Synthesis and Characterisation of New Arsonium Salts and Crystal Structures of Trimethylarsonium Undecafluorodiarsenate $(CH_3)_3AsH^+As_2F_{11}^-$ and Trimethylarsonium Hexafluoroantimonate $(CH_3)_3AsH^+SbF_6^-$

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The reaction of trimethylarsane in the superacidic systems hydrogen/fluoride antimony pentafluoride and hydrogen fluoride/arsenic pentafluoride leads to trimethylarsonium fluorometallates. These salts are stable up to 60 °C and 5 °C, respectively. Structures were successfully elucidated in the cases of trimethylarsonium undecafluorodiarsenate and trimethylarsonium hexafluoroantimonate. $(CH_3)_3AsH^+As_2F_{11}^-$ crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell with the dimensions a = 7.362(1), b = 12.589(1), c = 13.598(1) Å and β = 95.37(1)°. $(CH_3)_3AsH^+SbF_6^-$ crystallizes in the monoclinic space group $P2_1/m$ with four formula units per unit cell with the dimensions a = 8.313(1), b = 8.855(1), c = 13.285(1) Å and β = 94.358(1)°.

Introduction

Arsanes are much weaker bases than amines, although they do demonstrate nucleophilic properties. For instance, arsane is protonated during the reaction with hydrogen bromide or hydrogen iodide (Equation 1).[1]

$$AsH_3 + HX \rightarrow AsH_4^+X^- \quad X = Br, I \tag{1}$$

However, these salts are only stable up to −123°C (Br⁻) and −83°C (I⁻), respectively.

Stabilisation to −40°C (SbF_6^-) and −75°C (AsF_6^-) is achieved by exchanging the anions by hexafluoroantimonate or hexafluoroarsenate (Equation 2).[2]

$$AsH_3 + HF + MF_5 \rightarrow AsH_4^+MF_6^- \quad M = As, Sb \tag{2}$$

Dimethylarsane reacts with hydrogen chloride with formation of dimethylarsonium chloride (Equation 3), which is completely dissociated into the starting materials at 20°C.[3]

$$(CH_3)_2AsH + HCl \rightleftharpoons (CH_3)_2AsH_2Cl \tag{3}$$

Trimethylarsane and, for example, methyl halogenides (CH_3Cl, CH_3Br, CH_3I) form stable tetramethylarsonium salts i.e. $(CH_3)_4As^+Br^-$ and $(CH_3)_4As^+I^-$ which have been identified by their crystal structures.[4][5]

Although attempts to protonate triphenylarsane in sulfuric acid failed, the reaction of triphenylarsane with hydrogen chloride, yielding the triphenylarsonium salt (Equation 4), nevertheless succeeded.[6][7]

$$Ph_3As + HCl \xrightarrow{HCl} Ph_3AsH^+Cl^- \tag{4}$$

Hence, the protonation of trimethylarsane in the superacidic systems hydrogen fluoride antimony pentafluoride and arsenic pentafluoride, respectively, should lead to salts which are more stable than dimethylarsonium chloride but less stable than the tetramethylarsonium salts.

Not only will the series of $(CH_3)_nAsH_{4-n}^+$ salts with $n = 1-4$ be completed but new pnikogenium salts which are analogous to trimethylphosphonium salts will also be formed. The crystal structure of trimethylphosphonium hexachloroantimonate is well-known and could be compared to the structures of prepared trimethylarsonium undecafluorodiarsenate and trimethylarsonium hexafluoroantimonate.[8]

