Protonated Trithiocarbonic Acid − Synthesis, Spectroscopic Characterization and the Crystal Structure of $C(SH)_3^+AsF_6^-$

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Protonation of trithiocarbonic acid H_2CS_3 in the superacidic system HF/MF_5 (M = As, Sb) results in the generation and isolation of the extremely water-sensitive salts $C(SX)_3^+MF_6^-$ (M = As, Sb; X = H, D). The slightly yellow salts decompose above 233 K with the formation of $SX_3^+MF_6^-$ and CS_2. These new salts are characterized by vibrational and NMR spectroscopy and $C(SH)_3^+AsF_6^-$ by X-ray diffraction.

Introduction

The NMR spectroscopic evidence that protonated carbonic acid is stable in the superacidic system HSO_3F/SbF_5 below 273 K was found in 1968 by Olah. Based on his extensive ^{13}C NMR investigations he proposed a trihydroxycarbenium ion structure and explained the remarkable thermal stability by comparison with the high resonance stability of protonated guanidine.[1,2] The existence of a symmetrical structure protonated at the carbonyl oxygen atom is supported by theoretical studies.[3−5] The crystal structure of protonated carbonic acid was recently determined by Minkwitz and co-workers [Equation (1)]; the IR spectra of free and sublimable carbonic acid were also reported.[6,7]

$$(Me_3SiO)_2CO + HF/MF_5 \rightarrow 2\ Me_3SiF + C(OH)_3^+MF_6^-\ (M = As, Sb) \qquad (1)$$

Formal replacement of the OH groups by SH groups leads to the mono-, di- and trithio-analogues compounds. The evidence for the existence of these species were given by ^1H-NMR studies in the super-acidic system HSO_3F/SbF_5 by Olah.[8] In contrast to the carbonic acid, trithiocarbonic acid can easily be synthesized and isolated from the reaction of barium trithiocarbonate with hydrochloric acid.[9] The physical and spectroscopic data as well as the crystal structures of the reaction products of trithiocarbonic acid with bromine, thiophosgene and chlorosulfane have been reported.[10−14]

In our investigations on protonated carbonic and thiocarbonic acids and their derivatives such as the $(MeO)_2COH^+$, $(MeO)(MeS)CSH^+$ and $(MeS)_2CSH^+$ cations, the determination of the crystal structure of trimercaptocarbenium hexafluoroarsenate was reported.[15−17]

Results and Discussion

Formation of $C(SX)_3^+$ Salts and NMR Spectra

Protonated trithiocarbonic acid is available by the reaction of trithiocarbonic acid with the superacid XF/MF_5 (X = H, D; M = As, Sb) [Equation (2)].

$$H_2CS_3 + HF/MF_5 \rightarrow H_3CS_3^+MF_6^- \qquad (2)$$

To avoid the formation of arsenate and antimonate sulfide it is necessary to condense hydrofluoric acid and the Lewis acid alternately in layers. The yellowish, unpleasant smelling and extremely water-sensitive hexafluorometallates decompose, in the case of the arsenate salt, at 208 K and in the case of the antimonate salt at 218 K. The salts are clearly more unstable than the trihydroxycarbenium salts (273 K), and after one day storage under inert conditions at 203 K the decomposition products $SX_3^+MF_6^-$ (X = H, D; M = As, Sb) and CS_2 can be observed spectroscopically [Equation (3)].[1,6]

$$C(SX)_3^+MF_6^- \rightarrow SX_3^+MF_6^- + CS_2\ (X = H, D; M = As, Sb) \qquad (3)$$

This is similar to the decomposition of the trihydroxycarbenium cation as reported by Olah.[1]

The ^1H NMR spectra of freshly prepared $C(SH)_3^+AsF_6^-$ and $C(SH)_3^+SbF_6^-$ dissolved in SO_2 with TMS as external standard at −60 °C show one signal at $\delta = 8.3$ and one at $\delta = 8.0$ for the equivalent mercapto groups. These results are similar to the chemical shifts reported previously by Olah and Minkwitz.[8,15,16] The difference of 0.49 ppm from the reported chemical shift by Olah is explainable by different solvents and temperatures. The ^{13}C NMR signals could not be measured because of poor solubility in SO_2. In solution, the new salts are about 20 K more stable than in the solid state.

