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Synthesis and Characterization of the Tris(methylthio)sulfonium Salt $[(CH_3S)_3S]^+SbF_6^-$[1]

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Abstract: $[(CH_3S)_3S]^+SbF_6^-$, the first example of a trithiosulfonium salt saturated with organyl groups, was prepared from $SH_3^+SbF_6^-$ and CH_3SCl and characterized by ^1H, ^{13}C NMR, infrared, and Raman spectroscopy. The colorless salt is stable up to 10 °C, but solutions in SO_2 decompose at −60 °C in a few hours. The structure of the cation was studied by ab initio calculations and a normal coordinate analysis based on four additional isotopic derivates $[(CH_3{}^{34}S)_3S]^+SbF_6^-$, $[(CH_3S)_3{}^{34}S]^+SbF_6^-$, $[(^{13}CH_3S)_3S]^+SbF_6^-$, and $[(CD_3S)_3S]^+SbF_6^-$. The cation possesses C_3 symmetry with a pyramidal trithiosulfonium unit with predicted geometry parameters of $r(SS) = 208.8$ pm and $\angle(SSS) = 104.06°$.

Introduction

Trithiosulfonium compounds in which a central sulfur cation is surrounded by three sulfur atoms should not be rare, since a large variety of analogous and isoelectronic phosphorus compounds are known.[2] In fact, only very few compounds containing the $[(RS)_3S]^+$ unit are known in the literature. Structure determination of sulfur-rich compounds is handicapped by the absence of suitable analytical methods. Most of the structures of, for example, phosphorus and boron compounds were elucidated by NMR spectroscopy. Although the ^{33}S nucleus is NMR active, its spectroscopic usefulness is strongly restricted due to its very low sensitivity and its nuclear quadrupole moment, which causes a large line broadening.[3] Thus, structure determinations of sulfur-rich compounds are usually restricted to X-ray diffraction studies and vibrational spectroscopy.

Although sulfur has a tendency to form homonuclear chains and rings, branched structures, such as the trithiosulfonium unit, were not known for a long time.[4] The first example of a trithiosulfonium cation was reported by Gillespie et al. in 1980.[5] They found by X-ray diffraction studies that the red sulfur cation, proposed in previous studies to be $S_{16}{}^{2+}$,[6−8] is in fact a $S_{19}{}^{2+}$ cation which consists of two seven-membered rings linked by a five-membered sulfur atom bridge. It is formed, in addition to the blue $S_8{}^{2+}$, during treatment of elemental sulfur with oxidizing agents such as AsF_5 or SbF_5.[5,9] The reaction mechanism for the conversion of S_8 compounds to the $S_{19}{}^{2+}$ cation is still poorly understood.

In the course of our studies of sulfur-rich compounds, synthetic pathways to trithiosulfonium salts were of general interest, since they contain the simplest structural fragment of a three-dimensional sulfur network. During our studies on reaction sequences for the formation of sulfur chains, connected to sulfonium cations, the condensation of S−H functional compounds with chlorosulfonium salts was found to be an excellent general pathway.[10−14] The condensation of trichlorosulfonium salts with hydrogen sulfide (eq 1) yielded unstable

$$SCl_3{}^+A^- + 3H_2S \rightarrow [(HS)_3S]^+A^- + 3HCl \quad A^- = AsF_6{}^-, SbCl_6{}^- \qquad (1)$$

trismercaptosulfonium salts,[15] but attempts to obtain more stable organyl derivates by the use of mercaptanes failed (eq 1).[16]

Experimental Section

Apparatus and Materials. All synthetic work and sample handling were performed by employing standard Schlenk techniques and a standard vacuum line. $H_2{}^{34}S$ was prepared from $^{34}S_8$ (Monsanto) by a known literature method.[13] $SH_3{}^+SbF_6{}^-$ and $^{34}SH_3{}^+SbF_6{}^-$ were obtained by protonation of the hydrogen sulfide in HF/SbF_5.[17] CH_3SCl was

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[1] Sulfur Halide Chemistry, part 73. For part 72, see: Meyer, C.; Mootz, D.; Bäck, B.; Minkwitz, R. *Z. Naturforsch.* **1997**, *52B*, 69.

[2] Corbridge, R. C. *Phosphorous*; Elsevier: Amsterdam, 1990.

[3] Hinton, J. F. *Annu. Rep. NMR Spectrosc.* **1987**, *19*, 1.

[4] Müller, A.; Krebs, B. *Sulfur*; Elsevier: Amsterdam, 1984.

[5] Burns, R. C.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1980**, *19*, 1423.

[6] Gillespie, R. J.; Passmore, J. *J. Chem. Soc., Chem. Commun.* **1969**, 1333.

[7] Barr, J.; Gillespie, R. J.; Ummat, P. K. *J. Chem. Soc., Chem. Commun.* **1970**, 264.

[8] Gillespie, R. J.; Passmore, J.; Ummat, P. K.; Vaidya, O. C. *Inorg. Chem.* **1971**, *10*, 1327.

[9] Faggiani, R.; Gillespie, R. J.; Sawyer, J. F.; Vekris, J. E. *Acta Crystallogr., Sect. C* **1989**, *45*, 1847.

[10] Minkwitz, R.; Gerhard, V.; Krause, R.; Prenzel, H.; Preut, H. *Z. Anorg. Allg. Chem.* **1988**, *559*, 154.

[11] Minkwitz, R.; Krause, R. *Z. Anorg. Allg. Chem.* **1990**, *587*, 193

[12] Minkwitz, R.; Krause, R.; Goesmann, H. *Z. Anorg. Allg. Chem.* **1990**, *591*, 150.