Moreover, a structure elucidation of a undecafluorodiarsenate salt succeeded. This anion was firstly mentioned by Brownstein in 1969, who examined the reaction of various hexafluoroantimonate and hexafluoroarsenate salts with AsF_5.[9] Further investigations by Raman spectroscopy, IR spectroscopy, NMR spectroscopy, cryoscopic and conductimetric measurements followed.[10−13] In spite of the fact that this kind of salt has been known since 1969, structural data, in comparison to the undecafluorodiantimonate, are scarce. Only a few crystal structures of salts with undecafluorodiarsenate as the anion are known up to now. To date, Christe has been able to determine the crystal structure of an $As_2F_{11}^-$ salt,[14] whilst we have crystallized salts of $HPCl_3^+As_2F_{11}^-$ (to be published), $(MeS)_2CSX^+As_2F_{11}^-$ (X = H, D) and $(CH_3)_3AsH^+As_2F_{11}^-$ reported now.[15]

Results and Discussion

Formation of $(CH_3)_3AsH^+$ Salts

The salts are prepared by protonation of trimethylarsane in superacidic media, hydrogen fluoride and antimony pentafluoride (Equation 5) or arsenic pentafluoride (Equation 6).

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$$As(CH_3)_3 + HF + SbF_5 \xrightarrow{HF/-78\,^{\circ}C} (CH_3)_3AsH^+SbF_6^- \quad (5)$$

$$As(CH_3)_3 + HF + 2AsF_5 \xrightarrow{HF/-78\,^{\circ}C} (CH_3)_3AsH^+As_2F_{11} \quad (6)$$

The fine colourless solids are stable for several months at −70°C under a nitrogen atmosphere, decomposing at 5°C in the case of the undecafluorodiarsenate and at 60°C in the case of the hexafluoroantimonate. The salts dissolve well in sulfur dioxide at −40°C.

Vibrational Spectra

The Raman and IR spectra of $(CH_3)_3AsH^+SbF_6^-$ are shown in Figure 1 and all observed wavenumbers of the salts are summarised in Table 1. The vibrational spectra are assigned according to C_{3v} symmetry for the $(CH_3)_3AsH^+$ cation. The cation has twenty-four fundamental modes consisting of eight A_1 vibrations, four A_2 vibration and twelve E vibrations. The A_2 modes are inactive in both Raman and IR spectra. The twenty active fundamentals can be divided into six modes which are largely associated with $HAsC_3$ skeletal vibrations and the remaining modes which can be considered as motions of the methyl group. The CH_3 stretching modes are found in the range of 3042 to 2949 cm^{-1} and the corresponding deformation modes from 1433 cm^{-1} to 1180 cm^{-1}. The As−H and As−D stretching modes are detected at 2290 cm^{-1} and 1650 cm^{-1}, respectively.

The assignment of the skeletal vibrations is much more difficult because both anion and cation have the same anticipated range of vibrations. However, the possible assignment is carried out by comparison with the AsH_4^+ cation and the isoelectronic trimethylgermane.[2][16] Only four modes of the expected six could be assigned. In the range of 950 cm^{-1} to 880 cm^{-1} the CAsH and CAsD deformation modes are observed. They are shifted up to 90 cm^{-1} to higher wavenumber in comparison to the analogous vibration in trimethylgermane. The out-of-phase stretching modes of the AsC_3 skeleton are assigned to the lines and bands around 655 cm^{-1} and the in-phase stretching modes to those at 600 cm^{-1}. The corresponding deformation modes are detected at 220 cm^{-1}. The remaining vibrations are possibly modes of the anions.

Crystal Structure of $(CH_3)_3AsH^+As_2F_{11}^-$

$(CH_3)_3AsH^+As_2F_{11}^-$ crystallises in the monoclinic space group $P2_1/n$ (no. 14) with a = 7.362(1), b = 12.589(1), c = 13.598(1) Å, β = 95.37(1)° and four formula units per unit cell. The crystal structure was solved via the Patterson method and successive difference Fourier syntheses. For refinement full-matrix least-squares methods were applied. All hydrogen atoms were taken from Fourier maps and refined with isotropic displacement parameters and all non-hydrogen atoms with anisotropic displacement parameters. For the data reduction, structure solution, and refinement, programs in the SHELXTL package, PLATON, MISSYM, and PARST were used.[17−21] The crystal data are summarised in Table 2. The cation has the shape of a trigonal pyramid and the anion has a distorted edge-linked dioctahedral structure. Bond lengths and selected angles are shown in Table 3. The structure of trimethylarsonium cation with weak hydrogen bonds [H···F: 2.44(7) Å to 2.55(5) Å] to the nearest fluorine atoms of the anions is shown in Figure 2.