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Raman Spectra of $C(SX)_3{}^+MF_6{}^-$ (M = As, Sb; X = H, D)

The observed Raman frequencies of the $C(SX)_3{}^+MF_6{}^-$ (X = H, D; M = As, Sb) are summarized in Table 1. The assignments for the $C(SX)_3{}^+$ cations were made by comparison with the calculated frequencies of $(CH_3S)_2CS$ and several alkylxanthogenates.[15,16,18–20] The recorded Raman frequencies of protonated, deuterated and free trithiocarbonic acid are also shown in Table 1. The IR spectra could not be measured due to the high reactivity and spontaneous decomposition on the IR window material (Si or CsBr) at 193 K.

Table 1. Raman frequencies and possible assignments of H_2CS_3 and $C(SH)_3{}^+MF_6{}^-$ (X = H, D; M = As, Sb)

$(HS)_2CS$	$(XS)_3C^+AsF_6{}^-$		$(XS)_3C^+SbF_6{}^-$		Possible assignment
	X = H	X = D	X = H	X = D	
2530 sh	2526		2569 w	1873 sh	ν SX
2512	2514 m	1837 m	2509 sh	1832 sh	
2493 m			2464 s	1810 sh	
2395 sh			2396 br	1754 br	
1116 sh	1123 w			1093 s	
1095 s			1101 s	1072 s	ν C=S
1082 sh		1040 w		1055 s	
1002 m	972 w	960 w	1003 w	972 m	δ CSX
879 m	862 w		882 m	888 m	ν_{as} CS
813 w			823 w	837 w	ν_s CS
654 w				690 m	τ CSX
501 s	517 s	512 s	506 m	508 s	δ SC=S
	459 w	476 m			
		435 w			δ SCS
431 w	404 w	404 w			
291 m	279 m	270 m	277 sh	277 sh	γ SCS
266 m		221 m			γ SCS
	683 m	685 m	655 w	661 m	$\nu_{(1)}$ $MF_6{}^-$
	575 w	573 w	580 vw	582 vw	$\nu_{(2)}$ $MF_6{}^-$
	370 w	370 w	296 w	298 m	$\nu_{(5)}$ $MF_6{}^-$

There are significant differences in the frequency of the SH and CS stretching modes between the spectra of the hexafluroantimonate and hexafluoroarsenate salts. The spectrum of $C(SH)_3{}^+SbF_6{}^-$ shows a broad, slightly split line between 2569 and 2396 cm^{-1} similar to the spectra of trithiocarbonic acid, whereas the hexafluoroarsenate spectrum shows a sharp line shifted to higher frequencies by about 70 cm^{-1}. This means that there is a similar association of the molecules due to hydrogen bonds between the antimonate species and the free acid. The sulfur atoms function as both proton and electron donors. The existence of two maximums in the broad SH line can be explained by different SH bonds, similar to the previously reported IR spectra of dialkylphosphinicdithio acids.[21] The annealing of H_2CS_3 and $C(SH)_3{}^+SbF_6{}^-$ results in a decreasing width and a shift to higher frequencies of the SH valence mode, as described by Allen and co-workers. The result of these effects is that there are weaker hydrogen bonds in the arsenate species than in the hexafluoroantimonate salts. The observed H/D shift of about 700 cm^{-1} is similar to the expected shift reported by Teller and Redlich.[22]

The second significant difference between the hexafluoroarsenate and -antimonate salts is observed in the C=S valence mode region. The strongest line in the spectra of $X_3CS_3{}^+SbF_6{}^-$ (X = H, D) is observed at 1100 cm^{-1} and, analogous to H_2CS_3, is assigned to the C=S stretching mode. However, in the spectra of $X_3CS_3{}^+AsF_6{}^-$ (X = H, D) only a very weak line is observed. The measured frequencies and intensities in the region of the C–S stretching mode are similar and independent of the anion. It is doubtful if this difference can be explained by different interactions in the solid state or by different structures in the solid depending on the superacid used. For all substances the characteristic SC=S deformation mode is observed as a very sharp and intense line at 500 cm^{-1}. The vibrational modes of the anions are observed in their typical regions assuming O_h symmetry.

