Protonated *O*,*S*-Dimethyl Dithiocarbonate − Synthesis, Spectroscopic Characterization and the Crystal Structure of $(CH_3O)(CH_3S)CSH^+SbF_6^-$

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Keywords: Carbocations / IR spectroscopy / Raman spectroscopy / NMR spectroscopy / Protonations

Dithiocarbonic acid *O*,*S*-dimethyl ester reacts with the super acidic system HF/MF_5 (M = As, Sb) to form $(MeO)(MeS)CSX^+MF_6^-$ (M = As, Sb; X = H, D). $(MeO)(MeS)CSH^+SbF_6^-$ crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 8.634(2) Å, b = 9.521(3)Å, c = 12.509(4) Å, β = 97.39 (2)° and 4 formula units per cell. The reaction of *O*,*S*-dimethyl dithiocarbonate with the super acidic systems XF/MF_5 (X = H, D; M = As, Sb) is discussed with regard to the formation of the salts, and Raman, IR, ^1H NMR, and ^{13}C NMR spectra of $(MeO)(MeS)CSX^+MF_6^-$ (M = As, Sb; X = H, D) are reported.

Introduction

In our investigations of mono-, di-, and trihydroxy carbenium ions and mercapto carbenium ions, we wanted to know how *O*,*S*-carbonic acids behave in super acidic media.[1−5] We had to fall back on derivatives of the acids, since the free monothio- and dithiocarbonic acids have not yet been isolated. Dialkylxanthogenic acids are well known in the literature, where the work of Gattow and co-workers in the area of the chalcogenocarbonic acids and sulfur chemistry should be mentioned.[6,7]

Nevertheless, until now, single-crystal X-ray investigations have only been conducted on metal xanthogenates, for example $Sn[S_2COMe]_2$ or $Cd[S_2COC_2H_5]_2$.[8,9] X-ray investigations of a positively charged OCS_2 skeleton are not known. Alkyl xanthogenates decompose in the presence of aqueous acids, since the alkyl xanthogenic acid intermediate is formed, which is not stable under normal conditions. To avoid decomposition in super acidic systems the use of dialkyl xanthogenates, which can be handled easily at ambient temperature, is recommended. As the crystal structures of the hydroxy dimethoxy carbenium cation and mercapto dimethylthio carbenium cation and Olah's NMR studies show, all methyl groups are located in *trans* positions.[4,5] The same configuration is expected for the cation formed by protonation of dimethyl xanthogenates. However, it remains to be determined whether a 1,3-methyl shift to form the $(MeS)_2COH^+$ cation (**I**), protonation to form an oxonium cation (**II**) or protonation to form a sulfonium cation (**III**) takes place (Figure 1). The X-ray structure and further investigations are of interest for this reason.

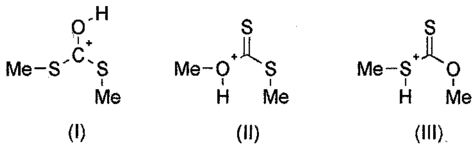

Figure 1. Potential reaction products

Results and Discussion

Formation of $(MeO)(MeS)CSH^+$ Salts

The best way to form the precursor (MeO)(MeS)CS for reaction in the super acidic system XF/MF_5 (M = As, Sb; X = H, D) is by the known reaction of NaOMe and CS_2 (Equation 1) followed by reaction with MeI[10] (Equation 2). Other reactions using alkali salts of dithiocarbonic acids such as $Na_2OC(S)S$ and methyl halides do not lead to uniform products (Equation 3).

$$NaOMe + CS_2 \rightarrow MeOC(S)SNa \tag{1}$$

$$NaS(S)COMe + MeI \rightarrow (MeO)(SMe)C{=}S \tag{2}$$

$$Na_2OC(S)S + 2MeI \rightarrow (MeO)(MeS)C{=}S + (MeS)_2C{=}O \tag{3}$$

Mercapto methoxy methylthio carbenium hexafluorometallate can be isolated from the protonation of (MeO)(MeS)CS in the super acidic systems HF, $(DF)/MF_5$ (M = As, Sb) (Equation 4).

$$(MeO)(MeS)C{=}S + HF/MF_5 \rightarrow (MeO)(MeS)CSH^+MF_6^- \; (M{=}\ As, Sb) \tag{4}$$

The resulting yellow salts, sensitive towards moisture and soluble in SO_2, decompose above −25 °C in the case of the arsenate and above −29 °C in the case of the antimonate into substances which were not further investigated. The salts can be stored without decomposition under inert conditions at −70 °C. Crystals of $(MeO)(MeS)CSH^+SbF_6^-$ suitable for X-ray diffraction studies could be isolated.

