The Crystal Structures of the Trihalogenphosphonium Salts $X_3PH^+As_2F_{11}^-$ (X = Cl, Br)

Rolf Minkwitz*[a] and Markus Dzyk[a]

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The X_3PH^+ ions (X = Cl, Br) were prepared as their $X_3PH^+As_2F_{11}^-$ salts by protonation of PX_3 with HF/AsF_5 at low temperature in anhydrous HF. Single crystals were obtained directly from this solvent. $Cl_3PH^+As_2F_{11}^-$ crystallises in the orthorhombic space group *Pnma* (No. 53) with a = 2350.6(1) pm, b = 837.7(1) pm, c = 1179.9(1) pm and eight formula units per cell. $Br_3PH^+As_2F_{11}^-$ crystallises in the monoclinic space group $P2_1/m$ (no. 14) with a = 617.7(1) pm, b = 872.4(2) pm, c = 1182.5(2) pm, β = 94.68(3)° and two formula units per cell.

Introduction

Salts with the phosphonium ion PR_4^+ are very well known, and R can be an organic or an inorganic group like hydrogen or halogen, amongst others. In contrast to phosphonium ions with organic groups relatively little is known about halogenated phosphonium salts. Only the fluorinated salts $F_{4-n}PH_n^+A^-$ (n = 0−3, A^- = anion) have been characterised by NMR and vibrational spectroscopy.[1−5] Recently Seppelt at al. prepared the salt $F_3PH^+SbF_5^-$ from a $PF_3/HF/SbF_5$ solution and determined its crystal structure by X-ray diffraction.[6]

Most of the corresponding chlorine and bromine compounds are not yet known. A few years ago our research group prepared a series of $X_3PH^+AsF_6^-$ salts (X = Cl, Br; M = As, Sb) by protonation of phosphorus trihalides with HF/MF_5.[7] The compounds were characterised by vibrational and NMR spectroscopy. Due to the negligible solubility no single crystals of these compounds were available. Within the scope of further investigations of the behaviour of phosphorus trihalides in the superacidic system HF/AsF_5 we have isolated single crystals of $X_3PH^+As_2F_{11}^-$ salts (X = Cl, Br) and determined their structures by X-ray diffraction.

Results and Discussion

Formation of $X_3PH^+As_2F_{11}^-$ (X = Cl, Br)

Protonation of phosphorus trichloride or phosphorus tribromide by the superacidic system HF/AsF_5 gives the corresponding phosphonium undecafluorodiarsenates [Equation (1)]:

$$X_3P + HF + 2AsF_5 \rightarrow X_3PH^+As_2F_{11}^- \quad (X = Cl, Br) \qquad (1)$$

The resulting colourless, moisture-sensitive salts decompose in the case of the trichlorophosphonium salt above −25 °C, and in the case of the bromine compound above −45 °C. They can be stored for several months without decomposition under inert conditions at −70 °C.

X-ray Crystal structure of $Cl_3PH^+As_2F_{11}^-$

Trichlorophosphonium undecafluorodiarsenate crystallises in the orthorhombic space group *Pnma* (no. 53) with eight units per cell (see Table 1).[8] For data collection and reduction, a semi-empirical correction determined from single ψ-scan data, and programs in the SHELXL package, PLATON, MISSYM and PARST, were used.[9−12] The solution of the crystal structure was done by the Patterson method with a subsequent difference Fourier synthesis. A final refinement with anisotropic (except H atoms) thermal parameters gave a value of R = 0.0314.

The orthorhombic unit cell contents two crystallographically independent anions and cations. Table 2 lists important bond lengths and angles. Figure 1 shows a trichlorophosphonium cation with weak interionic contacts to the nearest atoms of the anions and Figure 2 a section of the crystal structure. The cation has the shape of a trigonal pyramid and the anion has a distorted edge-linked dioctahedral structure. The P−Cl bond lengths [192.9(1)−193.6(1) pm] show no significant differences and they are shortened by about 10 pm relative to the precursor PCl_3 [PCl_3: P−Cl = 203.9(1) pm].[13] The Cl−P−Cl angles of 109.5(1)° to 110.1(5)° are wider than in phosphorus trichloride [PCl_3: Cl−P−Cl = 100.07(7)−100.19(7)°].[13]

The two independent cations form the same kind of interionic contacts to the fluorine atoms of neighbouring an-

[a] Anorganische Chemie, Fachbereich Chemie der Universität Dortmund
44221 Dortmund, Germany

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Table 1. Crystal data and structure refinement for $Cl_3PH^+As_2F_{11}^-$ and $Br_3PH^+As_2F_{11}^-$