Crystal Structure of $C(SH)_3{}^+AsF_6{}^-$

Trimercaptocarbenium hexafluoroarsenate crystallises in the triclinic space group $P\bar{1}$ (no. 2) with six units per cell and the dimensions $a = 800.8(2)$, $b = 1154.6(2)$, $c = 1499.7(3)$ pm, $\alpha = 107.74(3)°$, $\beta = 99.04(3)°$ and $\gamma = 104.35(3)°$ (Table 2).[23] The bond lengths and angles are listed in Table 3. Figure 1 shows the salt with atom labels, and the arrangement of the $C(SH)_3{}^+AsF_6{}^-$ in the unit cell is depicted in Figure 2. The antimony and sulfur atoms

Table 2. Crystal data and structure refinement for $C(SH)_3{}^+AsF_6{}^-$

Formula	$CH_3AsF_6S_3$
Space group	$P\bar{1}$
Unit cell dimensions	$a = 800.8(2)$ pm; $\alpha = 107.74(3)°$ $b = 1154.6(2)$ pm; $\beta = 99.04(3)°$ $c = 1499.7(3)$ pm; $\gamma = 104.35(3)°$
Volume [Å^3]	1238.1(4)
Density (calculated) [g cm^{-3}]	2.415
Z	6
Molecular weight [g mol^{-1}]	300.13
Absorption coefficient [mm^{-1}]	4.913
Temperature [K]	173
λ (Mo-K_α) [Å]	0.71069
Crystal size [mm]	0.1 × 0.05 × 0.08
θ range for data collection [°]	1.95–26.3
Index ranges	$-9 \le h \le 9$; $-12 \le k \le 14$; $-16 \le l \le 17$
$F(000)$	864
Reflections collected	6182
Independent reflections	4373 [R(int) = 0.047]
R[a] [$I > 2\sigma(I)$]	$R1 = 0.0328$, $wR2 = 0.0592$
R[a] (all data)	$R1 = 0.0636$, $wR2 = 0.0646$
Largest diff. peak and hole [e Å^3]	0.461/–0.853
Free parameter	337
Goodness-of-fit on F^2	0.838
Programs used	SHELX,[29,30] SHELXTL Plus,[31] PARST,[32] MISSYM,[33] PLATON,[34] DENZO,[35] SCALEPACK[36,37]
Refinement method	Full-matrix least-squares on F^2

Table 3. Bond lengths [Å], angles [°] and contacts [Å] for $C(SH)_3^+AsF_6^-$[a]