^1H and ^{13}C NMR Spectra of $(MeO)(MeS)CSH^+MF_6^-$ (M = As, Sb)

The ^1H NMR spectra at −60 °C of freshly prepared $(MeO)(MeS)CSH^+AsF_6^-$ and $(MeO)(MeS)CSH^+SbF_6^-$ in

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SO_2, with TMS as external standard, show singlets at $\delta = 4.98$ and 4.90, respectively, for the protons of the methoxy groups and singlets at $\delta = 3.09$ and 3.04, respectively, for the methylthio groups. The signals for the remaining mercapto groups are observed at $\delta = 6.99$ and 7.2. In the ^{13}C NMR spectra, the signals at $\delta = 17.79$ and 69.36 for the AsF_6^- species, and at $\delta = 17.68$ and 68.79 for the SbF_6^- species, are assigned to the $CH_3{-}S$ and $CH_3{-}O$ groups and the singlets at $\delta = 221.9$ and 221.4 are assigned to the carbon of the OCS_2 group. These results are comparable to the ^1H-NMR spectra of the $(HS)_3C^+$ and $(HO)(HS)_2C^+$ cations observed by G. A. Olah, as well as investigations of Barany et al. and our previous NMR investigations.[4,5,10,11]

Raman and IR Spectra of $(MeO)(MeS)CSX^+MF_6^-$ (M = As, Sb; X = H, D)

The infrared and Raman spectra of $(MeO)(MeS)CSD^+ AsF_6^-$ are depicted in Figure 2. The observed frequencies of the $(MeO)(MeS)CSX^+$ salts of AsF_6^- and SbF_6^- (X = H, D) are summarized in Table 1. The assignments for the $(MeO)(MeS)CSX^+$ cation were made by comparison to the frequencies of $(MeS)_2CS$ and the $[MeOCS_2]^-$ anion.[4,5,12−14] On the assumption that the $(MeO)(MeS)CSX^+$ cation (X = H, D) has a C_1 point symmetry, 33 Raman- and IR-active fundamental vibrations are expected. The antisymmetric and symmetric stretching modes of the methyl groups are observed in the region 2933−3035 cm^{-1}.

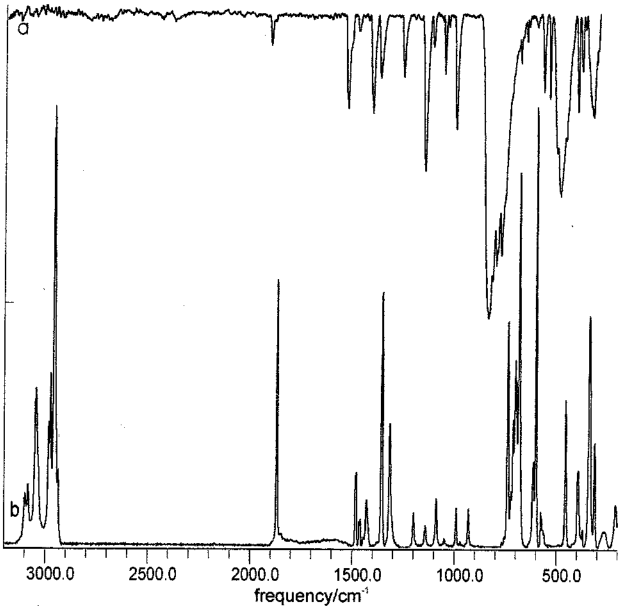

Figure 2. Infrared spectrum (trace A) and Raman spectrum (trace B) of $(MeO)(MeS)CSD^+AsF_6^-$

