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THE SYNTHESIS AND VIBRATIONAL SPECTRA OF THE ANTIMONY(V)FLUORIDE-
FLUOROSULFATES $SbF_3(SO_3F)_2$, $SbF_4(SO_3F)$ and $Sb_2F_9(SO_3F)$

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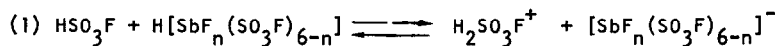
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SUMMARY

The synthesis of the title compounds by a variety of routes is described. These routes involve the oxidation of antimony(III)fluoride by bis(fluorosulfonyl)peroxide and the use of non-statistical ligand redistribution reactions. Complex formation with ClO_2SO_3F leads to $ClO_2[SbF_n(SO_3F)_{6-n}]$, with $n=3$ or 4. Polarized Raman data and low temperature infrared data are reported. All antimony(V)fluoride-fluorosulfates are found to have fluorosulfate bridges with $SbF_3(SO_3F)_2$ and $SbF_4(SO_3F)$ being polymers. Ionic formulations for the ClO_2^+ complexes are again based on vibrational spectra.

INTRODUCTION

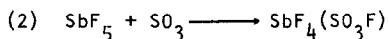
The superacid systems HSO_3F-SbF_5 and $HSO_3F-SbF_5-SO_3$ are among the strongest protonic acids known [1]. Their acidity is attributed to the presence of mono-protonic, monomeric acids of the type $H[SbF_n(SO_3F)_{6-n}]$, with $n=2,3,4$ and 5, and their ability to protonate the solvent HSO_3F according to



At higher SbF_5 concentrations, dimeric acids like $H[Sb_2F_{10}(SO_3F)]$ and $H[Sb_2F_8(SO_3F)_3]$ and the corresponding anions are also present [2,3]. Evidence for the acidity and the constitution is obtained primarily by conductometric methods [2] and by ^{19}F NMR spectra [2,3]. The use of Raman spectroscopy has been limited to the $HSO_3F + SbF_5$ system [3].

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Even though a number of mono- and dimeric complex acids and their anions have been identified in solution [2,3], synthetic efforts to obtain either the anhydro acids or complexes with above mentioned anions in substance, have been rather limited. The synthesis of antimony(V)tetrafluoride monofluorosulfate via



has been reported together with ^{19}F NMR and vibrational spectra [4]. The reaction of antimony(V)chloride with bis(fluorosulfonyl)peroxide, $\text{S}_2\text{O}_6\text{F}_2$, had yielded rather complex mixtures, possibly containing anions of the type $[\text{SbF}_n(\text{SO}_3\text{F})_{6-n}]^-$ [5].

The present study reports the synthesis of two additional antimony(V) fluoridefluorosulfates, $\text{SbF}_3(\text{SO}_3\text{F})_2$ and $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$, and of the chloronium complexes of the type $\text{ClO}_2[\text{SbF}_n(\text{SO}_3\text{F})_{6-n}]$ with $n=3$ or 4. Structural conclusions are based on Raman and IR spectra.

EXPERIMENTAL

I. Chemicals

Antimony(III)fluoride of technical grade was purified according to a method of Andersen et. al. [6]. Antimony(V)fluoride (Ozark Mahoning Company) was purified by repeated distillation, first at atmospheric pressure and finally in vacuo. Bis(fluorosulfonyl)peroxide [7], bromine(I)fluorosulfate [8] and chlorylfluorosulfate [9] were synthesized by literature methods. FSO_3F was formed as a by-product in the synthesis of $\text{S}_2\text{O}_6\text{F}_2$ [7].

II. Instrumentation

Infrared spectra were obtained on Perkin-Elmer 457 and 225 grating spectrophotometers for room temperature and low temperature spectra respectively. Details of the instrumentation used to obtain IR spectra at 80 K have been published [10]. At room temperature, spectra were recorded on thin films between BaF_2 and where possible AgCl and AgBr windows (all from Harshaw Chemicals).

Raman spectra were recorded on a Cary 81 spectrometer equipped with a Model 125 He-Ne gas laser (Spectra Physics Corp.). The samples were contained in 5-mm o.d. Pyrex tubes with flat bottom ends. The 6328 Å wavelength line was used as exciting light. Mass spectra were obtained on a AEI MS902 mass spectrometer. Hygroscopic materials were stored and handled in a 'Dri-Lab' Model No. HE-43-2 (Vacuum Atmosphere Corp.) filled with purified

dry nitrogen and equipped with 'Dri-Train' Model No. HE-93B. A Mettler top loading balance Model P160 was used inside the drybox for the preparation of reaction mixtures.