[13] Minkwitz, R.; Kornath, A. *Z. Anorg. Allg. Chem.* **1991**, *605*, 101.

[14] Minkwitz, R.; Kornath, A. *Z. Naturforsch.* **1994**, *49B*, 729.

[15] Minkwitz, R.; Krause, R.; Härtner, H.; Sawodny, W. *Z. Anorg. Allg. Chem.* **1991**, *593*, 137.

[16] Krause, R. Dissertation, University of Dortmund, 1990.

[17] Christe, K. O. *Inorg. Chem.* **1975**, *14*, 2230.

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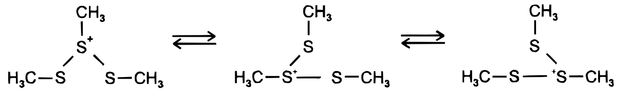
Table 1. NMR Spectroscopic Shifts of Methyl- and (Methylthio)Sulfonium Salts in SO_2

	T (°C)	^{1}H NMR		^{13}C NMR	
$[(CH_3S)_3S]^+SbF_6^-$	−60	3.39		15.9	
$[CH_3S(SCH_3)_2]^+SbF_6^-$	−50	3.38	3.0	16.5	32.0
$[CH_3S(SCH_3)_2]^+SbF_6^-$	−30	3.1		16.7	
$[CH_3S(SCH_3)_2]^+AsF_6^-$ [a]	−25	3.0		16.3	
$[CH_3S(SCH_3)_2]^+SbCl_6^-$ [b]	20	2.9			
$[(CH_3)_2SSCH_3]^+SbCl_6^-$ [a]	20	3.4	3.1	17.1	31.6
$[(CH_3)_2SSCH_3]^+AsF_6^-$ [a]	20	3.3	2.9		
$[(CH_3)_3S]^+AsF_6^-$ [a]	20		2.9		28.0

[a] Data from ref 16. [b] Data from ref 22.

Scheme 1



prepared from $(CH_3S)_2$ and SO_2Cl_2.[18] The preparation of CD_3SCl, $^{13}CH_3SCl$, and $CH_3{}^{34}SCl$ was carried out using the appropriate isotopically enriched $Ph_3Si*S*C*H_3$ which was obtained from Ph_3Si*SH and $*C*H_3I$.[19] Ph_3Si*SH was prepared from Ph_3SiH and S_8 or $^{34}S_8$, respectively.[20] $^{13}CH_3I$ and CD_3I were obtained from the appropriate isotopically enriched methanol (Merck) and PI_3.[21]

Infrared spectra were recorded on a Bruker ifs 113v spectrophotometer. Spectra of dry powders were obtained using a CsBr plate coated with the neat sample. The Raman spectra were recorded on a Coderg T800 using an Ar^+ laser (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. Mass spectra were recorded on a Varian CH5. The Sb/S analysis of an oxidized (HNO_3) sample dissolved in distilled water was carried out with an ICP (Leeman Lab).

Synthesis of $[(CH_3S)_3S]^+SbF_6^-$. A total of 270 mg (1 mmol) of $SH_3^+SbF_6^-$ was placed in a 30 mL glass vessel, and 410 mg (5 mmol) of freshly distilled CH_3SCl was condensed into the glass vessel at −196 °C. The reaction proceeds on thawing of the mixture and is completed within 15 min at −60 °C. The excess of CH_3SCl and the formed HCl were removed at −45 °C under a dynamic vacuum. The increase in weight (410 mg; calculated for $[(CH_3S)_3S]^+SbF_6^-$, 409 mg) of the

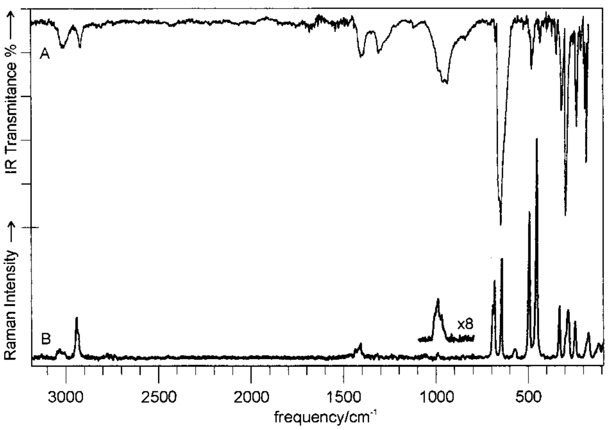


Figure 1. Infrared spectrum (trace A) and Raman spectrum (trace B) of solid $[(CH_3S)_3S]^+SbF_6^-$.

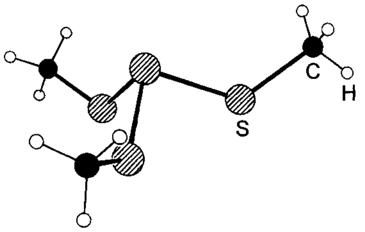


Figure 2. Calculated structure of the $[(CH_3S)_3S]^+$ cation. Geometry parameters: $r(SS) = 208.8$ pm; $r(SC) = 182.2$ pm; $d(CH) = 108.3$ pm; $\angle(SSS) = 104.1°$; $\angle(SSC) = 99.4°$; $\angle(SCH) = 110.9°$; $\angle(SCH') = 103.9°$; $\angle(HCH) = 109.6°$; $\angle(HCH') = 109.4°$.