	$Cl_3PH^+As_2F_{11}^-$	$Br_3PH^+As_2F_{11}^-$
Space group (no.)	*Pnma* (53)	$P2_1/m$ (14)
Crystal system	Orthorhombic	Monoclinic
a [pm]	2350.6(1)	6177.0(1)
b [pm]	837.7(1)	872.4(2)
c [pm]	1179.9(1)	1182.5(2))
β [°]	–	94.68(3)
Volume [nm^3]	2.3233(4)	0.6351(2)
Density (calcd.) [g cm^{-3}]	2.843	3.297
Z	8	2
Formula mass [g mol^{-1}]	497.15	630.49
Absorption coefficient [mm^{-1}]	6.698	14.932
Temperature [K]	173	173
F(000)	1856	572
Wavelength [pm]	71.069	71.069
Theta range for data collection [°]	1.73 to 28.78	2.90 to 25.56
Index range	$-31 \le h \le 31$	$-4 \le h \le 6$
	$-10 \le k \le 10$	$-10 \le k \le 10$
	$-15 \le l \le 15$	$-14 \le l \le 8$
Reflections collected/independent	16177/2949	1490/998
Parameters	187	94
Goodness-of-fit on F^2	0.977	1.013
R [$I > 2\sigma(I)$]	$R = 0.031$; $wR2 = 0.0572$	$R = 0.050$; $wR2 = 0.1160$
R (all data)	$R = 0.065$; $wR2 = 0.0622$	$R = 0.061$; $wR2 = 0.1199$
Largest diff. Peak and hole[e nm^3]	704/−495	897/−1596
Refinement method	Full-matrix, least-squares on F^2	Full-matrix, least-squares on F^2

Table 2. Bond lengths [pm], selected angles [°] and contacts [pm] for $Cl_3PH^+As_2F_{11}^-$[a]

P(1)−Cl(11)	192.9(1)	Cl(11)−P(1)−Cl(12)	109.9(9)
P(1)−Cl(12)	193.6(2)	Cl(11a)−P(1)−Cl(12)	109.9(5)
P(2)−Cl(21)	193.6(1)	Cl(22)−P(2)−Cl(21)	110.1(5)
P(2)−Cl(22)	193.1(2)	Cl(21)−P(2)−Cl(21a)	109.5(1)
As(1)−F(11)	168.4(3)		
As(1)−F(12)	169.6(2)	As(1)−F(14)−As(2)	145.6(2)
As(1)−F(13)	167.7(2)	F(14)−As(1)−F(11)	178.1(4)
As(1)−F(14)	193.7(3)	F(12)−As(1)−F(13)	89.7(1)
As(2)−F(21)	168.4(3)		
As(2)−F(22)	169.2(3)	As(3)−F(32)−As(4)	148.3(2)
As(2)−F(23)	169.5(2)	F(32)−AS(3)−F(34)	177.9(1)
As(2)−F(24)	170.2(3)	F(35)−As(3)−F(33)	89.2(7)
As(2)−F(14)	190.2(3)		
As(3)−F(31)	169.4(3)	Cl(21)···F(13)	302.0(2)
As(3)−F(32)	182.3(2)	Cl(22)···F(11)	280.4(3)
As(3)−F(33)	171.8(3)	P(2)···F(33)	300.4(2)
As(3)−F(34)	169.9(2)		
As(3)−F(35)	170.5(2)	Cl(11)···F(31)	308.7(2)
As(4)−F(41)	168.1(3)	Cl(12)···F(41)	312.5(3)
As(4)−F(42)	165.8(2)	P(1)···F(23)	321.9(2)
As(4)−F(43)	166.2(2)		
As(4)−F(32)	205.9(2)		

[a] Symmetry operation: a = x, $-y$, 0.5 + z.

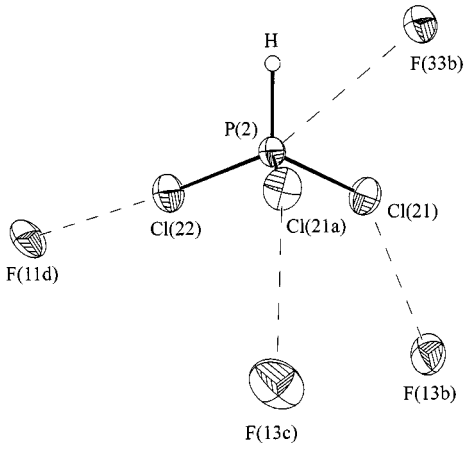

Figure 1. Fragment of the structure of $Cl_3PH^+As_2F_{11}^-$, showing the Cl_3PH^+ cation of the crystallographically independent unit 2 with interionic contacts (50% probability ellipsoids for the non-hydrogen atoms); symmetry operations: a = x, 0.5 − y, z; b = 0.5 − x, $-y$, $-0.5 + z$; c = 0.5 − x, 0.5 + y, $-0.5 + z$; d = $-0.5 + x$, y, 2.5 + z

ions, but with different strengths. There are chlorine-fluorine contacts of between 280.4(3) and 312.5(3) pm and P−F contacts of 300.4(2) pm and 321.9(2) pm, respectively. There are no contacts between hydrogen and fluorine atoms that are significantly below the sum of the van der Waals radii of 267 pm. The interionic contacts result in the formation of a three-dimensional linkage of anions and cations.