Volatile reactants were manipulated in a Pyrex vacuum line fitted with Kontes Teflon stem stopcocks. All reactions were carried out in one or two part Pyrex reactors of approximately 50 ml volume, fitted with Kontes Teflon stem stopcocks. B19 ground glass joints were used for the two part reactions.

III. Synthetic Reactions

Details regarding the stoichiometry, reaction conditions, time, and product are summarized in Table I. A typical reaction, the synthesis of $\text{SbF}_3(\text{SO}_3\text{F})_2$, is described in detail below.

TABLE I

The Synthesis of Antimony(V)fluoride-fluorosulfates

No.	Reactants mg [mmoles]	Rxn Temp °C	Rxn Time hr	Reaction Product	Method of Isolation
1	$\text{SbF}_3 + \text{S}_2\text{O}_6\text{F}_2$ 3162 [17.69]; 7388 [37.29]	+25 +65	240 36	$\text{SbF}_3(\text{SO}_3\text{F})_2$	Removal of volatile reactants in static vacuum
2	$\text{SbF}_3 + \text{FOSO}_2\text{F}$ 2979 [16.67]; 2585 [21.90]	+25	192	$\text{SbF}_4(\text{SO}_3\text{F})$	Removal of volatile reactants in vacuo
3	$\text{SbF}_5 + \text{SbF}_3 + \text{S}_2\text{O}_6\text{F}_2$ 3898 [17.98]; 3213 [17.98]; 10052 [50.1]	+25	24	$\text{SbF}_4(\text{SO}_3\text{F})$	In vacuo distillation of reaction mixture
4	$\text{SbF}_3(\text{SO}_3\text{F})_2 + \text{SbF}_5$ 3530 [9.367]; 2036 [9.38]	+25	192	$\text{SbF}_4(\text{SO}_3\text{F})$	Not required
5	$\text{SbF}_4(\text{SO}_3\text{F}) + \text{SbF}_5$ 1070 [3.60]; 782 [3.61]	+25	2	$\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$	Distillation in vacuo
6	$\text{Br}_2 + \text{S}_2\text{O}_6\text{F}_2 + \text{SbF}_5$ 1280 [8.01]; 797 [4.023]; 8876 [40.95]	+50	<1	$\text{Br}_2\text{Sb}_3\text{F}_{16}$, $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$	Removal of $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ in vacuo
7	$\text{ClO}_2\text{SO}_3\text{F} + \text{SbF}_3(\text{SO}_3\text{F})_2$ 407 [2.44]; 917 [2.43]	+50	2	$\text{ClO}_2[\text{SbF}_3(\text{SO}_3\text{F})_3]$	Not required
8	$\text{ClO}_2\text{SO}_3\text{F} + \text{SbF}_4(\text{SO}_3\text{F})$ 385 [2.32]; 687 [2.32]	+50	2	$\text{ClO}_2[\text{SbF}_4(\text{SO}_3\text{F})_2]$	Not required

To 3.162 g (17.69 mmoles) of purified SbF_3 were added 7.388 g (37.29 mmoles) of $\text{S}_2\text{O}_6\text{F}_2$. The reaction mixture was warmed to room temperature and then continually agitated, automatically, for approximately 10 days. During this time the white crystals (SbF_3) slowly changed into a viscous, dense liquid, which was seemingly not miscible with the supernatant $\text{S}_2\text{O}_6\text{F}_2$. To ensure complete reaction, the mixture was held for an additional three days at $+65^\circ\text{C}$.

Subsequently, most of the excess $\text{S}_2\text{O}_6\text{F}_2$ was removed in static vacuum with the reaction vessel at room temperature. In order to remove traces of $\text{S}_2\text{O}_6\text{F}_2$ dissolved in the extremely viscous reaction product, the mixture was heated briefly in a static vacuum to $+65^\circ\text{C}$. Small amounts of the very slightly volatile reaction product distilled over as well. The absence of a Raman band at 800 cm^{-1} (symmetric O-O stretch for $\text{S}_2\text{O}_6\text{F}_2$ [12]) was subsequently used as a purity check for the final product.

A total of 6.243 g (16.57 mmoles) of a viscous liquid remained in the reaction vessel. The product analysed as $\text{SbF}_3(\text{SO}_3\text{F})_2$.

IV. Analyses and Physical Properties

Chemical analysis for Sb, S and F was performed by A. Bernhard, Microanalytical Laboratories, Elbach, West Germany. The results are listed below in Table 2.