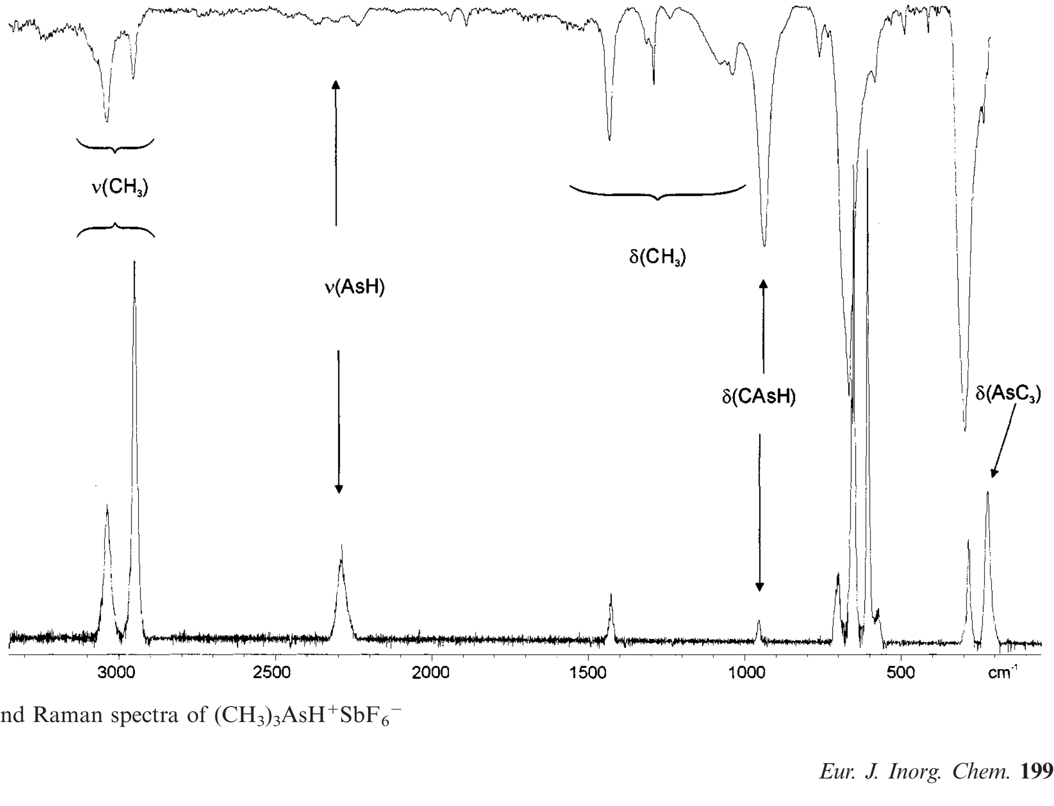

Figure 1. IR and Raman spectra of $(CH_3)_3AsH^+SbF_6^-$

Table 1. Vibrational wavenumbers of trimethylarsonium salts and Raman wavenumbers of trimethylgermane