As with the precursor, different conformations arise in the solid, whereby the large number of valence modes can be explained.[15] The ν(SH) mode is observed at 2570 cm^{-1}, and the H/D shift to ca. 1860 cm^{-1} is almost in accordance with the expected shift.[16] The ν(SH) vibration mode in the AsF_6^- salt is shifted ca. 20 cm^{-1} to higher frequencies because the interaction between the anion and cation is weaker than in the SbF_6^- compound. This results in the loss of anion symmetry, which can be seen in the many anion vibration modes of the AsF_6^- salt. The deformation and rocking modes of the methyl groups are observed in their normal ranges of 1480−1300 cm^{-1} and 1000−880 cm^{-1}. A sharp Raman line and IR band is detected at 570 cm^{-1} and is assigned to the OCS_2 skeleton out of plane deformation mode.

The symmetric degradation is responsible for the additional As−F stretching modes. A complete assignment of the vibrational frequencies would require force field calculations.

Crystal Structure of $(CH_3O)(CH_3S)CSH^+SbF_6^-$

Mercapto methoxy methylthio carbenium hexafluoroantimonate crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with four formula units per unit cell (Table 3).[17] The bond lengths and angles are listed in Table 2. Figure 3 shows the salt with atom labels, and the arrangement of $(MeO)(MeS)CSH^+SbF_6^-$ in the unit cell is depicted in Figure 4. For the data reduction, a semiempirical correction determined from ψ-scan data, and structure solution and refinement programs in the SHELXTL package and PARST were used.[18−21] The antimony and sulfur atoms were located 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 $R = 0.071$.

Both C(3)−S bond lengths of 1.702(7) Å and 1.692(7) Å and the C(3)−O(1) bond length of 1.293(9) Å lie in the range between typical single and double bonds.[22] If one takes the measured lengths as a basis, one comes to the conclusion that the positive charge is equally distributed over the central sp^2-hybridized C(3) carbon atom. The C(3)−O(1) bond length can be compared to the lengths of the CO bonds in the dihydroxy methyl carbenium cation and the $C(OH)_3^+$ cation. The C(3)−S(1) length, as well as the C(3)−S(2) bond length, is comparable with the corresponding lengths in the $(MeS)_2CSH^+$ cation.[1,2,4,5] The sum of angles around C(3) amounts to 360°, which indicates planar sp^2 hybridization. The torsion angles of the methyl groups, with a maximum deviation of 2.5°, indicate that they are not located in the OCS_2 plane.

The S(1)···F(4) distance of 2.903 Å indicates an S(1)−H(1)···F(4) hydrogen bond with an angle of 155°. A further donor−acceptor reciprocal effect exists between S(1) and F(2a) with a length of 2.903 Å, forming an eight-membered ring in a chair conformation (Figure 5). There are additional contacts but because of their longer interatomic distances, they are not considered. The ideal octahedron structure of the anion is not distorted, with almost ideal angles of 90° and lengths in the range of 1.863(5)−1.879(5) Å.

Table 1. Raman, IR frequencies, and possible assignment of $(CH_3O)(CH_3S)CSX^+MF_6^-$ (X = H, D; M = As, Sb)