The anion consists of two distorted octahedra which are linked at one corner. The As−F bond lengths involving the "bridging" fluorine atom are 205.9(2) pm and are thus significantly longer than the other As−F bond lengths of between 167.7(2) and 170.5(2) pm, which are in the normal range of As−F bond lengths of hexafluoroarsenate anions.[14−16] These unusually long As−F bonds are in the same range as in the other known $As_2F_{11}^-$ salts.[14−16] In both anions the two octahedral AsF_6 units are in a gauche arrangement. The average torsion angles F−As−As−F of

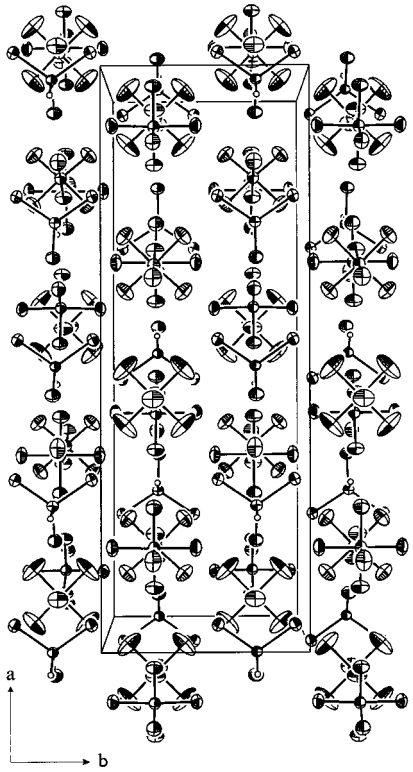

Figure 2. Projection of the $Cl_3PH^+As_2F_{11}^-$ salt

45.3° and 45.6° and the As−F−As bridge angles of 145.6(2)° and 148.3(2)° are similar to those found in other $As_2F_{11}^-$ salts.[14−16]

X-ray Crystal structure of $Br_3PH^+As_2F_{11}^-$

$Br_3PH^+As_2F_{11}^-$ crystallises in the monoclinic space group $P2_1/m$ (No. 14) with a = 617.7(1) pm, b = 872.4(2) pm, c = 1182.5(2) pm, β = 94.68(3)° and two formula units per unit cell.[17] The crystal structure was solved by direct methods and successive difference Fourier syntheses. For refinement full-matrix least-squares methods were applied. A final refinement with anisotropic (except H atoms) thermal parameters gave a value of R = 0.0504. For data reduction, structure solution, and refinement the same programs were used as for the structure solution of $Cl_3PH^+As_2F_{11}^-$.[9−12]

The crystal data are summarised in Table 1 and bond lengths and selected angles are shown in Table 3.

Table 3. Bond lengths [pm], selected angles [°] and contacts [pm] for $Br_3PH^+As_2F_{11}^-$[a]

Br(1)−P	211.1(2)	Br(1)−P−Br(2)	110.8(1)
Br(2)−P	211.1(4)	Br(1a)−P−Br(1)	110.3(2)
As(1)−F(11)	170.1(5)		
As(1)−F(12)	170.0(7)	As(1)−F(15)−As(2)	145.9(4)
As(1)−F(13)	171.0(6)	F(11)−As(1)−F(12)	89.8(2)
As(1)−F(14)	172.9(6)	F(13)−As(1)−F(14)	174.9(4)
As(1)−F(15)	183.6(6)		
As(2)−F(21)	168.5(5)	Br(1)·····F(13)	306.1(3)
As(2)−F(22)	168.5(7)	Br(1)·····F(21)	325.1(2)
As(2)−F(23)	167.8(6)	Br(2)·····F(22)	300.8(7)
As(2)−F(15)	202.0(6)		

[a] Symmetry operation: a = x, y − 1.5, z.