As(1)F(11)	1.687(4)	F(11)−As(1)−F(12)	87.6(3)
As(1)−F(12)	1.699(4)	F(11)−As(1)−F(13)	178.0(2)
As(1)−F(13)	1.670(4)	F(11)−As(1)−F(14)	89.9(3)
As(1)−F(14)	1.689(4)	F(11)−As(1)−F(15)	90.6(2)
As(1)−F(15)	1.708(3)	F(11)−As(1)−F(16)	89.4(2)
As(1)−F(16)	1.720(3)	F(12)−As(1)−F(13)	91.0(3)
As(2)−F(21)	1.704(3)	F(12)−As(1)−F(15)	90.6(2)
As(2)−F(22)	1.727(4)	F(12)−As(1)−F(16)	89.1(2)
As(2)−F(23)	1.706(3)	F(13)−As(1)−F(14)	91.6(3)
As(2)−F(24)	1.716(3)	F(13)−As(1)−F(15)	90.7(2)
As(2)−F(25)	1.722(3)	F(13)−As(1)−F(16)	89.3(2)
As(2)−F(26)	1.713(3)	F(14)−As(1)−F(12)	177.2(2)
As(3)−F(31)	1.719(4)	F(14)−As(1)−F(15)	90.5(2)
As(3)−F(31a)	1.719(4)	F(14)−As(1)−F(16)	89.8(2)
As(3)−F(32)	1.727(3)	F(15)−As(1)−F(16)	179.7(2)
As(3)−F(32a)	1.727(3)		
As(3)−F(33)	1.711(3)	F(21)−As(2)−F(22)	89.9(2)
As(3)−F(33a)	1.711(3)	F(21)−As(2)−F(23)	90.4(2)
As(4)−F(41)	1.710(3)	F(21)−As(2)−F(24)	90.1(2)
As(4)−F(41b)	1.710(3)	F(21)−As(2)−F(25)	89.8(2)
As(4)−F(42)	1.727(3)	F(21)−As(2)−F(26)	179.4(2)
As(4)−F(42b)	1.727(3)	F(22)−As(2)−F(23)	179.7(2)
As(4)−F(43)	1.729(3)	F(22)−As(2)−F(24)	89.6(2)
As(4)−F(43b)	1.729(3)	F(22)−As(2)−F(25)	89.4(2)
S(11)−C(1)	1.683(5)	F(22)−As(2)−F(26)	90.0(2)
S(12)−C(1)	1.708(6)	F(23)−As(2)−F(24)	90.5(2)
S(13)−C(1)	1.701(6)	F(23)−As(2)−F(25)	90.5(2)
S(11)−H(11)	1.135(2)	F(23)−As(2)−F(26)	89.8(2)
S(12)−H(12)	1.358(2)	F(24)−As(2)−F(25)	179.0(2)
S(13)−H(13)	1.329(2)	F(24)−As(2)−F(26)	90.5(2)
S(21)−C(2)	1.702(6)	F(25)−As(2)−F(26)	89.6(2)
S(22)−C(2)	1.692(6)		
S(23)−C(2)	1.694(6)	F(31)−As(3)−F(31a)	180.0
S(21)−H(21)	1.039(2)	F(31)−As(3)−F(32)	89.6(2)
S(22)−H(22)	1.197(2)	F(31)−As(3)−F(32a)	90.4(2)
S(23)−H(23)	1.217(2)	F(31)−As(3)−F(33)	89.5(2)
S(31)−C(3)	1.712(6)	F(31)−As(3)−F(33a)	90.5(2)
S(32)−C(3)	1.684(6)	F(31a)−As(3)−F(32)	90.4(2)
S(33)−C(3)	1.686(6)	F(31a)−As(3)−F(32a)	89.6(2)
S(31)−H(31)	1.160(2)	F(31a)−As(3)−F(33)	90.5(2)
S(32)−H(32)	1.261(2)	F(31a)−As(3)−F(33a)	89.5(2)
S(33)−H(33)	1.276(2)	F(32)−As(3)−F(32a)	180.000(2)
		F(32)−As(3)−F(33)	90.5(2)
C(1)−S(11)−H(11)	104.5(2)	F(32)−As(3)−F(33a)	89.5(2)
C(1)−S(12)−H(12)	101.4(2)	F(32a)−As(3)−F(33)	89.5(2)
C(1)−S(13)−H(13)	91.8(2)	F(32a)−As(3)−F(33a)	90.5(2)
		F(33)−As(3)−F(33a)	180.000(3)
C(2)−S(21)−H(21)	89.7(2)		
C(2)−S(22)−H(22)	95.1(2)	F(41)−As(4)−F(41b)	180.000(3)
C(2)−S(23)−H(23)	100.7(2)	F(41)−As(4)−F(42)	89.6(2)
		F(41)−As(4)−F(42b)	90.4(2)
C(3)−S(31)−H(31)	92.4(2)	F(41)−As(4)−F(43)	90.1(2)
C(3)−S(32)−H(32)	107.5(2)	F(41)−As(4)−F(43b)	89.9(2)
C(3)−S(33)−H(33)	86.9(2)	F(41b)−As(4)−F(42)	90.4(2)
		F(41b)−As(4)−F(42b)	89.6(2)
S(11)−C(1)−S(12)	120.3(3)	F(41b)−As(4)−F(43)	89.9(2)
S(11)−C(1)−S(13)	120.5(3)	F(41b)−As(4)−F(43b)	90.1(2)
S(13)−C(1)−S(12)	119.2(3)	F(42)−As(4)−F(42b)	180.000(1)
		F(42)−As(4)−F(43)	89.6(2)
S(22)−C(2)−S(21)	119.1(4)	F(42)−As(4)−F(43b)	90.4(2)
S(22)−C(2)−S(23)	120.6(3)	F(42b)−As(4)−F(43)	90.4(2)
S(23)−C(2)−S(21)	120.3(3)	F(42b)−As(4)−F(43b)	89.6(2)
		F(43)−As(4)−F(43b)	180.000(3)
S(32)−C(3)−S(31)	119.0(3)		
S(32)−C(3)−S(33)	121.5(3)		
S(33)−C(3)−S(31)	119.5(3)		
S(11)···F(15c)	2.896(1)	S(11)···F(24d)	3.394(1)
S(12)···F(33e)	3.371(1)	S(12)···F(41f)	3.329(2)
S(13)···F(22)	3.397(1)	S(21)···F(16g)	3.317(1)
S(21)···F(14g)	3.737(1)	S(23)···F(23)	2.990(1)
S(21)···F(32h)	2.954(1)	S(33)···F(43)	3.506(1)
S(31)···F(13)	3.362(1)	S(33)···F(16g)	3.343(2)
S(33)···F(25)	3.052(1)		