$As(CH_3)_3H^+As_2F_{11}^-$				$As(CH_3)_3D^+As_2F_{11}^-$				$As(CH_3)_3H^+SbF_6^-$				$As(CH_3)_3D^+SbF_6^-$				$(CH_3)_3GeH$	Assignment
IR −30°C		Raman −78°C		IR −30°C		Raman −78°C		IR room temp.		Raman room temp.		IR room temp.		Raman room temp.		Raman [19]	
3036	w	3041	m	3040	w	3042	m	3033	m	3035	m	3035	m	3038	m	2982	$\nu(CH_3)$
		2955	s	2958	vw	2956	s	2950	w	2947	s	2949	w	2950	s	2913	$\nu(CH_3)$
						2949	s										$\nu(CH_3)$
2372	vw							2361	w								$\nu(CH_3)$
2299	vw	2295	m			1649	m	2299	w	2297	m			1658	m	2036	ν(AsH), (AsD), (GeH)
2230	vw							2232	w								ν(AsH), (AsD), (GeH)
								1933	w								ν(AsH), (AsD), (GeH)
								1884	w								ν(AsH), (AsD), (GeH)
1432	m	1420	w	1432	w	1430	w	1425	m	1426	w	1429	m	1428	w	1419	$\delta(CH_3)$
				1418	sh												$\delta(CH_3)$
				1311	vw			1305	sh			1305	sh	1312	vw		$\delta(CH_3)$
														1295	vw	1247	$\delta(CH_3)$
1282	w			1281	w	1288	vw	1281	m			1281	w	1283	vw		$\delta(CH_3)$
								1230	w								$\delta(CH_3)$
								1073	sh			1086	w				$\delta(CH_3)$
								1028	w			1026	w				$\delta(CH_3)$
929	s	956	vw	937	m	940	vvw	929	s	950	vw	934	s	941	vw		δ(CAsH), (CAsD), (CGeH)
				884	m							884	m	888	vw	850	δ(CAsH), (CAsD), (CGeH)
																830	$\rho(CH_3)$
811	w			818	w												$As_2F_{11}^-$
791	vw																$As_2F_{11}^-$
		739	m			734	m	752	w			745	sh				
							723	vw			722	m					
698	vs	700	sh	699	vs	699	w			695	w						$As_2F_{11}^-$, SbF_6^-
679	sh	685	s	680	sh	682	m										$As_2F_{11}^-$, SbF_6^-
		657	m	655	sh	657	m	657	vs	650	sh	656	vs	656	sh	597	$\nu_{as}(AsC_3)$, (GeC_3)
										644	s			649	s		SbF_6^-
																626	$\rho(CH_3)$
		607	vs			604	s			600	s	591	vw	605	vs	573	$\nu_s(AsC_3)$, (GeC_3)
								571	vw	568	vw	570	vw	572	vw		$As_2F_{11}^-$, SbF_6^-
				535	w	540	m					536	w	537	m		$As_2F_{11}^-$, SbF_6^-
								476	w			475	m				$As_2F_{11}^-$, SbF_6^-
						443	vw										$As_2F_{11}^-$, SbF_6^-
						426	vw										$As_2F_{11}^-$, SbF_6^-
395	s	397	w	395	vs	394	w	400	w					372	vw		$As_2F_{11}^-$, SbF_6^-
						373	w					370	w				$As_2F_{11}^-$, SbF_6^-
		313	w			313	vw										$As_2F_{11}^-$, SbF_6^-
						284	vw	286	vs	280	mw	286	vs	282	m		$As_2F_{11}^-$, SbF_6^-
259	w			269	sh												$As_2F_{11}^-$, SbF_6^-
				235	sh							234	w				$As_2F_{11}^-$, SbF_6^-
219	vw	228	m	221	sh	224	m	224	w	219	m	220	vw	223	m	189	$\delta(AsC_3)$, (GeC_3)

For comparison, the sum of the van der Waals radii of fluorine and hydrogen amounts to 2.67 Å.[22] Only the hydrogen atoms of the methyl groups are involved in hydrogen bonds and not the hydrogen atom which is directly bonded to the arsenic atom. No contact between arsenic and fluorine atoms, which is significantly below the sum of the van der Waals radii of 3.32 Å, is formed. The weak hydrogen bonds result in a formation of ribbons and two "As−F contacts", in the range of the sum of the van der Waals radii, of 3.304(3) Å and 3.399(3) Å, lead to a weak linkage of these ribbons. The As−C lengths of 1.894(5) Å, 1.907(5) Å and 1.908(5) Å are comparable to those found in methyltrifluoroarsonium hexafluoroarsenate of 1.886(4) Å and dimethyldifluoroarsonium hexafluoroantimonate of 1.894(7) Å, but are significantly shorter than that in trimethylarsane of 1.98(2) Å.[23−25] Comparison of the C−As−C angles of 109.5(3)°, 109.8(3)° and 111.1(3)° to the analogous C−P−C angles in trimethylphosphonium hexachloroantimonate of 109.7(4)°, 110.4(4)° and 111.0(3)° show no significant difference.[8]