The phosphorus−bromine bond lengths are equal and shorter by about 10 pm than in the precursor [PBr_3: P−Br = 221.2(3) pm].[18] The Br−P−Br angles of 110.3(2)° and 110.8(1)° are wider than in phosphorus tribromide [PBr_3: Br−P−Br = 99.0(2)−101.3(2)°].[18]

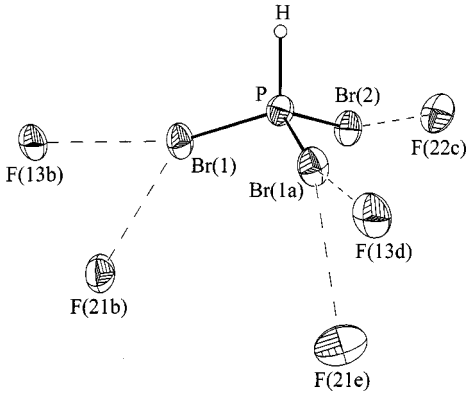

Figure 3. Fragment of the structure of $Br_3PH^+As_2F_{11}^-$, showing the Br_3PH^+ cation with interionic contacts (50% probability ellipsoids for the non-hydrogen atoms); symmetry operations: a = x, y − 1.5, z; b = 1 + x, 1 + y, z; c = −x, 1 − y, 1 − z; d = 1 − x, −y, −z; e = 1 + x, 0.5 − y, z

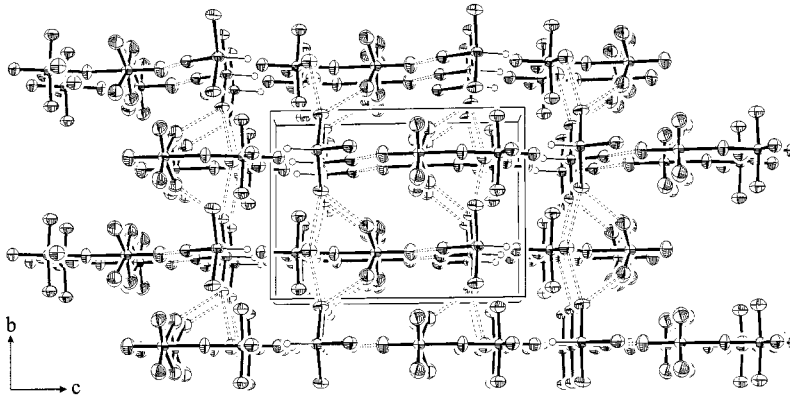

Figure 4. Projection of the $Br_3PH^+As_2F_{11}^-$ salt with interionic contacts

The cations form interionic contacts of different strengths to fluorine atoms of neighbouring anions (Figure 3). Two weak fluorine−bromine contacts of 300.8(7) pm and 325.1(2) pm result in the formation of chains in the *bc* plane. The chains of different *bc* planes are connected along the *c* axes by further weak fluorine−bromine contacts of 321.8(7) pm (Figure 4).

The undecafluorodiarsenate anion has the same distorted edge-linked dioctahedral structure as the anion in the $Cl_3PH^+As_2F_{11}^-$ salt. All bond lengths and angles of the anion (Table 3) are of the same order as the previous salt and similar to the other known $As_2F_{11}^-$ salts.[14−16]

Experimental Section

All synthetic work and sample handling was conducted by standard Schlenk techniques on a standard vacuum line (stainless steel or glass). Drying of HF was carried out with Fluorine (1.5 bar) in a stainless steel bomb. AsF_5 was synthesised from As and F_2.[19] The synthesis of PBr_3 was carried out by a known literature method from Br_2 (Riedel de Haen) and red phosphorous (Fluka).[20] PBr_3 and PCl_3 (Riedel de Haen) were distilled repeatedly before use. Reactions in HF were carried out in a KEL-F reactor fitted with a KEL-F valve. Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and an X-ray diffraction study was carried out at −100 °C using a Nonius Kappa CCD-(1152 × 1242 Pixel) diffractometer.

Preparation of $X_3PH^+As_2F_{11}^-$ (X = Cl, Br):

Caution! Avoid contact with these compounds and note that hydrolysis of $As_2F_{11}^-$salts forms HF, which burns the skin and causes irreparable damage. Safety precautions should be taken when using and handling these materials!

In a typical experiment AsF_5 (1 g, 5.9 mmol) was dissolved in HF (10 g) in a 50 mL KEL-F reactor. The solution was frozen at −196 °C and PX_3 (X = Cl, Br; 0.01 mmol) was added under an inert atmosphere (N_2). The mixture was warmed to −78 °C and kept for 30 minutes. The excess HF and AsF_5 were very slowly removed during 5 days under dynamic vacuum at −78 °C. The remaining colourless salts contained crystals suitable for X-ray diffraction studies and can be stored under inert conditions at −70 °C without decomposition.

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