Trichlorohydroxyphosphonium Hexafluorometallate — Synthesis, Spectroscopic Characterization and Crystal Structure of $Cl_3POH^+AsF_6^-$

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The reaction of trichlorophosphane oxide with the superacidic systems XF/MF_5 (X = H, D; M = As, Sb) leads to trichlorophosphonium hexafluorometallates. The structure of trichlorophosphonium hexafluoroarsenate was successfully determined. $Cl_3POH^+AsF_6^-$ crystallises in the orthorhombic space group *Pnma* (No. 53) with four formula units per unit cell with the dimensions *a* = 1286.7(1) pm, *b* = 842.2(1)pm and *c* = 822.2(1) pm. The Raman, IR, ^1H and ^{31}P NMR spectra of $Cl_3POX^+MF_6^-$ (X = H, D; M = As, Sb) are reported.

Introduction

The behaviour of trichlorophosphane oxide in strongly acidic solvents has been studied by various techniques since 1966.[1−8] Gillespie et al. found $POCl_3$ to be a non-electrolyte in 100% H_2SO_4, while Paul and co-workers, using mainly cryoscopy and conductance techniques, concluded that $POCl_3$ is incompletely protonated in HSO_3F, but completely protonated by $H_2S_2O_7$ to Cl_3POH^+.[1−4] Partial protonation of $POCl_3$ by chlorosulfuric acid has been reported by Zaidi et al.[5] Dillon et al. and Hibbert et al. used ^{31}P NMR spectroscopy to investigate the behaviour of $POCl_3$ in different acidic media.[6,7] Their studies suggested that an increase of the acidic strength leads to an increase in the degree of protonation of $POCl_3$ in the different acids. Dillon et al. observed the formation of the Cl_3POH^+ cation as an intermediate in the reaction of PCl_3 or PCl_5 with acidic solvents like H_2SO_4 (100%), oleum or HSO_3Cl.[6,8] No attempts were made to isolate the Cl_3POH^+ cation in the form of a phosphonium salt.

In recent years our research group has been successful in the isolation and characterisation of such unstable onium salts by protonation of various precursors at low temperature in the superacidic system HF/MF_5 (M = As, Sb).[9−11] Within the scope of our investigations of the behaviour of phosphorus compounds in the superacidic systems HF/MF_5 (M = As, Sb) we isolated a series of $Cl_3POX^+MF_6^-$ salts (X = H, D; M = As, Sb) and characterised them by X-ray diffraction, and vibrational and NMR spectroscopy.[12−14]

Results and Discussion

Formation of $Cl_3POX^+MF_6^-$ Salts (X = H, D; M = As, Sb)

The salts are prepared by protonation of trichlorophosphane oxide in superacidic media XF/MF_5 (X = H, D; M = As, Sb) [Equation (1)].

$$Cl_3PO + XF + MF_5 \rightarrow Cl_3POX^+MF_6^- \quad (X = H, D; M = As, Sb) \tag{1}$$

The colourless solids are stable for several months at −70 °C under nitrogen atmosphere, decomposing at −30 °C in the case of the hexafluoroarsenates and at −5 °C in the case of the hexafluoroantimonates. The salts are slightly soluble in sulfur dioxide at −60 °C and HF at −78 °C.

X-ray Crystal Structure of $Cl_3POH^+AsF_6^-$

Trichlorohydroxyphosphonium hexafluoroarsenate crystallises in the orthorhombic space group *Pnma* (No. 53) with *a* = 1286.7(1) pm, *b* = 842.2(1) pm, *c* = 822.2(1) pm and four formula units per unit cell. The crystal structure was solved by applying the Patterson method and successive difference Fourier syntheses. For refinement full-matrix least-square methods were applied. The hydrogen atom was taken from Fourier maps and refined with isotropic displacement parameters; all non-hydrogen atoms were refined with anisotropic displacement parameters. For the data reduction, structure solution, and refinement, programs in the SHELXTL package, PLATON, MISSYM, and PARST were used.[16−18] The crystal data are summarised in Table 1.[19] The cation has C_s symmetry and the anion a distorted octahedral structure. Bond lengths and selected angles are shown in Table 2. The structure of the trichlorohydroxyphosponium cation with a hydrogen bond