[a] Symmetry operations: (a) $1 - x, -y + 2, -z + 2$; (b) $-x, -y + 3, -z + 2$; (c) $x + 1, +y - 1, +z$; (d) $-x + 1, -y + 2, -z + 1$; (e) $x, +y, +z - 1$; (f) $-x, -y + 2, -z + 1$; (g) $x + 1, +y, +z$; (h) $x, +y + 1, +z$.

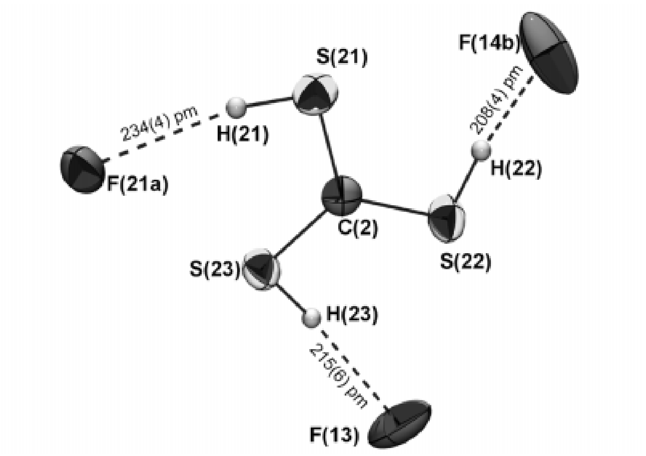

Figure 1. Projection of a selected $C(SH)_3^+$ cation with contacts; thermal ellipsoids are drawn at the 50% probability level

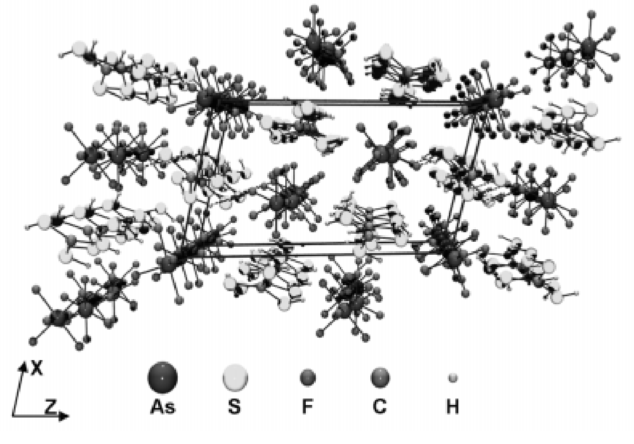

Figure 2. Projection of the $C(SH)_3^+AsF_6^-$ salt

were found by the Patterson method. All other atoms were determined by difference Fourier synthesis. A final refinement with anisotropic (except H atoms) thermal parameters gave a value of $R = 0.0328$.