TABLE 2
Analytical Results

Compound		% Sb	% S	% F
$\text{SbF}_3(\text{SO}_3\text{F})_2$	calc	32.31	16.79	25.21
	found	32.46	17.02	25.10
$\text{SbF}_4(\text{SO}_3\text{F})$	calc	41.02		32.00
	found	41.19		31.78
$\text{SbF}_4(\text{SO}_3\text{F}) \cdot \text{SbF}_5$	calc	47.42	6.24	36.99
	found	47.71	6.41	36.63
$\text{ClO}_2[\text{SbF}_4(\text{SO}_3\text{F})_2]$	calc	26.28	13.84	24.60
	found	26.46	13.68	24.47
$\text{ClO}_2[\text{SbF}_3(\text{SO}_3\text{F})_3]$	calc	22.41	17.70	20.98
	found	22.66	17.51	20.87

V. Molecular Weight Determination of Gaseous $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$

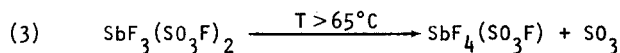
- vapour density measurements using fluorolube-oil of $d^{24}=1.92 \text{ g/cm}^3$
experimental 510 ± 30 calculated 513.54
- vapour pressure at room temperature 2.6 torr
- mass spectrum
parent ion peaks at 512, 514, 516 and 518 reflecting isotopic effects of ^{121}Sb , ^{123}Sb , ^{32}S and ^{34}S .

RESULTS AND CONCLUSIONS

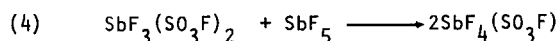
1. Synthesis

The oxidative addition of bis(fluorosulfonyl)peroxide to antimony(III) fluoride is found to yield quantitatively a clear viscous product of the composition $\text{SbF}_3(\text{SO}_3\text{F})_2$. The reaction has a precedent in the reported synthesis of $\text{CeF}_3(\text{SO}_3\text{F})$ from CeF_3 [11].

Antimony(V)trifluoridebisfluorosulfate is of limited thermal stability and the reaction temperature should not exceed $+65^\circ\text{C}$. Attempts to purify the viscous material by fractional distillation in a dynamic vacuum resulted in the quantitative conversion



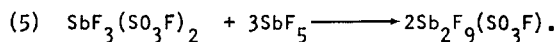
On the other hand, it was found necessary to heat the reaction mixture to $+65^\circ\text{C}$ for three days in order to ensure complete oxidation of SbF_3 . Small amounts of SbF_3 are soluble in $\text{SbF}_3(\text{SO}_3\text{F})_2$; however, the ligand redistribution reaction



provides a good purity check. Addition of SbF_5 to $\text{SbF}_3(\text{SO}_3\text{F})_2$ results in the formation of a white precipitate when SbF_3 is present, which can be isolated after removal of all volatiles in a dynamic vacuum. The solid, identified by chemical analysis and Raman spectrum, is a mixed valency fluoride of antimony, $\text{Sb}_{11}\text{F}_{43}$ [13][14].

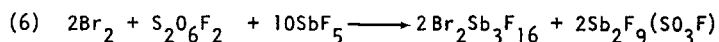
Additional new routes to $\text{SbF}_4(\text{SO}_3\text{F})$ besides the ligand redistribution reaction (4), are the addition of fluorinefluorosulfate, FSO_3F , to SbF_3 , and the oxidation of SbF_3 by $\text{S}_2\text{O}_6\text{F}_2$ in the presence of a stoichiometric amount of SbF_5 . Initial addition of SbF_3 to SbF_5 results in the formation of a solid intermediate, which is subsequently oxidized by $\text{S}_2\text{O}_6\text{F}_2$ to clear viscous $\text{SbF}_4(\text{SO}_3\text{F})$.

Addition of a further mole of SbF_5 , or the reaction



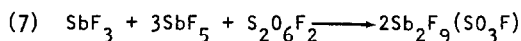
results in the formation of a clear colourless product of the composition $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$. However, in contrast to both $\text{SbF}_3(\text{SO}_3\text{F})_2$ and $\text{SbF}_4(\text{SO}_3\text{F})$ this material is sufficiently volatile to permit molecular weight determinations.

First indications that a rather volatile fluoride-fluorosulfate may be found had come from a number of solvolysis reactions of fluorosulfates in liquid SbF_5 which we had investigated previously [15-17]. The synthesis of $\text{Br}_2\text{Sb}_3\text{F}_{16}$ [18] by this method according to

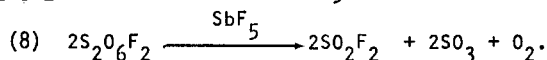


can be used to synthesize $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$, provided the reactants are used in the correct molar ratios. Without doubt other solvolysis reactions of fluorosulfates [15], [16] can be utilized in the same manner.

