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FLUORIDE-FLUOROSULFATES OF ARSENIC (V) AND ARSENIC (III)

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SUMMARY

The synthesis of $AsF_3(SO_3F)_2$ by the reaction $AsF_3 + S_2O_6F_2 \longrightarrow AsF_3(SO_3F)_2$ is described. Various alternate routes leading to similar arsenic (V) fluoride-fluorosulfates are discussed. All materials are clear, viscous, strongly associated liquids of the general formula $AsF_n(SO_3F)_{5-n}$, with n ranging from about 2 to 4. The presence of fluorosulfate bridges is ascertained by IR and Raman spectra.

The spectroscopic investigation is also extended to arsenic (III) fluoride-fluorosulfates.

INTRODUCTION

Whereas binary fluorosulfates of arsenic (III) or -(V) are hitherto unknown, a number of mixed fluoride-fluorosulfates of arsenic have been mentioned in the literature. An As (III) derivative of the composition $2AsF_3 \cdot 3SO_3$ is first reported by Engelbrecht et al. in 1951 (1), with structural conclusions based on ^{19}F nmr spectra reported subsequently (2) (3). No neutral As (V) derivative seems to have been isolated, but an intermediate formulated as $AsF_2(SO_3F)_3$ is reportedly (4) formed in the reaction of As_2O_5 with HSO_3F, a reaction ultimately leading to $S_2O_5F_2$ and $As_2O_3F_4$. A conductometric study in fluorosulfuric acid (5) on the AsF_3-SO_3 mixtures postulates besides $AsF_2(SO_3F)_3$ also $AsF_4(SO_3F)$, both acting as acids in HSO_3F (5), and an anion of the type $[AsF_5(SO_3F)]^-$. Subsequently the synthesis and Raman spectrum of a compound of the composition $C\ell O_2[AsF_5(SO_3F)]$ is reported (6), and further evidence for $[AsF_5(SO_3F)]^-$ ion is found in a recent low temperature ^{19}F nmr study (7).

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The present study is aimed at the synthesis and characterisation of $AsF_3(SO_3F)_2$. Its possible existence is suggested by the recently reported oxidation of antimony (III) fluoride by an excess of bis(fluorosulfuryl)peroxide (8) according to:

$$SbF_3 + S_2O_6F_2 \xrightarrow[25^\circ C]{240\,h} SbF_3(SO_3F)_2,$$

where antimony trifluoride-bis(fluorosulfate) is obtained as a clear, viscous liquid.

RESULTS AND DISCUSSION

Synthesis

The oxidation of AsF_3 proceeds indeed in a similar fashion leading to AsF_3(S but two important differences to the SbF_3reaction are noted: a) the oxidation of AsF_3 by $S_2O_6F_2$ takes place immediately and exothermically at room temperature and it becomes advisable to allow the reaction mixture to warm up slowly overnight from -78°C to room temperature in order to moderate the reaction b) A product of the correct composition is best obtained, when stochiometric amounts of reactants are used, or if $S_2O_6F_2$ is in a slight excess. As for SbF_3(S (8), it is found difficult to remove all $S_2O_6F_2$ in vacuo with the sample at room temperature, while heating results in SO_3 and $S_2O_5F_2$ elimination and partial decomposition of the sample. On the other hand an excess of AsF_3 is found to undergo a fluoride-fluorosulfate redistribution, resulting in clear viscous material with substantial amounts of As (III). Again such ligand redistribution had been observed in the antimony (V) system as well (8).

The resulting $AsF_3(SO_3F)_2$ is a clear viscous liquid, virtually non-volatile in vacuo at room temperature and of limited thermal stability. All samples prepared showed very small amounts of As (III) present, about 1-3% of the total arsenic contents, in spite of all efforts to achieve complete oxidation to As (V).