The undecafluorodiarsenate anion with hydrogen bonds is shown in Figure 3. The As−F bond lengths involving the "bridging" fluorine atom are asymmetrical and amount to 1.855(3) Å and 1.983(3) Å. They are significantly longer than the other As−F bond lengths of 1.675(3) Å up to 1.696(3) Å, which are in the normal range of As−F bond lengths of hexafluoroarsenate anions.[26−28] The As−F bond lengths involving the "bridging" fluorine atom in $(CH_3S)_2CSH^+As_2F_{11}^-$ of 1.867(4) Å and 1.920(6) Å are in the same range as in the presented salt.[15] By projection along the As(1)−As(2) axes of the $As_2F_{11}^-$ anion (Figure 4) the gauche arrangement of the two octahedral AsF_6 units is visible, the overage torsion angle F−As−As−F of 45.0° being comparable to that found in $(CH_3S)_2CSH^+As_2F_{11}^-$.[15] The As(1)−F(1)−As(2) angle of 146.1(2)° is comparable to the Sb−F−Sb angle of 146.2(4)° and 147.6(3)° found in $(CF_3)_2C(F)OH_2^+$ $Sb_2F_{11}^-$ and $[Hg(CO)_2][Sb_2F_{11}]_2$, respectively, but smaller than the As−F−As angle of 159.1(6)° in $(CH_3)_2CSH^+As_2F_{11}^-$.[15,29,30]

Crystal Structure of $(CH_3)_3AsH^+SbF_6^-$

$(CH_3)_3AsH^+SbF_6^-$ crystallises in the monoclinic space group P2₁/*m* (no. 14) with *a* = 8.313(1), *b* = 8.855(1), *c* = 13.285(1) Å, β = 94.358(1)° and four formula units per unit cell. The crystal structure was solved via direct methods and successive difference Fourier syntheses. For refinement full-matrix least-squares methods were applied. All hydro-

Table 2. X-ray diffraction data of $(CH_3)_3AsH^+As_2F_{11}^-$ and $(CH_3)_3AsH^+SbF_6^-$

	$(CH_3)_3AsH^+As_2F_{11}^-$	$(CH_3)_3AsH^+SbF_6^-$
Space group	$P2_1/n$	$P2_1/m$
Crystal system	monoclinic	monoclinic
a [Å]	7.362(1)	8.313(1)
B [Å]	12.589(1)	8.855(1)
C [Å]	13.598(1)	13.285(1)
β [°]	95.37(1)	94.358(1)
Volume [Å^3]	1254.7(2)	975.1(2)
$D_{calcd.}$ [g cm^{-3}]	2.540	2.430
Z	4	4
Formula weight [g mol^{-1}]	479.87	356.78
Absorption coefficient [mm^{-1}]	8.055	6.231
Temperature [K]	173(2)	173(2)
F(000)	904	664
Wavelength [Å]	0.71069	0.71069
θ range for data collection [°]	$2.21 \leq \theta \leq 29.54$	$1.54 \leq \theta \leq 26.67$
Index ranges	$-10 \leq h \leq 10$ $-15 \leq k \leq 15$ $-18 \leq l \leq 18$	$-7 \leq h \leq 7$ $-10 \leq k \leq 10$ $-15 \leq l \leq 15$
Reflections collected/ independent	10064/3087 [R(int) = 0.0635]	5952/1607 [R(int) = 0.0480]
Parameters	194	162
Goodness-of-fit on F^2	0.955	1.011
Final R indices [$I<2\sigma(I)$]	$R1 = 0.0384$ $wR2 = 0.0722$	$R1 = 0.0318$ $wR2 = 0.0759$
R indices (all data)	$R1 = 0.0831$ $wR2 = 0.0842$	$R1 = 0.0558$ $wR2 = 0.0809$
Largest diff. peak and hole, e. Å^{-3}	0.596 and −1.180	0.615 and −1.095
Refinement method	full matrix, least-squares on F^2	full matrix, least-squares on F^2