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[O···F(2): 249.5(9) pm] and weak interionic contacts to the nearest fluorine atoms of the anions is shown in Figure 1. Figure 2 shows a section of the crystal structure. The hydrogen bond and the strongest interionic Cl···F contact result in the formation of chains parallel to the *ac* plane, and the other weaker Cl···F contacts lead to a linkage of these chains. One of the chlorine atoms [Cl(1)] forms more contacts to fluorine atoms than the others. This different environment of the Cl atoms correlates with more vibrational modes for the PCl_3 group in the IR and Raman spectra (see below). The PO bond length of 150.6(7) pm is lengthened relative to the precursor [$POCl_3$: 145.6(1) pm] and lies in the range between typical single and double bonds.[20,21] In comparison to the precursor the phosphorus-chlorine bond lengths are equal and shortened [$POCl_3$: 196.6(1) pm to 199.0(1) pm].[20] The phosphorus has a distorted tetrahedral environment with angles between 107.4(2)° and 111.9(3)°.

Table 1. Crystal data and structure refinement for $Cl_3POH^+AsF_6^-$

	$Cl_3POH^+AsF_6^-$
Space group (no.)	*Pnma* (53)
Crystal system	Orthorhombic
a [pm]	1286.7(1)
b [pm]	841.2(1)
c [pm]	822.2(1)
V [nm^3]	0.8899(4)
Density (calcd.) [g cm^{-3}]	2.562
Z	4
Formula mass [g mol^{-1}]	343.2
Absorption coefficient [mm^{-1}]	4.947
T [K]	173
F(000)	648
Wavelength [pm]	71.069
Theta range for data collection [°]	2.94 to 30.53
Index range	$-18 \le h \le 18$ $-11 \le k \le 11$ $-11 \le l \le 11$
Reflections collected/independent	7937/1430
Parameters	71
Goodness-of-fit on F^2	1.167
R [$I > 2\sigma(I)$]	$R1 = 0.0626$; $wR2 = 0.1492$
R (all data)	$R1 = 0.0743$; $wR2 = 0.1527$
Largest diff. Peak and hole [e nm^3]	1145/−1077
Refinement method	Full-matrix, least-squares on F^2

Table 2. Bond lengths [pm] and selected angles [deg] for $Cl_3POH^+AsF_6^-$

P−O	150.6(7)	O−P−Cl(1)	111.9(3)
P−Cl(1)	193.6(4)	O−P−Cl(2)	109.4(2)
P−Cl(2)	193(1)	Cl(2)−P−Cl(1)	109.3(1)
As−F(1)	171.6(6)		
As−F(2)	175.7(7)	F(1)−As−F(2)	86.9(3)
As−F(3)	169.2(8)	F(1)−As−F(3)	92.5(4)
As−F(4)	169.6(6)	F(1)−As−F(4)	176.3(3)
As−F(5)	169.6(6)	F(1)−As−F(5)	89.4(2)
F(2)···O	249(1)	F(2)−As−F(3)	179.3(4)
Cl(1)···F(1)	294.3(7)	F(2)−As−F(4)	89.4(3)
Cl(1)···F(4)	310.6(7)	F(2)−As−F(5)	89.2(3)
Cl(1)···F(5)	311.6(6)	F(3)−As−F(4)	91.3(4)
Cl(2)···F(1)	306.9(3)		

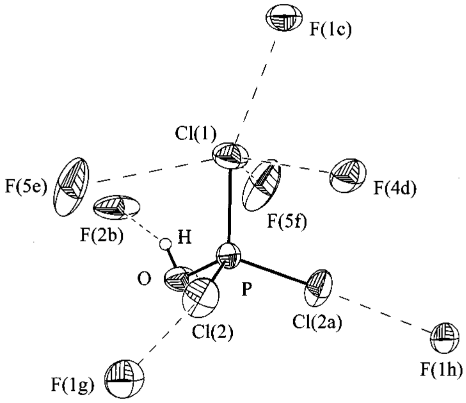

Figure 1. Fragment of the structure of $Cl_3POH^+AsF_6^-$, showing the Cl_3POH^+ cation with interionic contacts (50% probability ellipsoids for the non hydrogen atoms); symmetry operations: a = *x*, −0.5 − *y*, 1 + *z*; b = −0.5 + *x*, *y*, −0.5 − *z*; c = −0.5 + *x*, *y*, 1.5 − *z*; d = *x*, +*y*, 1 + *z*; e = 0.5 − *x*, *y*, 0.5 + *z*; f = 0.5 − *x*, 0.5 + *y*, 0.5 + *z*

