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Preparation of the Fluorosulfonium Hexafluorometalates $CH_3S(H)F^+MF_6^-$ and $CF_3S(H)F^+MF_6^-$ and the Chlorofluoromethylsulfonium Salts $CH_3S(Cl)F^+MF_6^-$ (M = As, Sb)[1]

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The new salts $CH_3S(H)F^+MF_6^-$ and $CF_3S(H)F^+MF_6^-$ (M = As, Sb) have been prepared by reacting RSH (R = CH_3, CF_3) with $XeF^+MF_6^-$ in liquid anhydrous HF and characterized by NMR (^1H, ^{19}F, ^{13}C), Raman, and IR spectroscopic methods. The spectral data are compared with those of the known compounds $R_2SF^+MF_6^-$ (R = CH_3, CF_3). The preparation of $CH_3S(Cl)F^+MF_6^-$ is also reported; these salts were formed by reacting $CH_3S(H)F^+MF_6^-$ with Cl_2 in HF.

Introduction

In the course of our investigations of the synthetic potential of $XeF^+MF_6^-$ (M = As, Sb) we succeeded in preparing the monofluorinated sulfonium salts $CF_3S(Cl)F^+MF_6^-$,[2] $SCl_2F^+MF_6^-$,[3] and $(CF_3)_2SF^+MF_6^-$[4] (M = As, Sb). In all cases the behavior of $XeF^+MF_6^-$ as an extremely mild and selective fluorinating agent with a high oxidation potential is observed. These properties are especially important in the preparation of $H_2SF^+SbF_6^-$,[5] which is a very unstable compound.

The high oxidation potential of $XeF^+MF_6^-$ is demonstrated by the formation of monofluorooxonium salts $H_2OF^+MF_6^-$,[6] which we have recently reported.

$$H_2O + XeF^+MF_6^- \rightarrow H_2OF^+MF_6^- + Xe \qquad (1)$$
$$M = As, Sb$$

In continuation of our investigations on sulfanes, it seemed likely that SH derivatives should also be fluorinated oxidatively to form fluorosulfonium salts. Thermolysis reactions of them might lead to new fluorosulfuranes.

With the preparation of $CH_3S(H)F^+MF_6^-$, the spectroscopic series of $(CH_3)_{2-n}S(H)_nF^+$ salts (n = 0–2) is now complete.[5,15] In this context the comparison of their reactivities with those of the homologous oxygen compounds $(CH_3)_{2-n}O(H)_nF^+MF_6^-$ is of interest. The stabilities of these recently prepared monofluorooxonium cations[6,7] differ greatly. While $CH_3O(H)F^+MF_6^-$ and $(CH_3)_2OF^+MF_6^-$ are extremely explosive, $H_2OF^+MF_6^-$ is absolutely harmless.

We therefore felt it important to study the behavior of the homologous S compounds.

Experimental Section

Materials and Apparatus. Literature methods were used for the synthesis of $XeF^+MF_6^-$ (M = As, Sb),[8] CF_3SH,[9] and DF.[10] HF (Bayer) was treated with F_2; CH_3SH (Merck) was used as received. Cl_2 (Messer Griesheim) was stored over CaO. Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques. All reactions were carried out in a KEL-F reactor fitted with a KEL-F valve. Infrared spectra were recorded on a Bruker IFS 113v spectrometer between NaCl or polyethylene plates in an IR low-temperature cell[11] at 135 K. Raman spectra were run on a Coderg T 800 spectrometer equipped with an Ar^+ laser operating at 514.5 nm and 400-mW laser power level and using a low-temperature cuvette at 195 K. The maximum resolution was 5 cm^{-1}, and all vibrational spectroscopic measurements showed reproducibility within ±5 cm^{-1}. The NMR spectra of HF solutions were recorded on a Bruker Model AM 300 spectrometer (^{13}C, 75.5 MHz; ^{19}F, 282.5 MHz; ^1H, 300 MHz) with positive shifts being downfield from the external standards TMS (^{13}C, ^1H) and CCl_3F (^{19}F). The pulse width was 2 μs (^{19}F), 2.5 μs (^{13}C), and 1.4 μs (^1H). A total of 256 scans were run for each spectrum; the maximal resolution was 4.3 Hz (^{19}F), 1.2 Hz (^{13}C), and 1.1 Hz (^1H) per data point. Mass spectra were recorded with IE = 70 eV on a Finnigan MAT 8230 instrument. For the measurements the samples were thermolyzed in a high vacuum from a glass vessel, fitted with a Young valve, into the mass spectrometer.