$(CH_3O)(CH_3S)CSX^+AsF_6^-$				$(CH_3O)(CH_3S)CSX^+SbF_6^-$			
X = H		X = D		X = H	X = D		
IR	Raman	IR	Raman	Raman	IR	Raman	Possible Assignment
	3097(9)		3097(12)				ν CH_3
	3082(10)		3082(13)	3068(9)		3069(16)	ν CH_3
	3044(32)		3045(35)	3039(13)		3029(32)	ν CH_3
						3007(10)	ν CH_3
	2982(24)		2982(28)			2993(24)	ν CH_3
	2974(34)		2973(39)			2976(27)	ν CH_3
	2956(95)		2957(100)	2961(22)		2961(40)	ν CH_3
			2937(17)	2939(15)		2943(53)	ν CH_3
						2922(54)	ν CH_3
2566m	2569(59)	1864w	1869(60)	2538(63)	1846m	1850(53)	ν SX
1481m	1483(16)	1479sh	1483(16)	1480(9)		1481(23)	δ CH_3
1475m	1480(16)	1474m	1479(17)		1478s		δ CH_3
1461m	1465(7)		1464(6)	1460(10		1460(8)	δ CH_3
1454m	1458(7)	1458sh	1458(6)		1459m	1452(9)	δ CH_3
				1434(10)	1438m	1437(10)	δ CH_3
1426m	1428(12)	1426w	1429(11)		1428m		δ CH_3
				1419(8)	1420m	1420(8)	δ CH_3
1352m	1356(54)	1348m	1354(57)	1350(35)	1349s	1349(65)	δ CH_3
1313m	1317(26)	1312m	1316(28)	1310(20)	1305s	1312(33)	δ CH_3
					1227s	1222(5)	ν $O-CS$
1200m	1201(13)	1193m	1198(8)	1196(10)		1195(10)	ν CH_3-O
					1191m	1190(10)	ν CH_3-O
					1160m	1165(24)	ν CH_3-O
	1148(5)		1141(5)	1142(3)	1142sh		ν CH_3-O
1095m	1096(18)	1083s	1087(11)	1087(6)			ν $C-S$
					1069vs		ν $C-S$
1054m	1055(4)	1044w	1048(2)		1040m		ν $C-S$
996m	998(15)	988s	991(9)	996(8)	986m	989(7)	ρ CH_3
				972(3)	973m	974(7)	ρ CH_3
957m	959(7)			958(3)		940(22)	ρ CH_3
		926s	930(9)		929s		ρ CH_3
882w	885(7)			887(7)			ρ CH_3
						732(20)	ν $S-CH_3$
				702(18)	696m	708(31)	ν $S-CH_3$
610m		613sh	613(19)				ν $S-COS$
	605(100)	600m	602(99)	601(53)	599w	601(65)	ν $S-COS$
	575(7)	570w	575(8)	572(10)	568m	572(9)	γ OCS_2 out of plane
517w		516w					δ OCS
482m		482m			482w		δ OCS
453m	455(37)	452m	455(33)	450(15)	449m	452(43)	γ OCS_2 in plane
417s		414sh					δ SCS
				400(7)			δ SCS
						361(11)	δ SCS
	342(54)		339(52)	346(38)		345(29)	δ SCS
274s	268(5)	275m	263(4)				δ SCS
244s		240sh					δ SCS
		229m		229(4)		221(13)	τ CH_3
	208(11)		209(10)				τ CH_3
753vs		758vs		648(100)	662vs		ν MF_6
	737(45)	739vs	738(51)		654vs	650(100)	ν MF_6
719vs	720(11)	719vs	722(12)		646sh	640(77)	ν MF_6
	713(25)		713(29)				ν MF_6
			702(42)				ν MF_6
694vs	698(39)	693vs	697(37)	278(35)		282(31)	ν MF_6
680s	683(78)	678sh	684(85)				ν MF_6
	590(11)						ν MF_6
396m	394(18)	394s	393(17)				ν MF_6
370m	370(6)	367sh	371(4)				ν MF_6
309s	311(22)	309m	312(23)				ν MF_6

Conclusion

The protonation of (MeO)(MeS)CS succeeds in super acidic systems, forming the expected carbenium ion. A clear statement about the structure of the cation can be made due to X-ray structure analysis. The Raman spectra of the salts show that in the solid state several conformations are present, which makes assignment of the spectra more difficult. The NMR spectra in SO_2 were assigned, and only one conformation was observed. If the solvent is carefully removed, crystals with a single conformation, in the all-*trans* position, are formed, as was shown by the X-ray diffraction study.