Whereas it had been found feasible to generate $\text{SbF}_4(\text{SO}_3\text{F})$ by adding $\text{S}_2\text{O}_6\text{F}_2$ to a preformed mixture of $\text{SbF}_3/\text{SbF}_5$, a reaction similar to this to prepare $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ did not succeed. Surprisingly, the reaction

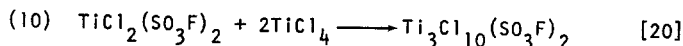
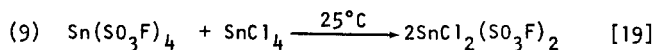


was found unsuitable because of a complicating side reaction—the decomposition of $\text{S}_2\text{O}_6\text{F}_2$ in the presence of SbF_5 —



This reaction proceeds quantitatively when $\text{S}_2\text{O}_6\text{F}_2$ is mixed with antimony(V) fluoride at room temperature. The occurrence of O_2 in the reaction products is readily detected. Decomposition of $\text{S}_2\text{O}_6\text{F}_2$ is avoided by either mixing SbF_3 and SbF_5 first to form the solid intermediate as in reaction 2, Table 1, or by oxidizing Br_2 with $\text{S}_2\text{O}_6\text{F}_2$ before adding SbF_5 as in reaction 6, Table 1.

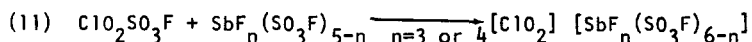
Ligand rearrangement reactions have several precedents in the chemistry of fluorosulfates. Two relevant examples involve fluorosulfates of tin(IV) and titanium(IV).



In the rearrangement reactions reported here a non-statistical redistribution of ligands is observed, hence the synthetic usefulness of these reactions; that is, the equilibrium reactions given here are shifted virtually entirely to the right. All reactions proceed in the same direction, from higher to lower fluorosulfates products, and in the absence of catalysts or solvents. However, since antimony(V)fluoride is not readily separated from the reaction products in such ligand scrambling reactions, it becomes necessary to react exact stoichiometric amounts.

The existence of $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ is not too surprising because the fluoro-sulfate bridged anion $[\text{Sb}_2\text{F}_{10}(\text{SO}_3\text{F})]^-$ had been detected in the superacid system $\text{HSO}_3\text{F} + \text{SbF}_5$ [2],[3].

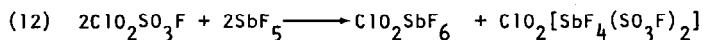
Complexation reactions of both $\text{SbF}_3(\text{SO}_3\text{F})_2$ and $\text{SbF}_4(\text{SO}_3\text{F})$, with $\text{ClO}_2\text{SO}_3\text{F}$ as SO_3F^- ion donor, follow the general equation



$\text{ClO}_2\text{SO}_3\text{F}$ was chosen because the material is a supercooled liquid at room temperature, which allows quantitative addition by pipetting inside a drybox. In addition, the vibrational spectrum of the chloronium cation, ClO_2^+ , is well known [21].

In both cases rather viscous materials are obtained which solidified to light yellow glasses on cooling. The occurrence of a reaction is indicated by a colour change from dark red to light yellow immediately after the addition of $\text{ClO}_2\text{SO}_3\text{F}$ and by changes in the vibrational spectrum (to be discussed later).

Attempts to extend the complexation reaction (11) to SbF_5 and $\text{ClO}_2\text{SO}_3\text{F}$ were not successful. When equimolar amounts were reacted, an inhomogeneous mixture of a white solid and a yellow liquid resulted. The liquid was identified by chemical analysis and by Raman spectroscopy as $\text{ClO}_2[\text{SbF}_4(\text{SO}_3\text{F})_2]$. The solid was tentatively identified as ClO_2SbF_6 and the reaction seemed to have followed the equation



The reaction is consistent with an earlier observation [15] on the same system, where $\text{ClO}_2\text{SO}_3\text{F}$ is converted by an excess of SbF_5 into $\text{ClO}_2\text{Sb}_2\text{F}_{11}$. Similar observations were made by Dean and Gillespie [22] on approximately equimolar mixtures of HSO_3F and SbF_5 by ^{19}F NMR. Here the formation of the ions $[\text{SbF}_4(\text{SO}_3\text{F})_2]^-$ and $\text{Sb}_2\text{F}_{11}^-$ was attributed to ligand redistribution, which seems to be the most logical explanation for our observations as well.