gen atoms were taken from Fourier maps and refined with isotropic displacement parameters and all nonhydrogen atoms with anisotropic displacement parameters. For the data reduction, structure solution, and refinement the same programs were used as for the structure solution of $(CH_3)AsH^+As_2F_{11}^-$.[21] The monoclinic unit cell consists of two crystallographically independent cations and anions. The crystal data are summarised in Table 2 and bond lengths and selected angles are shown in Table 3.

The arsenic−carbon bond lengths of 1.779(10) and 1.765(9) Å in the two cations are significantly shorter than the remaining arsenic−carbon bond lengths of 1.910(9) and 1.935(9) Å and the analogous bond lengths of 1.894(5), 1.907(5) and 1.908(5) Å in trimethylarsonium undecafluorodiarsenate. The C−As−C angles of average 107.7(4) and 109.1(6)° are comparable to the C−P−C angles found in trimethylphosphonium hexachloroantimonate [110.4(4)°]. The interionic contacts are stronger than in trimethylarsonium undecafluorodiarsenate. The two independent cations form different contacts to fluorine atoms of neighbouring anions. In one case hydrogen fluorine contacts of 2.36(9) up to 2.47(6) Å and one arsenic fluorine contact of 3.060(5) Å result in formation of ribbons in the *ac* plane without connection along the *b* axes. In the other case only one hydrogen fluorine contact of 2.36(10) Å leads to a connection of cations and anions

Table 3. Selected bond lengths [Å], selected angles [°] and contacts [Å] for $(CH_3)_3AsH^+As_2F_{11}^-$ and $(CH_3)_3AsH^+SbF_6^-$[a]

$(CH_3)_3AsH^+As_2F_{11}^-$		$(CH_3)_3AsH^+SbF_6^-$	
As(3)−C(1)	1.908(5)	As(1)−C(1)	1.779(10)
As(3)−C(2)	1.907(5)	As(1)−C(2)	1.910(9)
As(3)−C(3)	1.894(5)	As(2)−C(3)	1.765(9)
As(3)−H(1)	1.30(4)	As(2)−C(4)	1.935(9)
		As(1)−H(1)	1.46(9)
		As(2)−H(2)	1.49(8)
C(1)−As(3)−C(2)	111.1(3)	C(1)−As(1)−C(2)	107.3(4)
C(1)−As(3)−C(3)	109.8(3)	C(1)−As(1)−C(2e)	107.3(4)
C(2)−As(3)−C(3)	109.5(3)	C(2)−As(1)−C(2e)	108.4(4)
		C(3)−As(2)−C(4)	110.3(3)
		C(3)−As(2)−C(4e)	110.3(3)
		C(4)−As(2)−C(4e)	106.7(6)
As(1)−F(1)	1.855(3)	Sb(1)−F(1)	2.008(5)
As(2)−F(1)	1.983(3)	Sb(1)−F(2)	1.810(4)
As(1)−F(7)	1.685(3)	Sb(1)−F(3)	1.986(6)
As(1)−F(8)	1.689(3)	Sb(1)−F(4)	1.804(4)
As(1)−F(9)	1.695(3)	Sb(2)−F(5)	1.782(5)
As(1)−F(10)	1.696(3)	Sb(2)−F(6)	1.953(5)
As(1)−F(11)	1.691(3)	Sb(2)−F(7)	1.776(5)
As(2)−F(2)	1.685(3)	Sb(2)−F(8)	1.862(4)
As(2)−F(3)	1.683(3)	Sb(2)−F(9)	1.956(6)
As(2)−F(4)	1.687(3)		
As(2)−F(5)	1.682(3)		
As(2)−F(6)	1.675(3)		
As(1)−F(1)−As(2)	146.1(2)	F(1)−Sb(1)−F(2e)	85.9(2)
F(1)−As(1)−F(7)	85.38(13)	F(2d)−Sb(1)−F(4)	177.6(2)
F(8)−As(1)−F(11)	173.5(2)	F(7)−Sb(2)−F(9)	98.2(2)
F(1)−As(2)−F(5)	83.34(13)	F(8)−Sb(2)−F(8e)	177.0(2)
F(4)−As(2)−F(5)	168.63(13)	F(7)−Sb(2)−F(9)	98.2(2)
As(3)···F(8a)	3.399(3)	F(2)···H(12)	2.47(6)
As(3)···F(10b)	3.304(3)	F(3)···H(1f)	2.45(9)
F(5)···H(12c)	2.53(6)	F(5)···H(1g)	2.36(9)
F(5)···H(23c)	2.44(7)	As(1)···F(5h)	3.060(5)
F(10)···H(21b)	2.52(6)		
F(11)···H(31d)	2.54(5)		