Table 2. Vibrational Frequencies (cm^{-1}) of $[S(SCH_3)_3]^+SbF_6^-$ and ist Isotopomers[a]

$[S(SCH_3)_3]^+SbF_6^-$			$[S(^{34}SCH_3)_3]^+SbF_6^-$	$[^{34}S(SCH_3)_3]^+SbF_6^-$	$[S(S^{13}CH_3)_3]^+SbF_6^-$	$[S(SCD_3)_3]^+SbF_6^-$
IR	Ra	ρ[b]	Ra	Ra	Ra	Ra
	3039 (10)	0.60	3040 (23)	3041 (26)	3040 (31)	2279 (30)
3027 m						
	3006 (6)	0.60	3004 (sh)	3004 (sh)	3005 (sh)	
	2943 (18)	0.72	2944 (24)	2946 (28)	2934 (27)	2144 (61)
2934 m	2934 (11)	0.21	2934 (18)	2936 (15)	2926 (16)	
1438 m	1438 (5)	0.70	1437 (5)	1438 (4)	1432 (3)	1017 (9)
1224 m						
	1412 (3)					
1313 w						
1297 m						
1000 m	996 (4)	0.27				
976 m	974 (1)					
951 m						
	702 (18)	0.25	690 (15)	701 (19)	626 (20)	
694 w	691 (29)	0.25	681 (19)	691 (22)	677 (32)	659 (sh)
656 s*						
	653 (32)*	0.13	651 (37)*	653 (39)*	653 (40)*	652 (31)*
	579 (7)*	0.70	580 (11)*	580 (12)*	581 (8)*	581 (6)*
496 m	502 (58)	0.50	490 (62)	497 (63)	501 (67)	498 (65)
462 w	463 (100)	0.20	451 (100)	463 (100)	463 (100)	461 (100)
330 m	333 (22)	0.38	331 (27)	331 (25)	327 (21)	312 (31)
302 s*						
290 w	297 (sh)*		292 (sh)*	295 (sh)*	295 (sh)*	290 (27)*
	289 (40)*		286 (25)*	288 (32)*	287 (33)*	276 (15)*
245 m	249 (20)	0.44	247 (18)	233 (25)	245 (21)	224 (24)
183 s	175 (23)	0.54	175 (29)	170 (29)	175 (25)	164 (31)
	121 (15)		117 (20)	124 (19)	115 (11)	111 (15)
	85 (52)		81 (55)	86 (69)	83 (47)	79 (57)

[a] Anion vibrations are marked with an asterisk. [b] Polarization measurement in SO_2 at −75 °C; Lines below 150 cm^{-1} were not detectable because of a low stray light rejection.

Table 3. Calculated Bond Distances (Experimental Values in Parentheses) and Stretching Force Constants for Molecules and Ions Containing SS and CS Bonds

	r(SS) (pm)	*f*(SS) (N cm^{-1})	*r*(CS) (pm)	*f*(CS) (N cm^{-1})
$[(CH_3S)_3S]^+$	208.8	2.20	182.2	3.06
$[(HS)_3S]^+$ [a]	217.1	2.29		
$[S_2H_3]^+$ [b]	210.8	2.44		
S_2H_2 [c]	208.2 (206.1)	2.65		
$S_2(CH_3)_2$ [d]	206.4 (202.7)	2.40	180.5 (181.2)	2.84
$S(CH_3)_2$ [e]			181.0 (180.2)	3.19
$[S(CH_3)_3]^+$ [f]			180.7 (179−181)	

[a] Data from ref 15. [b] Data from ref 28. [c] Data from refs 29 and 30. [d] Data from refs 31 and 32. [e] Data from refs 33 and 34. [f] Data from refs 35 and 36.

Table 4. Sequence of Symmetry Coordinates in Species A_1 and E of the $[(CH_3S)_3S]^+$ Cation

A		E	
S_1	ν_s (SS)	S'_1	ν_{as} (SS)
S_2	ν_s (CS) ip[a]	S'_2	ν_{as} (CS) op[b]
S_3	ν (CH) ip	S'_3	ν (CH) op
S_4	ν (CH) ip	S'_4	ν (CH) op
S_5	ν (CH) ip	S'_5	ν (CH) op
S_6	δ_s (SSS)	S'_6	δ_{as} (SSS)
S_7	δ (SSC) ip	S'_7	δ (SSC) op
S_8	τ (SSSC) ip	S'_8	τ (SSC) op
S_9	δ (SCH) ip	S'_9	δ (SCH) op
S_{10}	τ (SSCH) ip	S'_{10}	τ (SSCH) op
S_{11}	δ_{as} (CH_2) ip	S'_{11}	δ_{as} (CH_2) op
S_{12}	δ (SCH) ip	S'_{12}	δ (SCH) op
S_{13}	δ_s (CH_2) ip	S'_{13}	δ_s (CH_2) op
S_{14}	δ_{as} (CH_2) ip	S'_{14}	δ_{as} (CH_2) op

[a] ip, in phase. [b] op, out of phase.

remaining colorless solid and the amount of formed HCl (2.97 mmol) indicate the quantitative formation of $[(CH_3S)_3S]^+SbF_6^-$. The salt was identified by NMR and vibrational spectroscopy. It is sensitive toward moisture and decomposes at 10 °C. It is soluble in SO_2, but the solutions undergo rapid decomposition at −60 °C. In solvents such as CS_2, CH_2Cl_2, $(CH_3)_2S$, and $CHCl_3$, spontaneous decomposition takes place at the melting point of the solvents.