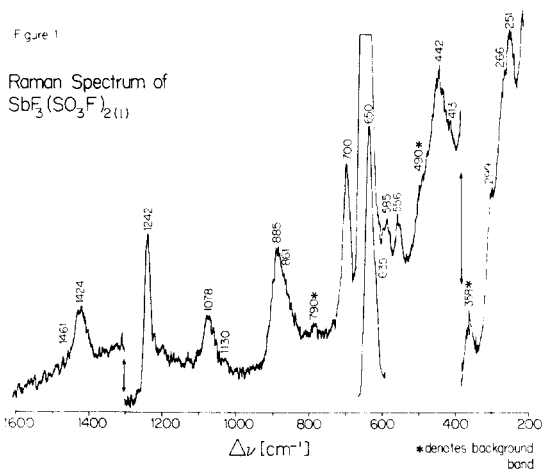
All compounds are hygroscopic viscous liquids which solidify to glasses on cooling.

Of the antimony(V)fluoride-fluorosulfates only $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ has a measurable vapour pressure at room temperature i.e., 2.6 torr. The compound appears to be monomeric in the gas phase. The rather strong association of one mole of SbF_5 with one mole of $\text{SbF}_4(\text{SO}_3\text{F})$ to form $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ is even evident under mass spectrometric conditions. The highest observable mass peaks are due to the parent ion with a small group of peaks at masses higher than the parent ion peaks by 19 mass units, suggesting the gain of a F atom. As the low vapour pressure of 2-4 torr for SbF_5 [23], [24] itself indicates, association of SbF_5 in the gas phase has also been confirmed [24], [25] with polymeric association being assumed for the Sb atoms via fluorine atom bridging.

The lack of appreciable vapour pressure for $\text{SbF}_4(\text{SO}_3\text{F})$ and for $\text{SbF}_3(\text{SO}_3\text{F})_2$, suggest even more than before polymeric structures for these compounds. A previous study on $\text{SbF}_4(\text{SO}_3\text{F})$ [4] had suggested association via fluorosulfate bridges with both cis or trans orientation.

II. Vibrational Spectra

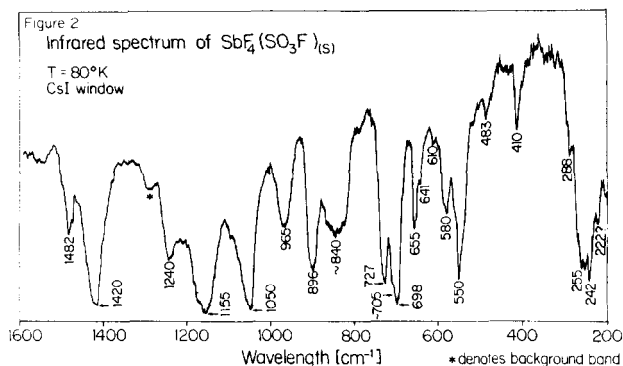
Reliable vibrational spectra of the rather viscous, reactive materials are not easily obtained. Raman spectra, as illustrated in Figure 1, show



rather broad bands. Consequently low intensity bands are often poorly resolved and detectable only with difficulties. In addition, unambiguous polarization measurements are not possible for these weak bands. Infrared spectra at room temperature, obtained on thin films, are only possible when

BaF_2 plates are used, thus restricting the transmission range to about 800 cm^{-1} . The use of AgCl , AgBr or KRS-5 plates resulted in window attack.

Only $\text{SbF}_4(\text{SO}_3\text{F})$ and $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ were sufficiently volatile and thermally stable to allow condensation onto a CsI window cooled to about 80 K . For these two compounds well resolved infrared spectra are obtained, as illustrated in Figure 2 for $\text{SbF}_4(\text{SO}_3\text{F})$.



The observed vibrational frequencies, together with estimated intensities, an approximate assignment and where possible the qualitative results of polarization measurements are listed in Table 3 for $\text{SbF}_3(\text{SO}_3\text{F})_2$, $\text{SbF}_4(\text{SO}_3\text{F})$ and $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$, and in Table 4 for $\text{ClO}_2[\text{SbF}_3(\text{SO}_3\text{F})_3]$ and $\text{ClO}_2[\text{SbF}_4(\text{SO}_3\text{F})_2]$.

Fig. 3 shows a tracing of the Raman spectrum of $\text{ClO}_2[\text{SbF}_3(\text{SO}_3\text{F})_3]$.