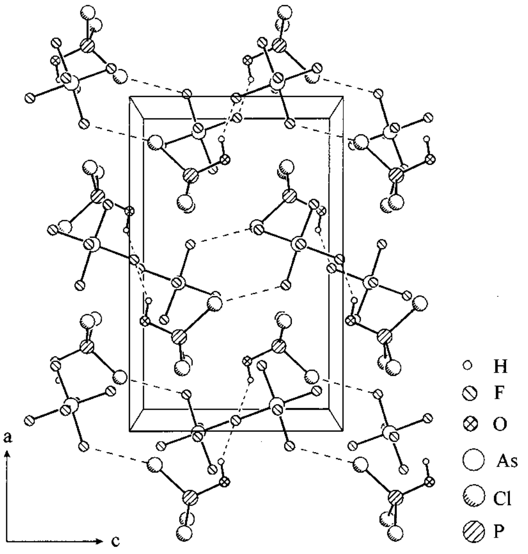

Figure 2. Structure of $Cl_3POH^+AsF_6^-$, showing the arrangement in the crystal lattice

The As−F bond lengths of the anion that is involved in the hydrogen bond and the short Cl···F contacts are longer than the other As−F lengths. A distorted octahedral structure is found for the AsF_6^- anions in the $Cl_3POH^+AsF_6^-$ salt, with deviations from an ideal octahedron of up to 3.3°.

Vibrational Spectra

The Raman and IR spectra of $Cl_3POD^+AsF_6^-$ are shown in Figure 3 and all observed wavenumbers of the salts are summarised in Table 3. The vibrational spectra are assigned according to C_s symmetry for the Cl_3POX^+ cation (X = H, D) and by comparison with the precursor and IR matrix spectra of the isoelectronic trichlorohydroxysilane.[22−24] The cation has twelve fundamental modes consisting of eight A_1 vibrations and four A_2 vibrations. All vibration modes are active in both the Raman