Data for $[(CH_3S)_3S]^+SbF_6^-$: ^{1}H NMR (300 MHz, SO_2, −60 °C, TMS) δ 3.39 (s), ^{13}C satellites $^1J(^{13}C,H) = 127$ Hz; ^{13}C NMR (75.47 MHz, SO_2, −60 °C, TMS): δ 15.9 (q, $^1J(^{13}C,H) = 133$ Hz); MS (70 eV, −40 °C) *m/z* (%)): 45 (60) $[SCH^+]$, 46 (35) $[SCH_2^+]$, 47 (31) $[SCH_3^+]$, 61 (15) $[SC_2H_5^+]$, 64 (11) $[S_2^+]$, 79 (61) $[S_2CH_3^+]$, 94 (100) $[S_2C_2H_6^+]$, 126 (15) $[S_3C_2H_6^+]$, Analysis: found % (calc %): S 31.0 (31.5), Sb 29.3 (29.8).

Synthesis of $[(CH_3{}^{34}S)_3S]^+SbF_6^-$, $[(CH_3S)_3{}^{34}S]^+SbF_6^-$, $[(^{13}CH_3S)_3S]^+SbF_6^-$, and $[(CD_3S)_3S]^+SbF_6^-$. The syntheses of the isotopomers were carried out on a 0.2 mmol scale in the same manner as described above.

Results and Discussion

Synthesis of $[(CH_3S)_3S]^+SbF_6^-$. The synthesis of $[(CH_3S)_3S]^+SbF_6^-$ was achieved according to eq 2. The salt is formed in

$$SH_3^+SbF_6^- + 3CH_3SCl \rightarrow [(CH_3S)_3S]^+SbF_6^- + 3HCl \quad (2)$$

quantitative yield by reacting an excess of CH_3SCl with $SH_3^+SbF_6^-$ at −60 °C. The absence of a solvent is important to obtain the $[(CH_3S)_3S]^+$ salt. All attempts to prepare the salt using a solvent, such as SO_2, resulted in the formation of methylbis(methylthio)sulfonium salts and sulfur, according to eq 3.

$$[(CH_3S)_3S]^+SbF_6^- \rightarrow [CH_3S(SCH_3)_2]^+SbF_6^- + {}^1/_8S^8 \quad (3)$$

The $[(CH_3S)_3S]^+SbF_6^-$ is a colorless salt, stable below 10 °C. At room temperature, it decomposes with formation of an orange-yellow product that contains sulfur, antimony sulfide, and various unidentified organosulfur compounds. The

Table 5. Ab Initio Force Field Calculated for the $[(CH_3S)_3S]^+$ Cation (Scaled Diagonal Constants in Parentheses)

A:	2.715	0.132	−0.046	0.007	0.011	0.314	0.159	−0.002	0.074	0.002	0.006	−0.005	0.013	−0.014
	(2.386)	3.277	0.097	0.063	0.060	0.039	0.170	−0.002	−0.110	−0.002	0.004	0.001	0.464	0.071
		(3.062)	5.837	0.033	0.031	−0.008	−0.005	0.002	0.098	−0.001	−0.002	0	−0.052	−0.124
			(4.908)	5.918	0.033	0.016	0.005	0.004	−0.018	0.008	−0.100	−0.015	−0.084	0.051
				(4.976)	5.919	−0.008	−0.006	−0.008	−0.018	−0.010	0.094	0.014	−0.085	0.055
					(4.977)	1.395	0.237	0.205	0.051	−0.012	−0.014	−0.029	0.039	0.009
						(1.036)	1.122	−0.005	0.227	−0.016	−0.005	−0.012	0.067	0.013
							(0.997)	0.111	−0.002	0	0.004	−0.013	0.006	0.001
								(0.099)	0.751	−0.008	−0.005	−0.002	−0.015	−0.028
									(0.644)	0.067	0.068	0.011	0.002	0.003
										(0.059)	0.661	−0.006	0.003	0.004
											(0.538)	0.756	0	0
												(0.602)	0.707	0.028
													(0.553)	0.624
														(0.511)
E:	2.401	0.128	−0.038	0.004	0.009	0.008	0.084	−0.032	0.052	0.003	0.005	0.002	0.002	−0.021
	(2.110)	3.269	0.097	0.064	0.061	0.006	0.149	0.019	−0.113	−0.001	0.005	−0.003	0.466	0.068
		(3.054)	5.837	0.033	0.031	0.002	0.001	0.002	0.100	−0.001	−0.003	0	−0.051	−0.125
			(4.908)	5.917	0.033	0.001	0.002	−0.004	−0.019	0.008	−0.099	−0.015	−0.084	0.051
				(4.975)	5.919	0	−0.008	−0.008	−0.018	−0.010	0.095	0.013	−0.086	0.055
					(4.977)	0.898	0.222	0.064	0.056	0.010	0.015	−0.012	0.021	0.002
						(0.667)	1.136	0.007	0.227	−0.007	0.006	−0.010	0.058	0.012
							(1.010)	0.063	−0.001	0.002	0.004	−0.010	0.006	−0.004
								(0.056)	0.749	−0.006	−0.003	0.002	−0.018	−0.027
									(0.642)	0.067	0.067	0.010	0.002	0.004
										(0.059)	0.660	−0.008	0.003	0.005
											(0.537)	0.758	−0.003	−0.001
												(0.603)	0.705	0.027
													(0.552)	0.623
														(0.511)
sf[a]	0.879	0.934	0.841	0.841	0.841	0.743	0.889	0.887	0.857	0.887	0.813	0.796	0.783	0.819

[a] sf, scaling factors (identical for A and E species) for the diagonal constants.