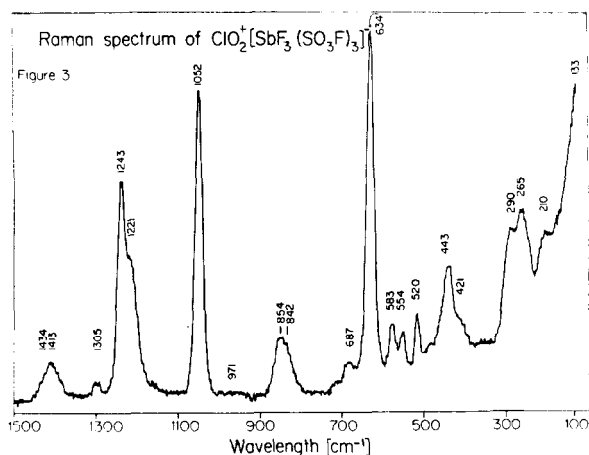


TABLE 3

Vibrational frequencies for some antimony(V)fluoride-fluorosulfates

$\text{SbF}_4(\text{SO}_3\text{F}) \cdot \text{SbF}_5$		$\text{SbF}_4(\text{SO}_3\text{F})$		$\text{SbF}_3(\text{SO}_3\text{F})_2$		Assignments
low-temp Infrared	Raman	low-temp Infrared	Raman	room-temp Infrared	Raman	Description of Mode
		1482 mw		1440 s	1461 w	$\nu_{\text{asym}} \text{SO}_2$ M
1425 vs	1430 (p) m	1420 vs 1240 m	1424 (p) m	1408 vs 1225 s	1424 (p) m 1242 (p) s	νSO_3 B $\nu_{\text{sym}} \text{SO}_2$ M
1095 vs		1155 vs,b	\sim 1150 vw	1125 vs,b		νSO_2 B
1060 vs	1068 (p) m	1050 vs 965 m	1080 (p) m	1060 s,sh 1000 s	1078 (p) m 1030 w	νSO_3 B νSO_3 M
900 s	898 (p) s	896 s	900 (p) s	870 vs,b	885 (p) s	νSF B
		\sim 840 s,b			861 s,sh	νSF M
731 vs		727 s				
\sim 715 sh	710 (p) vs	\sim 705 s,sh	699 (p) vs		700 (p) s	νSbF +
700 vs	700 s,sh	698 vs	664 sh			
662 m	661 (p) vs	655 s	653 (p) vs		650 (p) vs	νSbO
{648 ms}		641 m,sh			635 s,sh	
{635 w }	606 w	610 w	606 (dp) vw			
581 s	590? vw	580 m			585 (p) w	$\delta \text{SO}_3\text{F}$
549 s	556 (dp) w	550 s	555 (dp) w		556 (dp) w	$\delta \text{SO}_3\text{F}$
485 s	472 w	483 w	464 w,sh			$\delta \text{SO}_3\text{F}$
444 mw	434 (p) m		443 (p) m		442 (p) s	$\delta^+ \text{SbF}_{\text{m}} \text{O}_{\text{n}}$
410 w		410 m			413 w,sh	
341 ms						
285 w	302 w	288 m	300 w		299 m,sh	$\gamma_{\text{deform}} \text{SO}_3\text{F}$ +
265 w	271 s	255 s	268 w		266 m,sh	
235 w	245 s	242 s	249 (p) s		251 s	$\gamma_{\text{deform}} \text{SbF}_{\text{m}} \text{O}_{\text{n}}$
215?w		222?w				
	201 ms		199 w			
	129 w,sh		130 w,sh			

Explanation: vs = very strong, s = strong, m = medium, w = weak,
 vw = very weak, sh = shoulder, b = broad, (p) = polarized,
 (dp) = depolarized, M = monodentate, B = bidentate

Agreement with previously reported Raman data for $\text{SbF}_4(\text{SO}_3\text{F})$ [4] is fair. Infrared data, obtained by using AgCl windows [4], disagree with both the Raman and the low temperature infrared data. As confirmed by experiment, window attack is the cause for the unexpected discrepancy.