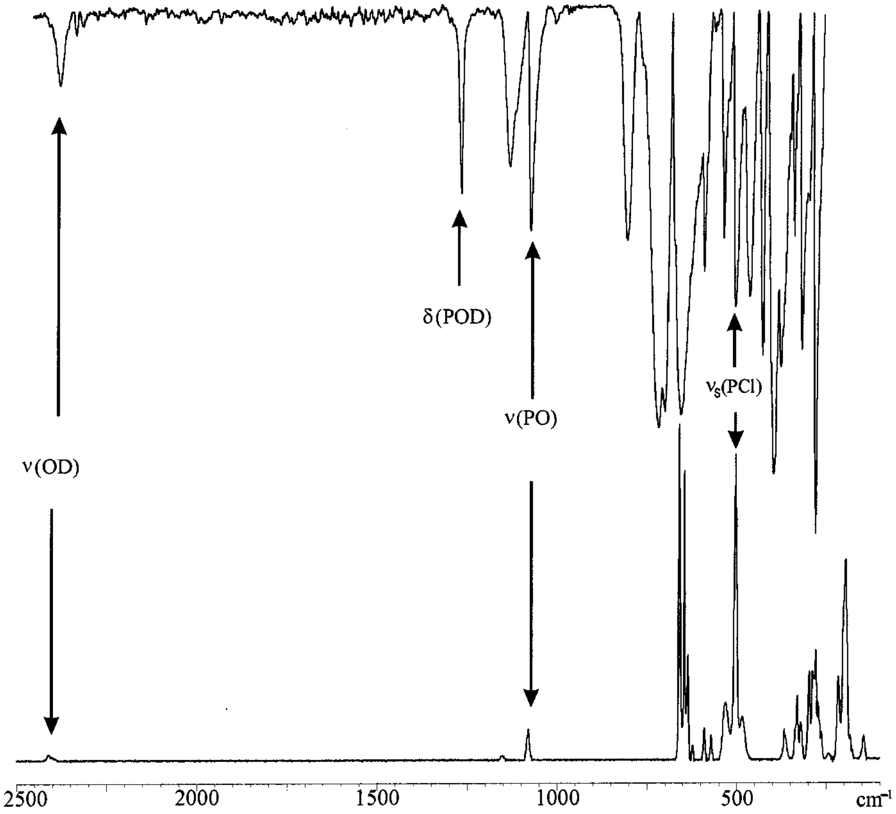

Figure 3. IR and Raman spectra of $Cl_3POD^+AsF_6^-$

and IR spectra. Due to the different interactions between the chlorine and fluorine atoms (see above) we observed more vibrational modes for the PCl_3 group than would have been expected without the X-ray studies. Altogether fifteen vibrational modes for the Cl_3POX^+ cation (X = H, D) were detected. Vibrational modes below 220 cm^{-1} were not detectable on account of the window material used in the low temperature cuvette for IR measurements (CsBr). The fifteen detected modes can be divided into four modes which are associated with the OH and PO modes, with the remaining modes being considered as motions of the PCl_3 group.

The OH and OD stretching modes are found at 3135 cm^{-1} and 2410 cm^{-1}, respectively. The corresponding POX (X = H, D) deformation modes were only observed by IR spectroscopy (at 1280 cm^{-1}) due to their low Raman intensity. The position of the PO stretching mode is important for the spectroscopic confirmation of the Cl_3POX^+ cation. The PO stretching mode is shifted to lower wavenumbers by 200 cm^{-1}, relative to the precursor, corresponding to protonation of Cl_3PO at the O atom.[22] The PCl stretching modes are observed in the range of 501 to 667 cm^{-1}. They are shifted by up to 80 cm^{-1} to higher wavenumbers relative to the analogous vibrations in trichlorophosphane oxide.[22] The PCl_3 deformation modes are found between 193 and 430 cm^{-1}. Two OPCl deformation modes are detected at 800 cm^{-1} and 1150 cm^{-1}, respectively, due to the interionic interactions between the Cl atoms and the F atoms of the anions.

Because of cation−anion interactions, the MF_6^- ions (M = As, Sb) do not show ideal O_h symmetry. This lowered symmetry causes a splitting of the anion vibrational modes.[25]

^1H and ^{31}P NMR Spectra of $Cl_3POH^+MF_6^-$ (M = As, Sb)

The ^1H NMR spectra of freshly prepared $Cl_3POH^+MF_6^-$ (M = As, Sb) dissolved in SO_2 with TMS as external standard at −60 °C show a singlet at $\delta = 10.7$ (AsF_6^-) and $\delta = 10.8$ (SbF_6^-) for the hydroxyl group. In the ^{31}P NMR spectra a singlet at $\delta = 55.5$ for the arsenate and $\delta = 55.2$ for the antimonate are observed. These signals are shifted to lower field by more than 51 ppm relative to the precursor. This result is similar to the results of Dillon and Hibbert (Table 4).[6,7]

Experimental Section

Caution: *Avoid contact with these compounds and note that the hydrolysis of AsF_6^- and SbF_6^- salts forms HF, which burns the skin and causes irreparable damage. Safety precautions should be taken when using and handling these materials!*

General: 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.[26] SbF_5 (Merck) and $POCl_3$ (Merck) were distilled repeat-

Table 3. Vibrational wavenumbers of trichlorohydroxyphosphonium salts and their possible assignments[a]