Table 6. Calculated and Experimental Frequencies and Assignments for the $[(CH_3S)_3S]^+$ Cation

	$[(CH_3S)_3S]^+$			$[(CH_3{}^{34}S)_3S]^+$			$[(CH_3S)_3{}^{34}S]^+$			$[({}^{13}CH_3S)_3S]^+$			$[(CD_3S)_3S]^+$			main character
	calc[a]	calc[b]	exp[c]	calc[a]	calc[b]	exp[c]	calc[a]	calc[b]	exp[c]	calc[a]	calc[b]	exp	calc[a]	calc[b]	exp[c]	
A:	3318	3043	3039	3318	3031	3040	3318	3043	3041	3305	3043	3040	2467	2262	2279	ν(CH)
	3295	3022	3006	3295	3011	3005	3295	3022	3004	3283	3022	3004	2445	2242	2234	ν(CH)
	3200	2935	2934	3200	2932	2926	3200	2935	2936	3198	2935	2936	2291	2101	2144	ν(CH)
	1586	1437	1438	1586	1434	1432	1586	1437	1438	1583	1437	1437	1154	1041		$\delta_{as}(CH_2)$
	1575	1418	1418	1575	1416		1575	1418		1573	1418		1138	1024	1017	$\delta_{as}(CH_2)$
	1491	1317	1313	1491	1310		1491	1317		1484	1317		1125	1000		$\delta_s(CH_2)$
	1082	1000	998	1081	992		1082	999		1075	998		843	783		δ(SCH)
	1076	963	975	1075	957		1076	963		1069	962		813	726		δ(SCH)
	721	697	702	714	681	686	721	697	701	705	691	690	679	653	659	ν_s(CS)
	499	465	463	492	465	463	492	459	463	499	458	451	486	453	461	ν_s(SS)
	256	232	(247)	252	230	(245)	255	231	233	254	229	(247)	247	223	224	δ_s (SSC)
	189	178	175	188	178	175	189	178	170	188	178	175	148	137	(164)	τ(SSCH)
	149	134	(121)	148	132	(115)	148	133	(124)	146	133	(117)	124	114	111	δ_s(SSS)
	70	66	85	69	65	83	69	66	86	69	65	81	63	60	79	τ(SSSC)
E:	3318	3043	3039	3318	3031	3040	3318	3043	3041	3305	3043	3040	2467	2262	2279	ν(CH)
	3294	3022	3006	3295	3010	3005	3295	3022	3004	3283	3022	3004	2444	2242	2234	ν(CH)
	3200	2935	2843	3200	2932	2934	3200	2935	2946	3198	2935	2944	2290	2101	2144	ν(CH)
	1587	1438	1438	1587	1435	1432	1587	1438	1438	1585	1438	1437	1153	1041		$\delta_{as}(CH_2)$
	1575	1418	1418	1575	1416		1575	1418		1572	1418		1137	1024	1017	$\delta_{as}(CH_2)$
	1488	1315	1297	1488	1308		1488	1315		1481	1315		1123	998		$\delta_s(CH_2)$
	1080	997	998	1079	990		1080	997		1074	996		839	781		δ(SCH)
	1076	963	951	1075	958		1076	963		1069	963		812	725		δ(SCH)
	719	696	691	713	680	677	719	696	691	703	689	681	676	650	652	ν_{as}(CS)
	538	503	499	532	503	501	529	495	497	538	497	490	533	499	498	ν_{as}(SS)
	265	246	247	261	243	245	264	245	(233)	262	243	247	247	228	224	δ_{as}(SSC)
	197	185	183	196	185	(175)	197	185	(170)	197	184	(175)	159	146	164	τ(SSCH)
	139	123	121	137	122	115	139	123	124	138	121	117	117	107	111	δ_{as}(SSS)
	49	46		49	45		49	46		48	46		44	41		τ(SSSC)

[a] Frequencies calculated from the ab initio force field. [b] Frequencies from force field scaled down to fit experimental data. [c] Values in parentheses: accidental degeneracy with similar vibration of alternate vibrational species assumed.

$[(CH_3S)_3S]^+SbF_6^-$ is quite soluble in SO_2 at low temperatures. Solutions of the $[(CH_3S)_3S]^+$ salt are stable for few hours at −70 °C. At −45 °C, rapid decomposition takes place according to eq 3.

The successful synthesis of the $[(CH_3S)_3S]^+$ cation is probably due to the heterogeneous reaction conditions yielding solid $[(CH_3S)_3S]^+SbF_6^-$, which is insoluble in CH_3SCl.

NMR Spectroscopy of the $[(CH_3S)_3S]^+$ Cation. The ^1H NMR spectrum of the $[(CH_3S)_3S]^+$ salt, dissolved in SO_2 at −60 °C, shows a singlet at 3.39 ppm and ^{13}C satellites with a coupling constant ($^1J(^{13}C,H) = 127$ Hz) that is typical for methyl groups. The observation of a single resonance in the ^{13}C NMR spectrum at 15.9 ppm confirms the presence of equivalent methylthio groups (Table 1). The $[(CH_3S)_3S]^+$ cation undergoes slow decomposition at −60 °C, which results in the appearance of another peak in the ^1H NMR and ^{13}C NMR spectra, respectively. After complete decomposition at −50 °C, the NMR spectra possess the expected intensity ratio and chemical shifts for the $[CH_3S(SCH_3)_2]^+$ cation. On further warming of the sample, coalescence of the peaks was observed. This effect had already been observed by Capozzi et al. and is explained by Scheme 1.[22]

Vibrational Spectra and Force Field Calculations. An infrared and Raman spectrum was recorded for $[S(SCH_3)_3]^+SbF_6^-$ (Figure 1), additional Raman spectra were obtained for the isotopomers $[S(^{34}SCH_3)_3]^+SbF_6^-$, $[^{34}S(SCH_3)_3]^+SbF_6^-$, $[S(S^{13}CH_3)_3]^+SbF_6^-$, and $[S(SCD_3)_3]^+SbF_6^-$. The observed vibrational frequencies are summarized in Table 2. The assignment of the vibrations of the octahedral SbF_6^- ion poses no problems (marked with an asterisk in Table 2) and needs no further discussion.

