HF$ and $PF_3H^+SbF_6^-\cdot HF$ are very similar; possibly the compounds are isomorphous. For matters of comparison, the experimental data of $SF_3^+SbF_6^-\cdot HF$ are included in Table 1.

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Supporting Information Available: Listings of crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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