Preparation of $RS(H)F^+MF_6^-$ (R = CH_3, CF_3; M = As, Sb). A 1-mmol amount of $XeF^+MF_6^-$ (M = As, Sb) was dissolved in 5 mL of HF in a KEL-F reactor. After the addition of equimolar amounts of RSH (R = CH_3, CF_3) at 77 K the reaction mixtures were stirred for 2–3 h at 213 K. Then all volatile compounds were removed by pumping at 213 K, and yellowish solids remained. These were stable at temperatures below 233 K.

NMR Data. $CH_3S(H)F^+MF_6^-$: ^{19}F NMR $\delta(SF) = -177.0$ ppm; ^{13}C NMR $\delta(CH_3) = 24.3$ ppm; ^1H NMR $\delta(SH) = 4.27$ ppm, $\delta(CH_3) = 3.45$ ppm. $CF_3S(H)F^+MF_6^-$: ^{19}F NMR $\delta(SF) = -133.2$ ppm, $\delta(CF_3) = -52.3$ ppm, $^1J(CF) = 325$ Hz; ^{13}C NMR $\delta(CF_3) = 124.3$ ppm (q), $^1J(CF) = 327$ Hz; ^1H NMR $\delta(SH) = 4.83$ ppm.

Preparation of $RS(D)F^+MF_6^-$ (R = CH_3, CF_3; M = As, Sb). The same reactions as described above were carried out in DF, and the remaining solids were washed three times with the DF solvent to complete the H/D exchange.

Preparation of $CH_3S(Cl)F^+MF_6^-$ (M = As, Sb). An equimolar amount of Cl_2 was condensed at 77 K onto a solution of $CH_3S(H)F^+$-MF_6^- (M = As, Sb) in HF. The reaction mixture was stirred for 3 h at 213 K. After removal of the HCl and the solvent by pumping at 183 and then 213 K, yellowish white solids remained. These were stable at temperatures below 223 K.

NMR Data: ^{19}F NMR $\delta(SF) = -119.3$ ppm, $^3J(HF) = 13.7$ Hz; ^{13}C NMR $\delta(CH_3) = 34.4$ ppm; ^1H NMR $\delta(SH) = 4.1$ ppm, $^3J(HF) = 14.2$ Hz.

MS Data. $CH_3S(Cl)F^+AsF_6^-$: m/e = 86 (5%) ($SClF^+$), 82 (60) (CH_3SCl^+), 67 (100) (SCl^+), 47 (48) (CH_3S^+), 51 (10) (SF^+), 151 (7.7) (AsF_4^+), 132 (5.7) (AsF_3^+), 113 (5) (AsF_2^+), 94 (8) (AsF^+). CH_3S-$(Cl)F^+SbF_6^-$: m/e = 86 (4.6%) ($SClF^+$), 82 (56) (CH_3SCl^+), 67 (100) (SCl^+), 47 (48) (CH_3S^+), 51 (6.9) (SF^+), 197 (3.4) (SbF_4^+), 178 (5) (SbF_3^+), 140 (5.5) (SbF^+), 121 (3) (Sb^+).