To aid in the assignment of normal mode vibrations of the $[S(SCH_3)_3]^+$ cation, an ab initio calculation of its geometry and force field was carried out at the RHF/6-311G(d,p) level of theory.[23-26]

The minimal energy was found for a pyramidal arrangement of C_3 symmetry with $r(SS) = 208.8$ pm and $\angle(SSS) = 104.06°$ (Figure 2). The CH_3 groups are bent toward the central S atom with $r(SC) = 182.2$ pm and $\angle(SSC) = 99.4°$, but tilted in the opposite direction [$>(SC\grave{H}) = 103.9°$, $>(SCH) = 110.9°$, respectively 111.0°, with $\grave{H}$ in trans position to the central S atom, but rotated by 2.23° from the SSC plane, thus reducing the overall symmetry from C_{3v} to C_3]. The geometrical data of the CH_3 groups are otherwise close to a regular tetrahedron with $r(C\grave{H})$ only slightly longer (108.3 pm) than $r(CH)$ (108.0 pm)

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(18) Brintzinger, H.; Pfannstiel, K.; Koddebush, H.; Kling, K.-E. *Chem. Ber.* **1950**, *83*, 87.

(19) Birkhofer, L.; Ritter, A.; Goller, H. *Chem. Ber.* **1963**, *96*, 3289.

(20) Becker, B.; Wojnowski, W. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 565.

(21) Becker, B. *Organikum*; DVW: Berlin, 1986; p 190.

(22) Capozzi, G.; DeLucchi, O.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 900.

(23) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(24) Krishnan, R.; Bleinky, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(25) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(26) Francl, M. M.; Pietro, W. J.; Hehre, W. J. Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(27) Minkwitz, R.; Kornath, A.; Sawodny, W. *Inorg. Chem.* **1996**, *35*, 3622.

(28) Marsden, C. J.; Smith, B. J. *Phys. Chem.* **1988**, *92*, 347.

(29) Anharmonic force field calculated by the authors.

(30) Sutter, D.; Dreizler, H.; Rudolph, H. D. *Z. Naturforsch.* **1965**, *20A*, 1676.

(31) Meyer, M. *J. Mol. Struct.* **1992**, *273*, 99.

(32) Rudolph, H. D.; Dreizler, H.; Maier, W. *Z. Naturforsch.* **1960**, *15A*, 742.

Table 7. Potential Energy Distributions (PED)[a] for $[(CH_3S)_3S]^+$ and $[(CD_3S)_3S]^+$