Table 2. Bond lengths [Å] and angles [°] for (MeO)(MeS)-$CSH^+SbF_6^-$

Bond	Length [Å]	Angle	[°]
Sb(1)−F(1)	1.863(5)	F(1)−Sb(1)−F(2)	88.7(2)
Sb(1)−F(5)	1.868(5)	F(1)−Sb(1)−F(3)	178.6(2)
Sb(1)−F(3)	1.870(5)	F(1)−Sb(1)−F(4)	90.2(2)
Sb(1)−F(2)	1.871(5)	F(1)−Sb(1)−F(5)	90.5(3)
Sb(1)−F(4)	1.873(5)	F(1)−Sb(1)−F(6)	89.6(2)
Sb(1)−F(6)	1.879(5)	F(3)−Sb(1)−F(6)	89.9(2)
S(1)−C(3)	1.702(7)		
S(1)−H(1)	1.39(9)	C(3)−S(1)−H(1)	98(4)
S(2)−C(3)	1.692(7)	C(3)−S(2)−C(2)	101.3(4)
S(2)−C(2)	1.783(10)	C(3)−O(1)−C(1)	120.2(7)
O(1)−C(3)	1.293(9)	O(1)−C(3)−S(1)	120.5(5)
O(1)−C(1)	1.469(11)	O(1)−C(3)−S(2)	118.3(5)
		S(2)−C(3)−S(1)	121.2(4)

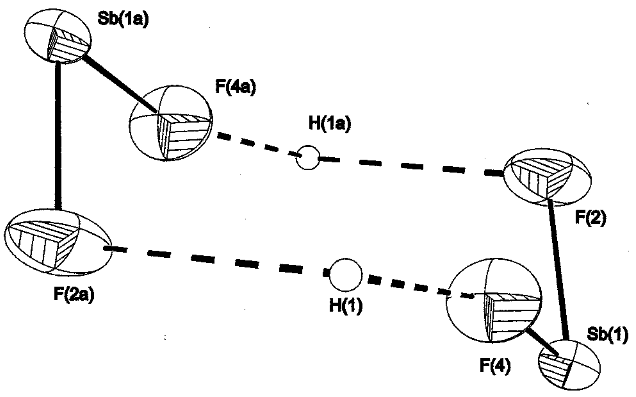

Figure 5. Structure of the chair-conformation 8-membered ring

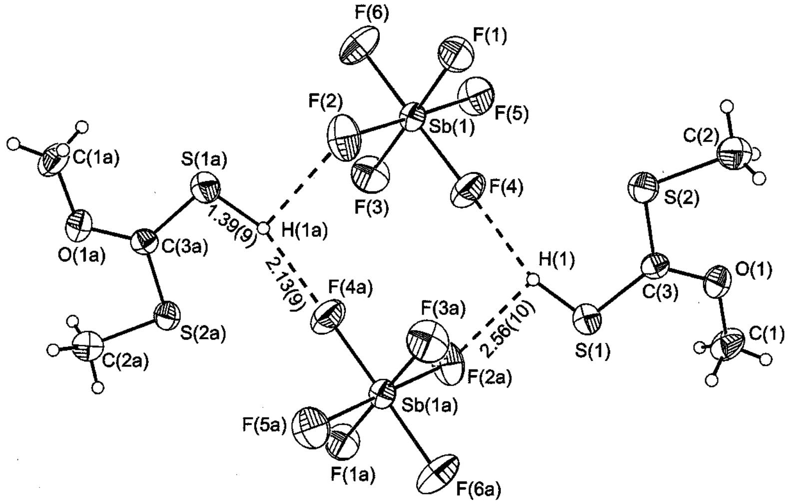

Figure 3. ORTEP of $(MeO)(MeS)CSH^+SbF_6^-$ with contacts; thermal ellipsoids are drawn at the 50% probability level