Results and Discussion

Monofluorinated sulfonium salts $RS(H)F^+MF_6^-$ (R = CH_3, CF_3; M = As, Sb) are formed by the reaction between RSH (R = CH_3, CF_3) and $XeF^+MF_6^-$ (M = As, Sb) in HF at 218 K (eqs 2 and 3). Their characterization has been carried out by NMR

$$CH_3SH + XeF^+MF_6^- \rightarrow CH_3S(H)F^+MF_6^- + Xe \qquad (2)$$

$$CF_3SH + XeF^+MF_6^- \rightarrow CF_3S(H)F^+MF_6^- + Xe \qquad (3)$$

and vibrational spectral studies. For unequivocal assignment of the S–H vibrations, H/D isotope exchange reactions were carried out at the SH groups.

Both salts are extremely sensitive to hydrolysis. Decomposition is observed above 233 K with formation of $S_8^{2+}(MF_6^-)_2$, which is recognizable by its blue color. The thermal stabilities of these $RS(H)F^+$ salts are considerably lower than those of the already known members of the series RSX_2^+ (R = CH_3, CF_3; X = H, F), which are all stable at room temperature.[12,13] The same effect

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(1) Chemistry of Sulfur Halides. 50. Part 49: Minkwitz, R.; Molsbeck, W. *Z. Naturforsch.*, in press.
(2) Minkwitz, R.; Nowicki, G.; Preut, H. *Z. Anorg. Allg. Chem.* **1989**, *573*, 185.
(3) Minkwitz, R.; Nowicki, G. *Z. Naturforsch.* **1989**, *44B*, 1343.
(4) Minkwitz, R.; Werner, A. *J. Fluorine Chem.* **1988**, *39*, 141.
(5) Minkwitz, R.; Nowicki, G. Unpublished results.
(6) Minkwitz, R.; Nowicki, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 688.
(7) Minkwitz, R.; Nowicki, G. Manuscript in preparation.
(8) Gillespie, R. J.; Landa, B. *Inorg. Chem.* **1973**, *12*, 1383.
(9) Zack, N. R.; Shreeve, J. M. *Synth. Commun.* **1974**, *4*, 233.
(10) Brauer, G., Ed.; *Handbuch der präparativen anorganischen Chemie*; F. Enke Verlag: Stuttgart, Germany, 1975.
(11) Bayersdorfer, L.; Minkwitz, R.; Jander, J. *Z. Anorg. Allg. Chem.* **1972**, *392*, 137.

0020-1669/92/1331-0225$03.00/0

Table I. Vibrational Frequencies (cm^{-1}) of $RS(X)F^+MF_6^-$ ($R = CH_3, CF_3$; $X = H, D$; $M = As, Sb$)