TABLE 4

Vibrational frequencies for $\text{ClO}_2[\text{SbF}_4(\text{SO}_3\text{F})_2]$ and $\text{ClO}_2[\text{SbF}_3(\text{SO}_3\text{F})_3]^*$

$\text{ClO}_2[\text{SbF}_4(\text{SO}_3\text{F})_2]$			$\text{ClO}_2[\text{SbF}_3(\text{SO}_3\text{F})_3]$			Assignments
Infrared		Raman	Infrared		Raman	
cm^{-1}	Intensity	cm^{-1} Intensity	cm^{-1} Intensity	cm^{-1} Intensity		
1398	s	{1405} {1397}	1405	s	{1434} {1413}	$\nu_{\text{asym}}\text{SO}_2$
{1325}	sh	1302	{1330}	sh	1305	$\nu_{\text{asym}}\text{ClO}_2$
{1295}	s	{1232}	{1290}	m	{1243}	$\nu_{\text{sym}}\text{SO}_2$
{1225}	sh	{1222}	{1225}	s	{1221}	$\nu_{\text{sym}}\text{ClO}_2$
{1205}	sh		{1200}	sh		ν_{SO}
{1103}	w,sh	1053	{1100}	sh	1052	
{1080}	sh		{1080}	sh		
{1025}	s	980	{1025}	sh	971	
{1000}	sh		{985}	s		
~ 820	sh on BaF ₂ cutoff	{853} {838}	~ 835	sh on BaF ₂ cutoff	{854} {842}	ν SF
		683			687	$\nu + \text{SbF}$
		637			634	$\nu + \text{SbO}$
		585			583	$\delta_{\text{bend}}\text{SO}_2$
		557			554	$\gamma_{\text{rock}}\text{SO}_2$
		519			520	$\delta_{\text{bend}}\text{ClO}_2$
		441			443	$\delta_{\text{bend}}\text{SbF}_{0n}$
		412			421	$\gamma_{\text{wag}} + \text{SF}$
		291			290	$\gamma_{\text{deform}}\text{SbF}_{0n}$
		262			265	$\gamma_{\text{deform}}\text{SO}_3$
		213			210	$\gamma_{\text{deform}}\text{SO}_3$

* For abbreviations see Table 3

The area of primary interest in the vibrational spectra is the SO_3F stretching range ($1500\text{--}750\text{ cm}^{-1}$). In the lower frequency range, a clear distinction between bands due to Sb-F and Sb-O stretching vibrations and, to a degree, SO_3F bending modes is difficult, because all of them should fall into the $780\text{--}500\text{ cm}^{-1}$ range. Further complication in this region may arise from the type of bridging (fluorosulfate or fluoride bridging) and the resulting geometry around antimony.

Extensive help in assigning the SO_3F modes reported here may be found in a number of fluorosulfate derivatives of tin, where ^{119}Sn Mossbauer spectroscopy has provided support for vibrational assignments. Bidentate bridging SO_3F groups, leading to polymers with octahedral coordination around tin, are found for compounds of the type $\text{X}_2\text{Sn}(\text{SO}_3\text{F})_2$ with $\text{X}=\text{CH}_3$, Cl, F, etc. [26 — 28]. In addition the molecular structure of $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ is known in detail [29]. Both bidentate bridging and monodentate fluorosulfate groups are found in $\text{Sn}(\text{SO}_3\text{F})_4$ [28] and only monodentate $-\text{OSO}_2\text{F}$ groups are found in the anion $[\text{Sn}(\text{SO}_3\text{F})_6]^{2-}$ [30].

As can be seen in Table 5, vibrational bands due to a bidentate, presumably bridging, fluorosulfate group are found for $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$, $\text{SbF}_4(\text{SO}_3\text{F})$ and $\text{SbF}_3(\text{SO}_3\text{F})_2$, and tentative assignments for all nine fundamentals is possible. Good similarity to the spectra for the corresponding $\text{SnX}_2(\text{SO}_3\text{F})_2$, with $\text{X}=\text{CH}_3$, Cl or F, compounds is observed.

An interesting pattern is observed in the SO_3 stretching range. The two highest frequency bands ν_1 and ν_2 , produced by the splitting of the degenerate SO_3 mode (E) at $\sim 1280\text{ cm}^{-1}$ for the SO_3F^- ion, are widely split (by $\sim 300\text{ cm}^{-1}$). As a consequence, ν_2 and ν_3 almost coincide and in the Raman spectra of $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ and $\text{SbF}_3(\text{SO}_3\text{F})_2$, ν_2 is not observed due to accidental degeneracy. The frequency difference between ν_1 and ν_2 seems to increase with increasing electronegativity of substituents on Sn or Sb, best reflected in observed trends for the tin compounds [27].