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[a] Symmetry operations: a = −1 + *x*, *y*, *z*; b = −*x*, 1 − *y*, −*z*; c = 1/2 + *x*, 1/2 − *y*, 1/2 + *z*; d = −1 − *x*, 1 − *y*, −*z*; e = *x*, 1/2 − *y*, *z*, f = −1 + *x*, *y*, *z*; g = −1 + *x*, *y*, 1 + *z*; h = −1 + *x*, *y*, −1 + *z*.

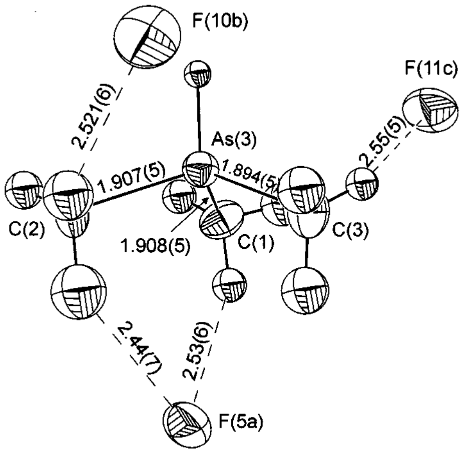

Figure 2. Fragment of the structure of $(CH_3)_3AsH^+As_2F_{11}^-$, showing the $(CH_3)_3AsH^+$ cation with hydrogen bonds (50% probability ellipsoids for the carbon, fluorine and arsenic atoms, 25% probability ellipsoids for the hydrogen atoms); bond lengths are given in Å; symmetry operations: a = −0.5 + *x*, 0.5 − *y*, −0.5 + *z*; b = −*x*, 1 − *y*, −*z*; c = −1 − *x*, 1 − *y*, −*z*

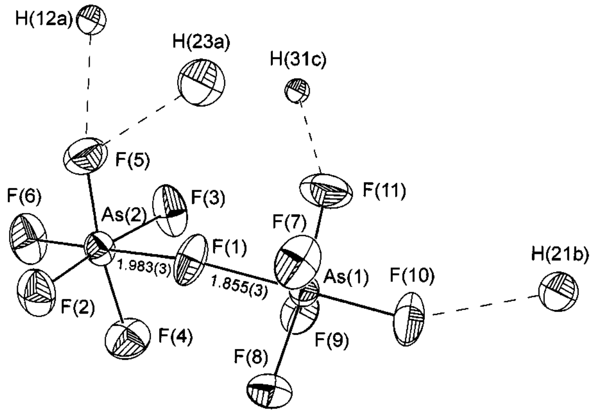

Figure 3. Structure of the $As_2F_{11}^-$ anion with hydrogen bonds (50% probability ellipsoids for the arsenic and fluorine atoms, 25% probability ellipsoids for the hydrogen atoms); bond lengths are given in Å; symmetry operations: a = 0.5 + x, 0.5 − y, 0.5 + z; b = −x, 1 − y, −z; c = −1 − x, 1 − y, −z