$CH_3S(H)F^+$				$CH_3S(D)F^+$				$CF_3S(H)F^+$				$CF_3S(D)F^+$				
AsF_6^-		SbF_6^-		AsF_6^-		SbF_6^-		AsF_6^-		SbF_6^-		AsF_6^-		SbF_6^-		
IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	assgnt
2980 s	2984 (1.3)	2980 s	2980 (1.5)	2981 s	2981 (1.4)	2980 s	2981 (1.3)									$\nu_{as}(CH_3)$
2948 s	2950 (0.9)	2950 s	2945 (1.0)	2950 s	2950 (0.9)	2948 s	2941 (0.9)									$\nu_s(CH_3)$
2540 s	2540 (1.1)	2548 s	2540 (1.1)	1808 s	1810 (1.2)	1811 s	1809 (1.2)	2500 s	2490 (1.1)	2495 s	2490 (1.1)	1780 s	1783 (1.0)	1780 s	1780 (1.2)	$\nu(SX)$
1410 m	1400 (0.9)	1405 m	1399 (1.0)	1410 m	1408 (0.9)	1405 m	1404 (1.0)									$\delta_{as}(CH_3)$
1390 m	1391 (0.9)	1392 m	n.b.	1389 m	1390 (0.2)	1390 m	1390 (0.2)									$\delta_s(CH_3)$
1322 m	n.b.	1320 m	n.b.	1320 m	1318 (0.2)	1327 m	n.b.									$\delta(CH_3)$
								1145 m	1145 (0.6)	1148 m	1145 (0.5)	1142 m	1141 (0.6)	1145 m	1145 (0.6)	$\nu_{as}(CF_3)$
								1050 m	1040 (1.1)	1048 m	1048 (1.2)	1040 m	1042 (1.1)	1042 m	1040 (1.5)	$\nu_s(CF_3)$
1080 w	1080 (0.6)	1083 w	1080 (0.5)	789 w	787 (0.5)	785 w	787 (0.5)	1003 mw	1000 (0.6)	1005 mw	1008 (0.7)	711 mw	715 (1.0)	710 mw	710 (0.7)	$\delta(XSF)$
989 w	982 (0.7)	985 m	980 (0.8)	990 w	985 (0.75)	985 w	987 (0.8)									$\rho(CH_3)$
820 s	817 (1.1)	820 s	815 (1.0)	813 s	815 (1.3)	813 s	813 (1.1)	810 s	806 (1.3)	810 s	808 (1.1)	801 s	804 (1.3)	804 s	804 (1.3)	$\nu(SF)$
								745 m	744 (3.1)	745 m	746 (3.0)	744 m	742 (3.0)	742 s	742 (3.2)	$\delta(CF_3)$
720 m	718 (3.3)	720 m	715 (3.5)	515 m	513 (3.5)	515 m	515 (3.4)	600 m	605 (2.2)	600 m	603 (2.3)	a	a	a	a	$\delta(CSX)$
665 m	670 (7.7)	671 m	670 (8.0)	660 m	665 (7.9)	666 m	665 (7.9)									$\nu(CH_3S)$
								562 m	562 (1.3)	560 m	560 (1.5)	555 m	557 (1.4)	555 m	555 (1.4)	$\delta(CF_3)$
								500 m	498 (0.6)	500 m	501 (0.7)	489 m	497 (0.6)	499 m	498 (0.8)	$\delta(CF_3)$
460 mw	465 (8.0)	465 mw	465 (8.3)	450 mw	455 (7.9)	455 mw	455 (8.0)	425 m	427 (1.1)	428 m	428 (1.1)	422 m	422 (1.1)	420 m	422 (1.3)	$\delta(CSF)$
								475 s	476 (6.1)	475 s	476 (6.0)	472 s	470 (6.1)	470 s	470 (6.3)	$\nu(CF_3S)$
								347 m	347 (0.9)	348 m	348 (1.0)	342 m	344 (0.9)	340 m	340 (1.2)	$\rho(CF_3)$
	244 (0.3)		245 (0.3)		243 (0.2)		245 (0.3)									$\rho(CH_3)$
700 s		650 s		700 s		660 s		700 s		655 s		700 s		660 s		$\nu_3(MF_6^-)$
	680 (10)		651 (10)		685 (10)		650 (10)		681 (10)		650 (10)		681 (10)		650 (10)	$\nu_1(MF_6^-)$
	575 (3.5)		575 (1.7)		577 (3.5)		570 (1.3)		573 (3.1)		570 (1.0)		572 (3.0)		570 (1.5)	$\nu_2(MF_6^-)$
400 s		280 s		402 s		280 s		400 s		290 s		403 s		290 s		$\nu_4(MF_6^-)$
	380 (6.3)		280 (6.4)		390 (6.2)		290 (6.0)		380 (6.0)		280 (6.0)		380 (6.2)		280 (5.9)	$\nu_5(MF_6^-)$

[a] Covered by lower vibrations.