		$[(CH_3S)_3S]^+$	$[(CD_3S)_3S]^+$
A	ν_1	$48.4\ S_4 + 51.6\ S_5$	$48.3\ S_4 + 51.7\ S_5$
	ν_2	$57.2\ S_3 + 23.1\ S_4 + 19.7\ S_5$	$63.0\ S_3 + 20.3\ S_4 + 16.7\ S_5$
	ν_3	$43.0\ S_3 + 28.3\ S_4 + 28.7\ S_5$	$37.2\ S_3 + 31.4\ S_4 + 31.4\ S_5$
	ν_4	$7.4\ S_9 + 1.7\ S_{13} + 90.9\ S_{14}$	$1.5\ S_2 + 2.7\ S_9 + 9.9\ S_{13} + 85.9\ S_{14}$
	ν_5	$2.3\ S_{10} + 93.6\ S_{11} + 4.1\ S_{12}$	$2.6\ S_{10} + 95.9\ S_{11} + 1.5\ S_{12}$
	ν_6	$2.6\ S_2 + 97.3\ S_{13}$	$11.0\ S_2 + 82.5\ S_{13} + 6.5\ S_{14}$
	ν_7	$1.9\ S_2 + 2.0\ S_7 + 90.4\ S_9 + 5.7\ S_{14}$	$2.1\ S_2 + 9.4\ S_2 + 5.4\ S_7 + 81.9\ S_9 + 1.2\ S_{14}$
	ν_8	$6.2\ S_{11} + 93.8\ S_{12}$	$2.5\ S_{11} + 97.5\ S_{12}$
	ν_9	$94.3\ S_2 + 3.8\ S_9 + 1.9\ S_{13}$	$2.1\ S_1 + 85.3\ S_2 + 12.6\ S_9$
	ν_{10}	$68.7\ S_1 + 9.6\ S_6 + 18.1\ S_7 + 3.6\ S_9$	$67.4\ S_1 + 9.8\ S_6 + 14.6\ S_7 + 8.2\ S_9$
	ν_{11}	$22.5\ S_1 + 38.0\ S_6 + 27.1\ S_7 + 5.4\ S_9 + 7.0\ S_{10}$	$19.2\ S_1 + 47.7\ S_6 + 23.2\ S_7 + 1.2\ S_8 + 5.6\ S_9 + 3.1\ S_{10}$
	ν_{12}	$12.2\ S_7 + 85.6\ S_{10} + 2.2\ S_{11}$	$1.4\ S_1 + 11.8\ S_6 + 34.2\ S_7 + 1.4\ S_8 + 3.0\ S_9 + 46.8\ S_{10} + 1.4\ S_{11}$
	ν_{13}	$1.9\ S_1 + 51.8\ S_6 + 37.8\ S_7 + 3.2\ S_9 + 5.3\ S_{10}$	$1.4\ S_1 + 34.6\ S_6 + 19.3\ S_7 + 2.5\ S_9 + 42.2\ S_{10}$
	ν_{14}	$21.8\ S_6 + 3.8\ S_7 + 74.4\ S_8$	$21.2\ S_6 + 4.2\ S_7 + 74.6\ S_8$
E	ν'_1	$48.5\ S'_4 + 51.5\ S'_5$	$48.4\ S'_4 + 51.6\ S'_5$
	ν'_2	$57.1\ S'_3 + 23.2\ S'_4 + 19.7\ S'_5$	$63.0\ S'_3 + 20.2\ S'_4 + 16.8\ S'_5$
	ν'_3	$43.0\ S'_3 + 28.3\ S'_4 + 28.7\ S'_5$	$37.2\ S'_3 + 31.2\ S'_4 + 31.6\ S'_5$
	ν'_4	$7.3\ S'_9 + 2.3\ S'_{11} + 1.9\ S'_{13} + 88.5\ S'_{14}$	$1.4\ S'_2 + 2.8\ S'_9 + 1.3\ S'_{11} + 9.5\ S'_{13} + 85.0\ S'_{14}$
	ν'_5	$2.4\ S'_{10} + 91.4\ S'_{11} + 4.2\ S'_{12} + 2.0\ S'_{14}$	$2.6\ S'_{10} + 94.8\ S'_{11} + 1.6\ S'_{12} + 1.0\ S'_{14}$
	ν'_6	$2.4\ S'_2 + 96.6\ S'_{13} + 1.0\ S'_{14}$	$10.8\ S'_2 + 82.8\ S'_{13} + 6.4\ S'_{14}$
	ν'_7	$2.0\ S'_2 + 1.8\ S'_7 + 91.4\ S'_9 + 4.8\ S'_{14}$	$1.2\ S'_1 + 10.9\ S'_2 + 4.6\ S'_7 + 82.1\ S'_9 + 1.2\ S'_{14}$
	ν'_8	$1.0\ S'_{10} + 6.3\ S'_{11} + 92.7\ S'_{12}$	$2.6\ S'_{11} + 97.4\ S'_{12}$
	ν'_9	$95.6\ S'_2 + 2.3\ S'_9 + 2.1\ S'_{13}$	$1.2\ S'_1 + 84.2\ S'_2 + 14.6\ S'_9$
	ν'_{10}	$92.5\ S'_1 + 4.4\ S'_6 + 3.1\ S'_7$	$91.0\ S'_1 + 4.4\ S'_6 + 2.2\ S'_7 + 2.4\ S'_9$
	ν'_{11}	$5.1\ S'_1 + 9.8\ S'_6 + 74.0\ S'_7 + 10.1\ S'_9$	$4.7\ S'_1 + 13.8\ S'_6 + 68.4\ S'_7 + 13.6\ S'_9$
	ν'_{12}	$5.3\ S'_6 + 4.6\ S'_7 + 87.9\ S'_{10} + 2.2\ S'_{11}$	$30.0\ S'_6 + 16.4\ S'_7 + 1.9\ S'_9 + 50.3\ S'_{10} + 1.4\ S'_{11}$
	ν'_{13}	$67.7\ S'_6 + 20.0\ S'_7 + 1.6\ S'_8 + 10.7\ S'_{10}$	$44.1\ S'_6 + 14.1\ S'_7 + 41.8\ S'_{10}$
	ν'_{14}	$8.4\ S'_6 + 91.6\ S'_8$	$8.0\ S'_6 + 92.0\ S'_8$

[a] Scaled force field to fit experimental frequencies used. Only contributions more than 1% to the PED are listed.

and all >(CH_2) 109.4−109.6°. The SS and SC distances are of the same magnitude as found experimentally or by calculation for other molecules containing these bonds (Table 3).[15,27−36] The calculated angles show no unusual effects.

For the $[S(SCH_3)_3]^+$ cation with C_3 symmetry, 14 A and 14 E vibrations are expected, which can be divided into 5 A + 5 E modes for the $S(SC)_3$ skeleton and 9 A + 9 E modes for the internal vibrations of the CH_3 groups. The symmetry coordinates of pyramidal ($S(SC)_3$ skeleton) and tetrahedral (SCH_3 groups) entities are well known and are not repeated here. Only a list of their sequence together with the physical meaning is given (Table 4), which is identical in species A and E, as the former contains the symmetric and in-phase modes, the latter the corresponding antisymmetric and out-of-phase ones. Consequently, we used the same numbering (1−14) for both species, indicating the E modes by adding a prime to the S symbol for the symmetry coordinate.

The results of the force constant calculations are given in Table 5; the vibrational frequencies obtained from this force field are reported in column 1 of Table 6. These values, reduced by 10%, which is known to be a good estimate for the deviations caused by the Hartree−Fock limit and the use of truncated basis sets, were used to assign the experimental data given in column 3 of Table 6. The potential energy distribution for the scaled force field[37] is listed in Table 7 for the ions $[S(SCH_3)_3]^+$ and $[S(SCD_3)_3]^+$ only, as the deviations for the heavy atom isotopomers from the parent compound are negligible.