The ideal octahedron structure of the anion is not distorted (O_h symmetry), with almost ideal angles of 90° and lengths of nearly 171 pm, similar to those in known structures.[6,24]

The CS_3 skeleton is surrounded by sulfur atoms in a trigonal planar geometry with angles of about 120° and average bond lengths of 169 pm. The still small differences in the length of the CS bonds imply a non-equal allocation of the positive charge over the sp^2-hybridised CS_3 group. The protons are not located in the CS_3 planes, therefore the symmetry is lowered to C_1 explaining the split SH valence mode in the Raman spectra. This geometry is similar to the structures of the $(CH_3S)_2CSH^+$ and $(CH_3O)(CH_3S)CSH^+$ cations where all cations posses a central sp^2 carbon atom, a delocalised positive charge and terminal groups which are not located in the CX (X = O,S) plane. The three symmetry-independent $C(SH)^+$ cations develop hydrogen bonds with S···F contacts, 10% below the sum of the Van der Waals radii, of about 289.6 pm, 295.4 pm, 305.2 pm and 299 pm.[25]

Experimental Section

All synthetic work and sample handling was performed by employing standard Schlenk techniques and a standard vacuum line (stainless steel or glass). SbF_5 (Merck) was fractionally distilled. Drying of HF and SO_2 were carried out by known literature methods.[26] Reactions in HF/DF were carried out in a KEL-F reactor with a KEL-F valve.[27] Infrared spectra were recorded with a Bruker IFS 113V spectrophotometer. The spectra of dry powders were obtained on a CsI plate in a cooled IR cell.[28] The Raman spectra were recorded with a T64000 (ISA) using a CCD detector (EEV CCD15-11) and an Ar^+ laser tube (514.5 nm) from Spectra Physics. The spectra were recorded in a glass cell cooled with liquid nitrogen. The NMR spectra were recorded with a Bruker DPX 300 spectrometer with TMS as external standard. Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and the X-ray diffraction study was carried out at −100 °C using an Enraff Nonius Kappa-CCD Mach3 automated diffractometer with an Oxford Cryosystem cooling unit.

Preparation of $C(SX)_3{}^+MF_6{}^-$ (X = H, D; M = As, Sb)

Caution! All contact with these compounds should be avoided as 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.

In a typical experiment H_2CS_3 (0.22 g) and anhydrous XF (X = H, D; 4 g) were combined at −196° C in a KEL-F reactor. AsF_5 (0.34 g) or SbF_5 (0.44 g) was then added to this mixture at −196 °C and the contents of the reactor were warmed up to −78 °C. After 10 minutes, the slow removal of all volatile material at −78 °C in vacuum resulted in a slightly yellow solid residue that was identified as $C(SX)_3{}^+MF_6{}^-$ (X= H, D; M= As, Sb). The remaining $C(SH)_3{}^+AsF_6{}^-$ contained crystals suitable for X-ray diffraction studies. The salts can be stored for one day under inert conditions at −70 °C.