Table II. Vibrational Frequencies (cm^{-1}) of $CH_3S(Cl)F^+MF_6^-$ ($M = As, Sb$)

$CH_3S(Cl)F^+$					$CH_3S(Cl)F^+$				
AsF_6^-		SbF_6^-			AsF_6^-		SbF_6^-		
IR	RA	IR	RA	assgnt	IR	RA	IR	RA	assgnt
3030 vs	3030 (0.7)	3030 vs	3031 (0.8)	$\nu_{as}(CH_3)$	338 m	337 (1.6)	339 m	338 (2.0)	$\delta(ClSF)$
2940 s	2945 (3.2)	2943 s	2944 (3.5)	$\nu_s(CH_3)$	247 m	245 (2.3)	250 m	244 (2.0)	$\tau(CH_3)$
1414 mw	1417 (0.7)	1414 mw	1413 (0.6)	$\delta_{as}(CH_3)$	180 w	180 (2.6)	180 w	181 (2.7)	$\delta(CSCl)$
1330 mw	1331 (0.2)	1335 mw	1338 (0.2)	$\delta_s(CH_3)$	700 s		650 s		$\nu_3(MX_6^-)$
993 m	995 (0.6)	999 m	1000 (0.6)	$\rho(CH_3)$		680 (10)		650 (10)	$\nu_1(MX_6^-)$
805 ms	800 (0.8)	803 ms	794 (0.9)	$\nu(SF)$		570 (3.3)		581 (1.3)	$\nu_2(MX_6^-)$
681 m, sh	688 (4.8)	689 m	688 (5.0)	$\nu(CS)$	400 s		280 s		$\nu_4(MX_6^-)$
511 m	510 (5.5)	511 m	506 (5.4)	$\nu(SCl)$		380 (6.3)		290 (5.2)	$\nu_5(MX_6^-)$
461 m	462 (6.3)	460 m	463 (6.0)	$\delta(CSF)$					

occurs in the case of the mixed chlorine–fluorine substituted sulfonium cations $(CF_3)_nSCl_{2-n}F^+$ ($n = 0, 1$)[2,3] in contrast to the behavior of the pure chloro- or fluorosulfonium cations $(CF_3)_nSX_{3-n}^+$ ($n = 0, 1$; X = Cl, F).[12,13] By comparison to the analogous oxonium salts, $RO(H)F^+MF_6^-$ (R = CH_3, CF_3), the sulfonium salts are thermally more stable and nonexplosive.[7] The comparison of the NMR data of the new salts with those of the corresponding dimethyl- and bis(trifluoromethyl)sulfonium salts shows the expected tendency in the ^{19}F NMR chemical shifts for the SF groups. The new sulfonium salts show a downfield shift ($CH_3S(H)F^+$, $\delta(SF) = -177.0$ ppm; $CF_3S(H)F$, $\delta(SF) = -133.2$ ppm), in contrast to secondary halides known from the literature ($(CH_3)_2SF^+$, $\delta(SF) = -190.7$ ppm;[16] $(CF_3)_2SF^+$, $\delta(SF) = -159.4$ ppm[4]). This can be explained on the basis of a decreasing electron density at the F atoms of the SF group. The minor shielding effect of the F atoms corresponds well with a decreasing diamagnetic contribution to the chemical shift. The same effect is responsible for the downfield shift of the ^{19}F resonances on going from the methylated to the perfluoromethylated sulfonium salts. The other signals found in the NMR spectra are due to the CF_3 group in $CF_3S(H)F^+$ ($\delta(CF_3) = -52.3$ ppm) and to the anions ($\delta(AsF_6^-) = -56$ ppm,[14] $\delta(SbF_6^-) = -116$ ppm[14]). The ^{13}C NMR shifts of the CH_3 and CF_3 groups are found within the expected ranges ($\delta(CH_3) = 24.3$ ppm, $\delta(CF_3) = 124.3$ ppm). The ^1H NMR spectra of $CH_3S(H)F^+MF_6^-$ contain the signal at $\delta = 3.45$ ppm for the methyl group and a broad signal at 4.27 ppm due to the SH function. In $CF_3S(H)F^+$ a downfield shift of $\delta(SH)$ to 4.83 ppm occurs, which can be explained by a decrease of electron density at the H atom. All ^1H signals were found to be shifted more upfield than expected (i.e. $\delta(SH) = 6.4$ ppm in $SH_3^+AsF_6^-$[15]). This may be due to stronger interactions of these two cations with the solvent HF.