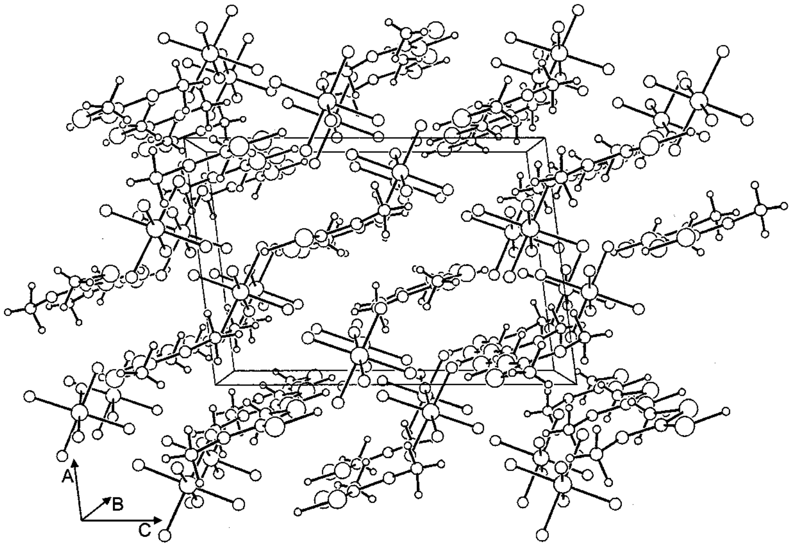

Figure 4. Structure of $(MeO)(MeS)CSH^+SbF_6^-$, showing the arrangement in the crystal lattice

Experimental Section

All synthetic work and sample handling was conducted by 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 literature methods. Reactions in HF/DF were carried out in a KEL-F reactor with a KEL-F valve. − Infrared spectra were recorded with a Bruker IFS 113V spectrophotometer. Spectra of dry powders were obtained on a CsI plate in a cooled IR cell. − The Raman spectra were recorded with a Yobin von 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 an X-ray diffraction study was carried out at −100 °C using an Enraf-Nonius Mach3 automated diffractometer.

Preparation of (MeO)(MeS)CS: *O,S*-Dimethyl dithiocarbonate was prepared by reaction of NaOMe (20 g, 0.37 mol) with excess dry CS_2 (35 g, 0.46 mol) in dry diethyl ether solvent. After filtration and drying under dynamic vacuum at room temperature the residue was treated with excess MeI (55 g, 0.38 mol) at 25 °C.[10] After 2 h, the excess MeI was removed under reduced pressure at −10 °C and the remaining yellow liquid distilled at 10 °C under dynamic vacuum in 89% yield based on NaOMe.

Preparation of $(MeO)(MeS)CSX^+MF_6^-$ (X = H, D; M = As, Sb): ***Caution! Avoid contact with these compounds and note that hydrolysis of AsF_6^- salts 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, *O,S*-dimethyl dithiocarbonate (0.24 g, 2 mmol) and anhydrous XF (X= H, D) (4 g, 0.2 mol) were combined at −196° C and placed in a KEL-F reactor. Arsenic pentafluoride (0.34 g, 2 mmol) or antimony pentafluoride (0.44 g, 2 mmol) was added to this mixture at −196 °C and the contents of the reactor were warmed to −78 °C. After 10 min, slow removal of all volatile material under vacuum at −78 °C gave a slightly yellow solid residue that was identified as $(MeO)(MeS)CSX^+MF_6^-$ (X= H, D; M= As, Sb). The remaining $(MeO)(MeS)CSH^+SbF_6^-$ contained crystals suitable for X-ray diffraction studies. The salts can be stored under inert conditions at −70 °C without decomposition.

Table 3. Crystal data and structure refinement for $(MeO)(MeS)CSH^+SbF_6^-$

Empirical formulae	$C_3H_7F_6OS_2Sb$
Molecular mass	358.96
Temperature	173(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.634(2) Å b = 9.521(3) Å, β = 97.39(2)° c = 12.509(4) Å
Volume	1019.8(5) Å^3
Z	4
Density (calculated)	2.338 Mg/m^3
Absorption coefficient	3.163 mm^{-1}
F(000)	680
Crystal size	0.3 × 0.2 × 0.3 mm
Theta range for data collection	3.06° to 25.97°
Index ranges	$-10 \leq h \leq 10$, $0 \leq k \leq 11$, $0 \leq l \leq 15$
Reflections collected	2085
Independent reflections	1994 [R_{int} = 0.0246]
Absorption correction	ψ scans
Max. and min. transmission	0.9982 and 0.8569
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1994/0/140
Goodness-of-fit on F^2	1.113
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.047$, $wR2 = 0.106$
R indices (all data)	$R1 = 0.071$, $wR2 = 0.113$
Largest diff. peak and hole	1.463 and −0.874 eÅ^{-3}

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[17] Crystallographic Data (excluding structure factors) for the structure of $(MeO)(MeS)CSH^+SbF_6^-$ included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145117. Copies of the data can be obtained free charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@cccdc.cam.ac.uk].

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Received March 3, 2000
[I00124]