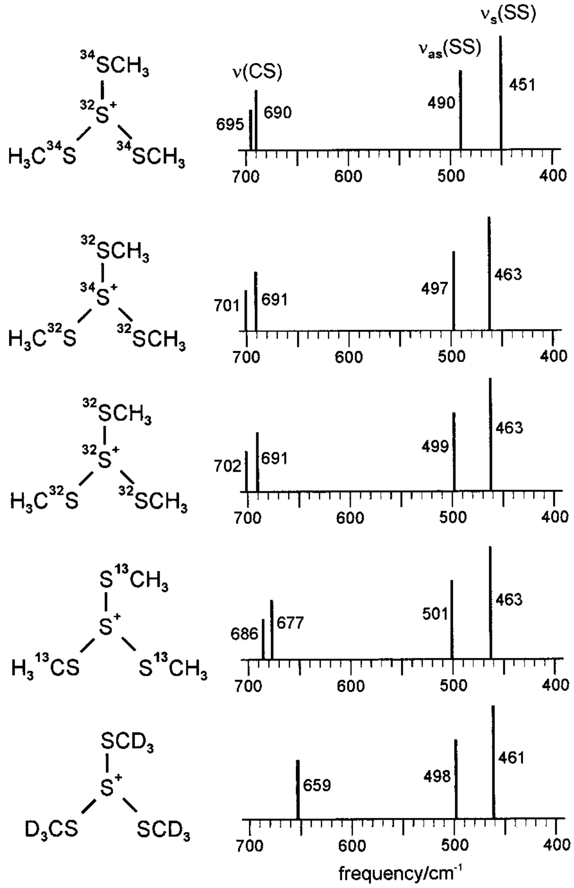

Figure 3. Isotopic shifts of the SS and CS stretching vibrations of the $[(CH_3S)_3S]^+$ isotopomers.

On the whole, the assignment of the normal modes poses no serious problem, as the inner vibrations of the CH_3 groups, even for CD_3, with the exception of the torsional modes all occur higher than 700 cm^{-1} and therefore well above even the stretching vibrations of the $S(SC)_3$ skeleton. In- and out-phase

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(33) Ellwood, J. A.; Steele, D.; Gerard, D. *Spectrochim. Acta* **1994**, *50A*, 913.

(34) Schumacher, C.; Schmidt, R. E.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *520*, 25.

(35) Knop, O.; Linden, A.; Vincent, B. R.; Chi, S. C.; Cameron, T. S. *Can. J. Chem.* **1989**, *67*, 1984.

(36) Markham, G. D.; Bock, C. W. *J. Phys. Chem.* **1993**, *97*, 5562.

(37) Herberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(38) Fritzkowsky, N.; Lentz, A.; Goubeau, J. *Z. Anorg. Allg. Chem.* **1971**, *386*, 67.

vibrations of the CH_3 groups are mostly accidentally degenerate; the deformational modes are so weak that they could not be found in the Raman spectra of the isotopomers with the exception of one $\delta_{as}(CD_3)$ for $[S(SCD_3)_3]^+$ at 1017 cm^{-1}.

The SC stretching vibrations are observed as a pair with a 10 cm^{-1} difference at 650−702 cm^{-1} (for $[S(SCD_3)_3]^+$, the lower vibration coinciding with the $\nu_1(a_{1g})$ of the SbF_6^- anion). The SS stretching vibrations with a difference of 34−39 cm^{-1} between the symmetric and asymmetric modes appear at 450−500 cm^{-1} (Figure 3). The agreement of calculated and experimental isotopic shifts (Table 6) seems satisfactoy, taking into account that the solid-state Raman spectra have been recorded without special precautions concerning the accuracy of the spectrometer.

There are some problems assigning the deformational modes of the skeleton, including the torsions of the CH_3 groups. According to the ab initio calculation, none of these vibrations can be expected above 270 cm^{-1}. Whereas a shoulder at ∼295 cm^{-1} may be interpreted as a splitting of $\nu_5(f_{2g})$ of the SbF_6^- anion at the 288 cm^{-1}, the Raman line at 312−333 cm^{-1}, which had been assigned to $\delta_{as}(PSC)$ in $P(SCH_3)_3$,[38] is left unexplained. Only one frequency is observed for each of the skeletal deformations and $\tau(CH_3)$, though a 7−10 cm^{-1} difference is predicted by the ab initio calculations between the symmetric and asymmetric modes. These differences may either not have been resolved at these low frequencies or only one of them appears in the spectra. The accidental degeneracy assumed for these pairs may not be valid. Therefore the experimental frequencies fitting less are given in parentheses in Table 6.

For the adaption of the force field to the experimental frequencies, decent scaling factors (identical for the proper A and E modes) of 0.78 to 0.89 had to be used,[37] with only two exceptions: a higher one (0.93) for ν(SC) and a lower one (0.74) for δ(SSS). It is not clear if the lowest Raman line observed at 79−85 cm^{-1} is a lattice mode or τ(SSSC) in species A. For a fit to the letter one would require a scaling factor of 1.43, which is not so unlikely as it seems at first glance, as the ab initio calculation was done for the free cation, but its integration in a crystal lattice may hamper especially the torsional mode and thus shift it to higher energy. But considering such an assignment is of minor influence on the rest of the force field, just increasing the mixing of the skeletal deformations, but leaving all diagonal force constants except the torsional one essentially unchanged.

The SC and SS stretching force constants calculated from the force field adopted to the experimental vibrational frequencies are included in Table 3. As the atomic distances, they fit into the range found for similar molecules and ions, though a correlation between these data is not extant, but also not expected because of the rather different methods of calculations used for these compounds.

Conclusion

The trithiosulfonium unit in cations of the type $[(RS)_3S]^+$ (R = alkyl) can be synthesized under heterogeneous reaction conditions. The tris(methylthio)sulfonium salt possesses moderate stability in the solid state, but in solution a rapid elimination of sulfur occurs. In previous attempts,[39,40] the instability of the tris(methylthio)sulfonium cation in solution has prevented its successful synthesis.

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(39) Minkwitz, R.; Prenzel, H.; Pritzkow, H. *Z. Naturforsch.* **1987**, *42B*, 750.

(40) Minkwitz, R.; Krause, R.; Preut, H. *Z. Anorg. Allg. Chem.* **1989**, *571*, 133.