The symmetry of the two $RS(H)F^+$ cations is C_1. A total of 15 vibrations are therefore expected in both the IR and the RA (RA = Raman) spectra. Of these 12 are observed in both spectra. Six of them are due to the CH_3 or CF_3 groups and are found within their typical ranges. The other six vibrations can be assigned to the stretching modes $\nu(SH)$, $\nu(CS)$, and $\nu(SF)$ and to the deformations $\delta(CSH)$, $\delta(CSF)$, and $\delta(HSF)$. In $CH_3S(H)F^+MF_6^-$, $\nu(SH)$ is shifted by 50 cm^{-1} to higher frequencies relative to $CF_3S(H)F^+$. Also the frequencies of the other stretching vibrations and of the deformation vibrations in the methylated compounds are found at higher values than those in the perfluoromethylated cation. A comparison of the cations containing the –S(H)F group with other fluorosulfonium cations shows that $\nu(SF)$ in $RS(H)F^+$ (R = CH_3, CF_3) occurs at lower frequencies than in all the known R_2SF^+ cations.[4,5,16] While the same tendency is observed for $\nu(H_3C–S)$, $\nu(F_3C–S)$ does not fit in a unique scheme. Also no unequivocal relationship between the measured frequencies of the deformations in the $RS(H)F^+$ and R_2SF^+ cations (R = CH_3, CF_3) and the nature of R is found. The frequencies observed for $\nu(SD)$ and $\delta(CSD)$ are as expected and in good agreement with the rule of Teller and Redlich.[17] Vibrational data are listed in Table I.

The mass spectra of the two salts $RS(H)F^+MF_6^-$ (R = CH_3, CF_3; M = As, Sb) give no evidence for dissociation into sulfuranes $RS(H)F_2$ and AsF_5 or SbF_5. Rather decomposition to MF_5, HF, and the corresponding sulfanes RSH is observed.

This behavior is significantly different from that of the previously investigated salts $CF_3S(Cl)F^+MF_6^-$ and $SCl_2F^+MF_6^-$. As shown by matrix-isolation techniques,[18] thermolysis of $CF_3S(Cl)F^+MF_6^-$ leads to the unusual sulfurane $CF_3S(Cl)F_2$, which contains one ligand of the third period. The existence of SCl_2F_2 was indicated by the fragments observed in the mass spectrum of $SCl_2F^+MF_6^-$.[3]

For a further characterization of the new sulfonium salts, reactions with chlorine were carried out (eqs 4 and 5). Beside the

$$CF_3S(H)F^+MF_6^- + Cl_2 \rightarrow CF_3S(Cl)F^+MF_6^- + HCl \quad (4)$$

$$CH_3S(H)F^+MF_6^- + Cl_2 \rightarrow CH_3S(Cl)F^+MF_6^- + HCl \quad (5)$$

$$M = As, Sb$$

formation of HCl in reaction 4, $CF_3S(Cl)F^+MF_6^-$ can be detected by vibrational and NMR spectroscopy.[2] The hitherto unknown chlorofluoromethylsulfonium hexafluorometalates can be prepared in the same way as bright yellowish hydrolyzable salts that are stable up to 233 K. They are slightly soluble in HF, while in SO_2 decomposition is observed.