$Cl_3POD^+AsF_6^-$		$Cl_3POD^+SbF_6^-$		$Cl_3POH^+AsF_6^-$		$Cl_3POH^+SbF_6^-$		Cl_3SiOH[23][24]	Possible Assignment
IR −50 °C	Raman −78 °C	Raman −78 °C	IR −50 °C	IR −50 °C	Raman −78 °C	IR −50 °C	Raman −78 °C	IR −253 °C	
2427 w	2410(3)	2407(2)	2426 w	3135 vs	n. o.	3120 s	n. o.	3693	ν(OX)
1283 m	n. o.	n. o.	1291 w	1289 m	n. o.	1252 w	n. o.	1330	δ(POX)
1149 m	1150 (3)	n. o.	n.o.	1159 w	n. o.	1152 w	n. o.		δ(OPCl)
1086 m	1078 (10)	1088 (9)	1077 m	1020 m	n. o.	1014 m	1026 (10)	960	ν(PO)
813 m	n. o.	n. o.	811 m	886 m	n. o.	868 m	n. o.	798	δ(OPCl)
657 vs	635 (32)	646 (10)	655 vs	667 s	655 (15)	645 vs	660 (55)		$\nu_{as}(PCl_3)$
592 m	589 (8)	592 (15)	588 m	593 m	593 (15)	585 s	591(10)	621	$\nu_{as}(PCl_3)$
535 m	530 (16)	531 (17)	536 m	534 m	529 (29)	532 s	531		δ(POX)
501 s	502 (83)	502 (100)	508 s	504 m	502 (100)	504 m	505 (100)	462	$\nu_s(PCl_3)$
424 s	n. o.	423 (6)	451 m	430 m	428 (7)	427 m	n. o.		$\rho(PCl_3)$
372 s	365 (10)	376 (38)	366 s	367 m	376 (38)	n. o.	378 (10)		$\rho(PCl_3)$
314 s	319 (13)	314 (24)	317 s	317 m	317 (35)	n. o.	324 (12)		$\delta(PCl_3)$
274 vs	279 (35)	273 (42)	289 vs	276 s	275 (58)	n. o.	277 (30)		$\delta_s(PCl_3)$
n. o.	217 (24)	211 (58)	n. o.	n. o.	212 (68)	n. o.	220 (25)		$\delta_{as}(PCl_3)$
n. o.	195 (58)	193 (55)	n. o.	n. o.	194 (50)	n. o.	197 (40)		$\delta_{as}(PCl_3)$
725 vs				723 s					MF_6^-
704 vs				705 s	703 (70)		700 (15)		MF_6^-
		700 (55)					685 (15)		MF_6^-
		673 (61)	660 vs		673 (83)	661 vs			MF_6^-
	659 (100)	661 (16)	631 s		662 (16)	630 s			MF_6^-
	645 (84)								MF_6^-
	570 (7)				569 (8)				MF_6^-
463 s	483 (12)			392 s		400 w			MF_6^-
394 vs									MF_6^-
335 m	331 (20)	337 (15)	333 m	346 m	347 (6)				MF_6^-
292 m	297 (31)							299 (25)	MF_6^-

[a] n. o. = not observed; vs = very strong; s = strong; m = medium; w = weak; X = H, D; M = As, Sb.

Table 4. ^1H and ^{31}P NMR spectroscopy data for $Cl_3POH^+MF_6^-$ (M = As, Sb) and literature data for Cl_3PO in acidic media

	$\delta(^{31}P)$[a]	$\delta(^1H)$
$Cl_3POH^+AsF_6^-$ [b]	55.5 (s)	10.7 (s)
$Cl_3POH^+SbF_6^-$ [b]	55.2 (s)	10.8 (s)
Cl_3PO in H_2SO_4 + 65% SO_3 [6][7]	55. 9 (s)	–
Cl_3PO in H_2SO_4 + 25% SO_3 [6][7]	35.3 (s)	–
Cl_3PO in H_2SO_4 [6], [7]	20.1 (s)	–
Cl_3PO [6], [7]	3.6 (s)	–

[a] (s) = Singlet. [b] Measured in SO_2 at −60 °C.

edly before use. Reactions in HF were carried out in a KEL-F reactor fitted with a KEL-F valve. The Raman spectra were recorded on a Jobin Yvon T64000 spectrometer using an Ar^+ laser (514.5 nm) from Spectra Physics. The spectra were obtained in a glass cell cooled with solid CO_2.[27] Infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra were obtained from a coated CsBr plate in a low-temperature cuvette.[28] NMR spectra were recorded with a Bruker DPX spectrometer and referenced to either TMS (^1H) or 85% H_3PO_4 (^{31}P) in SO_2 at −60 °C. Single crystals for the crystallographic studies were placed in Lindemann capilllaries 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 $Cl_3POX^+MF_6^-$ (X = H, D; M = As, Sb): In a typical reaction, 5 mL of XF (X = H, D) was distilled into the Kel-F reactor at −196 °C, followed by 0.2 mmol of MF_5 (M = As, Sb). The mixture was warmed to 20 °C to form the superacid. The reactor was then cooled to −196 °C, and $POCl_3$ (0.2 mmol) was added. The mixture was warmed to −78 °C. After removing the volatile compounds at −78 °C during 7 days colourless solids, stable up to −30 °C (arsenate) and −5 °C (antimonate) were obtained.

$Cl_3POH^+AsF_6^-$: ^1H NMR: δ = 10.7 (s). ^{31}P NMR: δ = 55.5(s).
$Cl_3POH^+SbF_6^-$: ^1H NMR: δ = 10.8 (s). ^{31}P NMR: δ = 55.2(s).

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