Polarization measurements indicate that ν_7 and possibly also ν_5 are depolarized. If one assumes that ν_2 would be the third depolarized band, C_s symmetry for the bidentate fluorosulfate group is confirmed. The remaining six fundamentals are polarized and of A' symmetry. Since bridging fluorosulfate groups were previously found only in solid compounds, polarization measurements had not been possible before. The postulated A' symmetry for ν_2 would suggest a weakly Raman active band. Our failure to observe this band in two instances would hence not be surprising. Good correspondence between Raman and low

TABLE 5

Normal vibrational modes due to bidentate SO_3F groups in tin and antimony compounds (cm^{-1})

Compound	Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	Reference
$(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ (s)	IR	1350	1180	1076	827	620	590	554	417	304	[27]
$\text{C}_4\text{Sn}(\text{SO}_3\text{F})_2$ (s)	IR	1385	1130	1087	864	628	586	555	446	312	[28]
$\text{F}_2\text{Sn}(\text{SO}_3\text{F})_2$ (s)	IR	1420	1101 ^a	1068	855	630	590	548	430	280	[26]
$\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ (l)	Ra	1430	n.o.	1068	898	606	590	556 ^b	434	302	this work
$\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ (s)	IR at 80°K	1425	1095	1060	900	n.o.	581	549	444	285	this work
$\text{SbF}_4(\text{SO}_3\text{F})$ (l)	Ra	1424	1150	1080	900	606 ^b	n.o.	555 ^b	443	300	this work
$\text{SbF}_4(\text{SO}_3\text{F})$ (s)	IR at 80°K	1420	1155	1050	896	610	580	550	410?	288	this work
$\text{SbF}_3(\text{SO}_3\text{F})_2$ (l)	Ra	1424	n.o.	1078	885	n.o.	585	556 ^b	413	299	this work
$\text{SbF}_3(\text{SO}_3\text{F})_2$ (l)	IR	1408	1125	1060	870	n.o.	n.o.	n.o.	n.o.	n.o.	this work

a) denotes average value,

b) depolarized Raman band,

c) n.o. = not observed

temperature infrared data is found for $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$. For $\text{SbF}_4(\text{SO}_3\text{F})$ additional low intensity infrared bands are found. These bands are assigned to a terminal, monodentate $-\text{OSO}_2\text{F}$ group. Apparently, condensation onto the cold CsI window prevents more extensive polymerization via SO_3F bridges. This view is confirmed by a decrease in intensity of these bands on allowing the sample to warm up to room temperature. Due to the reactivity of the material, BaF_2 windows were used in these experiments.

Strong bands due to terminal monodentate $-\text{OSO}_2\text{F}$ groups are found in both the IR and Raman spectra of $\text{SbF}_3(\text{SO}_3\text{F})_2$, and an assignment is possible in the SO_3F stretching range (see Table 3). But a polymeric structure with other bridging bidentate fluorosulfate groups seems also to be present. Consistent with earlier findings for $\text{SbF}_4(\text{SO}_3\text{F})$ [4], a number of isomers are possible and their presence may contribute to the broadness of some of the bands.

Finally, for both ClO_2^+ compounds only monodentate fluorosulfate groups are found as would be expected. The proliferation of some of the bands, in particular in the SO_3F stretching range, may suggest different isomers, again. The SO_3F stretches are found at slightly lower frequencies than for $\text{SbF}_3(\text{SO}_3\text{F})_2$ and in similar positions as for $[\text{Sn}(\text{SO}_3\text{F})_6]^{2-}$. The cation fundamentals agree well with published fundamentals [21] and formulation as $\text{ClO}_2^+[\text{SbF}_n(\text{SO}_3\text{F})_{6-n}]^-$, with $n=3$ or 4 , appears to be justified.

CONCLUSION

The presence of fluorosulfate bridges in all antimony(V)fluoride-fluorosulfates is evident from the vibrational spectra. This results in viscous, polymeric materials in the cases of $\text{SbF}_4(\text{SO}_3\text{F})$ and $\text{SbF}_3(\text{SO}_3\text{F})_2$. As in the case of tin(IV)fluorosulfate derivatives [27], [28] non-statistical ligand redistribution is observed and these scrambling reactions could involve fluorosulfate bridges initially.

As expected, both $\text{SbF}_4(\text{SO}_3\text{F})$ and $\text{SbF}_3(\text{SO}_3\text{F})_2$ act as SO_3F^- ion acceptors. The resulting ligand complexes may well be mixtures of different structural isomers hence their reluctance to crystallize.

$\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ may be regarded as a 1:1 complex between $\text{SbF}_4(\text{SO}_3\text{F})$ as O-donor and SbF_5 as acceptor. This view would either imply a coordinatively unsaturated antimony atom on the donor molecule or the more likely hexa-coordinated antimony atom that could result from a cyclic or polymeric structure via additional fluorine bridging. Even though the unusual volatility of $\text{Sb}_2\text{F}_9(\text{SO}_3\text{F})$ is more consistent with a cyclic than with a polymeric structure, no other direct experimental evidence besides that already discussed could be obtained to help resolve the situation.

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