The vibrational frequencies of $CH_3S(Cl)F^+MF_6^-$ are summarized in Table II. For the cation of C_1 symmetry 15 vibrations are expected of which 12 are observed as well in both the IR and the RA spectra. Six of these are due to the methyl group. The C–S stretching mode is found at 688 cm^{-1}, well within the range expected for S–CH_3 stretching modes.[19-21] The S–F and S–Cl stretching modes were both found at the lower limits of the expected ranges, and their frequencies are significantly lower than those found for the homologous trifluormethylated compound $CF_3S(Cl)F^+MF_6^-$ ($\nu(SF) = 851.5$ cm^{-1}, $\nu(SCl) = 546.5$ cm^{-1}).[2]

The ^{19}F NMR spectra of the salts show the signals due to the anions and also one additional quartet at $\delta = -119.3$ ppm with $^3J(HF) = 14$ Hz, which is due to the fluorine on sulfur coupled to the methyl protons. The coupling constant corresponds well to the value found for the doublet observed for the methyl group in the ^1H spectra with $\delta(CH_3) = 4.1$ ppm and $^3J(HF) = 14$ Hz. The ^{13}C NMR shift of 34.4 ppm for the CH_3 group is within the range expected for methyl groups.

Although the fragments $SClF^+$ and SF^+ were observed in the mass spectra, there is no further evidence for the presence of $CH_3S(Cl)F_2$ in the gaseous dissociation products.

Conclusion

In this paper it is shown that primary sulfanes can be fluorinated oxidatively without decomposition involving HF elimination. This step seems to be inhibited kinetically at low temperatures. With the formation of $CH_3S(H)F^+$ the spectroscopic series of $(CH_3)_{2-n}S(H)_nF^+$ cations (n = 0–2) is now completed and a comparison of their stabilities with those of the analogous oxonium salts has been carried out. Contrary to $CH_3O(H)F^+MF_6^-$ and $(CH_3)_2OF^+MF_6^-$, the homologous monofluorosulfonium salts are not explosive. Additional compounds $RS(Cl)F^+MF_6^-$ (R = CH_3, CF_3; M = As, Sb) have been synthesized quantitatively by the reactions of the new salts with equimolar amounts of chlorine in HF. This pathway provides an alternative route to $CF_3S(Cl)F^+$, which is also accessible from CF_3SCl and XeF^+.

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Registry No. Fluoroxenonium hexafluoroarsenate, 26024-71-5; fluoroxenonium hexafluoroantimonate, 36539-18-1; methanethiol, 74-93-1; trifluoromethanethiol, 1493-15-8; fluoromethylsulfonium hexafluoroantimonate, 137794-57-1; perfluoromethylsulfonium hexafluoroantimonate, 137794-58-2; fluoromethylsulfonium hexafluoroarsenate, 137794-53-7; perfluoromethylsulfonium hexafluoroarsenate, 137794-54-8; chlorofluoromethylsulfonium hexafluoroarsenate, 137794-56-0; chlorofluoromethylsulfonium hexafluoroantimonate, 137794-59-3.

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(12) Minkwitz, R.; Gerhard, V.; Norkat, T. *Z. Naturforsch.* **1989**, *44B*, 1337.
(13) Kramar, M.; Duncan, L. C. *Inorg. Chem.* **1971**, *10*, 647.
(14) Duncan, C. H.; van Wazer, J. R. *Compilation of Reported ^{19}F NMR Chemical Shifts*; Wiley-Interscience: New York, 1970.
(15) (a) Minkwitz, R.; Gerhard, V. Z. Naturforsch. **1989**, *44B*, 364. (b) Christe, K. O. *Inorg. Chem.* **1975**, *14*, 2330.
(16) Foster, A. M.; Downs, A. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2827.
(17) Siebert, H. *Anwendungen in der Schwingungsspektroskopie*; Springer: Berlin, 1966; p 21.
(18) Minkwitz, R.; Nowicki, G. Unpublished results.
(19) Minkwitz, R.; Nass, U.; Preut, H. *Z. Naturforsch.* **1985**, *40B*, 113.
(20) Prenzel, H. Dissertation, Universität Dortmund, 1986.
(21) Shamir, J. *J. Raman Spectrosc.* **1975**, *3*, 95.