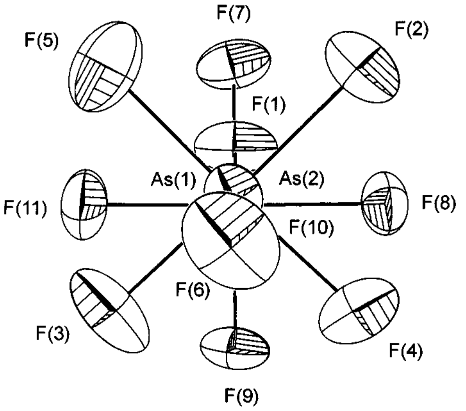

Figure 4. Projection along the As(1)−As(2) axes of the $As_2F_{11}^-$ anion (50% probability ellipsoids for the arsenic and fluorine atoms)

Experimental Section

Caution: Avoid contact with these compounds and note that the hydrolysis of $As_2F_{11}^-$ salts and SbF_6^- salts form 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 performed by employing standard Schlenk techniques and standard vacuum line (stainless steel or glass, respectively). Nonvolatile materials were handled under dry nitrogen and experiments in anhydrous HF were handled in Kel-F reactors with valves made of the same material. − The synthesis of $As(CH_3)_3$ was carried out by known literature methods out of $AsCl_3$ (Merck) and CH_3I (Merck).[31][32] Di-*n*-butyl ether (Fluka) was dried with sodium. AsF_5 was synthesised from As and F_2. SbF_5 (Merck) was distilled repeatedly before use. HF was dried in a stainless steel bomb using 1.5 bar of F_2. − 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.[33] − Infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra were obtained from a coated CsBr plate in a low-temperature cuvette.[34] − NMR spectra were recorded with a Bruker DPX 300 spectrometer. − Single crystals were obtained by slowly removing HF at −78 °C under vacuum and placed in Lindemann capillaries in a cooled stream of dry nitrogen. − X-ray diffraction studies were carried out using a Nonius Kappa CCD diffractometer.

Preparation of $(CH_3)_3AsH^+As_2F_{11}^-$ [$(CH_3)_3AsH^+SbF_6^-$]: In a typical reaction, 3 mL of HF was distilled into a Kel-F reactor at −196 °C, followed by 2 mmol (1 mmol) of AsF_5 (SbF_5). The mixture was warmed to 20 °C to form the superacid. The reactor was then cooled to −196 °C, and $As(CH_3)_3$ (1 mmol) was added. The mixture was warmed to −70 °C. After removing the volatile compounds at −78 °C colourless solids, stable up to 5 °C (60 °C) were obtained. − NMR spectra were recorded in SO_2 at −40 °C, standards are ^{75}As: 10% $KAsF_6$ in D_2O; ^{19}F: F11; $^{1\ \mathrm{H},}$ ^{13}C: TMS. The obtained data are as follows. **$(CH_3)_3AsH^+As_2F_{11}^-$:** ^{1}H NMR: δ = 1.92 (s), 10.27 (s). − ^{13}C NMR: δ = 4.13 (s). − ^{19}F NMR: δ = −52.24 (s). − ^{75}As NMR: δ = 138 (d), 131.1 (J_{AsH} = 507 Hz). − **$(CH_3)_3AsH^+SbF_6^-$:** ^{1}H NMR: δ = 2.00 (s). − ^{13}C NMR: δ = 4.42 (s). − ^{75}As NMR: δ = 138.6 (d, J_{AsH} = 498 Hz).

Preparation of $(CH_3)_3AsD^+As_2F_{11}^-$ [$(CH_3)_3AsD^+SbF_6^-$]: The preparations were analogous to those of the protonated species, but DF was used instead of HF. The colourless solids were stable up to 5 °C (60 °C).

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