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[1] G. A. Olah, M. White, *J. Am. Chem. Soc.* **1968**, *90*, 1884−1889.
[2] G. A. Olah, M. White, *J. Am. Chem. Soc.* **1969**, *91*, 5801−5810.
[3] G. Rasul, V. P. Reddy, L. Z. Zdunk, G. K. S. Prakash, G. A. Olah, *J. Am. Chem. Soc.* **1993**, *115*, 2236−2238.
[4] H. Egsgaard, C. Carlsen, *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 3403−3411.
[5] D. Ohlmann, C. M. Marchand, H. Grützmacher, G. S. Chen, D. Farmer, R. Glaser, A. Currao, R. P. H. Nesper, *Angew. Chem.* **1996**, *108*, 317−320; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 300−303.
[6] R. Minkwitz, S. Schneider, *Angew. Chem.* **1999**, *111*, 749−751; *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 713−715.
[7] W. Hage, K. R. Liedl, A. Hallbrucker, E. Mayer, *Science* **1998**, *279*, 1332−1335.
[8] G. A. Olah, A. T. Ku, M. White, *J. Org. Chem.* **1969**, *34*, 1827−1832.
[9] G. Gattow, B. Krebs, *Z. Anorg. Allg. Chem.* **1963**, *321*, 143−160.
[10] B. Krebs, G. Gattow, *Naturwiss.* **1964**, *51*, 554.
[11] B. Krebs, G. Gattow, *Z. Anorg. Allg. Chem.* **1965**, *340*, 294−311.
[12] G. Gattow, *Angew. Chem.* **1964**, *76*, 581−582.
[13] J. Wortmann, G. Kiel, G. Gattow, *Z. Anorg. Allg. Chem.* **1970**, *376*, 64−72.
[14] M. Schmidt, *Angew. Chem.* **1961**, *73*, 394−398.
[15] R. Minkwitz, F. Neikes, *Inorg. Chem.* **1999**, *38*, 5960−5963.
[16] R. Minkwitz, F. Neikes, *Eur. J. Inorg. Chem.* **2000**, 2283−2287.
[17] R. Minkwitz, F. Neikes, *Eur. J. Inorg. Chem.* **2000**, 1261−1265.
[18] K. Herzog, J. Fabian, *Z. Phys. Chem.* **1995**, *191*, 159−177.
[19] R. Mattes, G. Pauleickhoff, *Spectrochimica Acta* **1973**, *29A*, 1339−1344.
[20] K. Klaesser, G. Gattow, *Z. Anorg. Allg. Chem.* **1981**, *481*, 135−142.
[21] G. Allen, R. O. Coclough, *J. Chem. Soc.* **1957**, 3912−3915.
[22] J. Weidlein, U. Müller, K. Dehnicke, G. Thieme, Stuttgart **1982**.
[23] Crystallographic data (excluding structure factors) for the structure of $(HS)_3C^+AsF_6{}^-$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-411938. Copies of the data can be obtained free of charge onapplication to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk].
[24] R. Minkwitz, S. Schneider, M. Seifert, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1404−1410.
[25] A. Bondi, *J. Phys. Chem.* **1964**, *68 (3)*, 441.
[26] G. Brauer, *Handbuch der präparativen anorganischen Chemie*, 2 Aufl., F. Enke, Stuttgart **1975**.
[27] A. Werner, *Dissertation*, Universität Dortmund, **1988**.
[28] L. Bayerdorfer, R. Minkwitz, J. Jander, *Z. Anorg. Allg. Chem.* **1972**, *392*, 137−142.
[29] G. M. Sheldrick, *SHELXL 93*, Universität Göttingen, **1993**.
[30] G. M. Sheldrick, *SHELXS 86*, Universität Göttingen, **1986**.
[31] G. M. Sheldrick, *SHELXTL Plus Ver. 3.4*, An integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data., Universität Göttingen.
[32] M. Nardelli, *Comput. Chem.* **1993**, *7*, 95−98.
[33] Y. Le Page, *J. Appl. Crystallogr.* **1987**, *20*, 264−269.
[34] A. L. Spek, *The EUCLID Package*, Computational Crystallography, (Hrsg. D. Sayre), Claredon Press, Oxford, **1982**.
[35] *KappaCCD package*, NONIUS BV, Roentgenweg 1, Delft Netherlands.
[36] Z. Otwinowsky, W. Minor, *Methods in Enzymology* **1997**, *276*, 307−326.
[37] *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham 1974.

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