Like $SbF_3(SO_3F)_2$ (8) the arsenic analogue does not crystallize but solidifies on cooling to a glassy mass. Attempts to obtain crystalline, anionic derivatives by reaction with either NaF or $CsSO_3F$ in equimolar amounts according to

$$NaF + AsF_3(SO_3F)_2 \longrightarrow Na[AsF_4(SO_3F)_2]$$

or

$$CsSO_3F + AsF_3(SO_3F)_2 \longrightarrow Cs[AsF_3(SO_3F)_3]$$

resulted only in an increase in viscosity and in spectral changes in the Raman spectrum (to be discussed later) but no solid materials were obtained. It appears that the structure breaking effect of the addition of NaF or $CsSO_3F$ to the polymeric $AsF_3(SO_3F)_2$ is completely offset by electrostatic interaction between the ions formed. It is worthy of note that the addition of NaF to $AsF_3(SO_3F)$ does not result in gas evolution as long as an excess of NaF is avoided. When $2AsF_3.3SO_3$ is reacted with NaF, AsF_3 is reportedly (1) formed and separated from the mixture by distillation.

A number of alternate routes to fluoride-fluorosulfates of As (V) were attempted: The addition of SO_3 to AsF_5, the ligand redistribution reaction of AsF_5 and $AsF_3(SO_3F)_2$, the oxidation, and in some cases ligand substitution of $AsC\ell_3$, As_2O_3, elemental arsenic or the previously mentioned compound $2AsF_3.3SO_3$ (1) by bis(fluorosulfuryl)peroxide, all yield fluoride-fluorosulfates of arsenic, with both As (V) and some As (III) present in the materials produced by oxidation. All these materials are clear, colourless viscous liquids of the type $AsF_n(SO_3F)_{5-n}$ but n is rather variable, reflecting no well defined stoichiometry. Hence the oxidation of AsF_3 by $S_2O_6F_2$ remains as the only straightforward route to a well defined material of the composition $AsF_3(SO_3F)_2$.

The Characterisation of $AsF_3(SO_3F)_2$

$AsF_3(SO_3F)_2$ shows temperature dependant electrical conductance. Listed are the measured specific conductance values in $ohm^{-1}cm^{-1} \times 10^{-4}$ with the temperature in °C in parenthesis: 0.565 (25), 0.876 (30), 1.26 (35) and 1.84 (40). When dissolved in HSO_3F, $AsF_3(SO_3F)_2$ behaves like a moderately strong acid with conductivity values higher than for SbF_5 but below those reported for $AsF_2(SO_3F)_3$ (5)

The ^{19}F nmr spectrum at room temperature consists of two signals, a sharp line at -45.6 ppm indicative of fluorine bonded to sulfur in fluorosulfates (9) and a very broad signal at +37.2 ppm, with peak area integration of ~1.9 to 3.0 reflecting approximately the stoichiometry $AsF_3(SO_3F)_2$.

The observed Raman and IR bands for $AsF_3(SO_3F)_2$, the Raman bands for $2AsF_3.3SO_3$ (1) and the previously reported IR and Raman bands for $SbF_3(SO_3F)_2$ (8) are listed in the Table. While a complete assignment is impossible, due to the complexity of the system, a few general points may be made. The similarity of the vibrational spectra of $AsF_3(SO_3F)_2$ and $SbF_3(SO_3F)_2$ is rather striking. Different band positions are only noted in the region of 650 to 740 cm^{-1}, where ν Sb-F and ν As-F occur with the latter expected and found at slightly higher wave numbers. It must be concluded that a similar polymeric structure is present for both compounds, with intermolecular association occurring via bidentate bridging fluorosulfate groups. Bands at approximately 1425 and 1070 cm^{-1} (ν SO) and at 890 cm^{-1} (ν SF) are assignable to such a conformation (8). The third

TABLE: The Vibrational Spectra of $AsF_3(SO_3F)_2$, $2AsF_3 \cdot 3SO_3$ and $SbF_3(SO_3F)_2$

$AsF_3(SO_3F)_2$		$2AsF_3 \cdot 3SO_3$		$SbF_3(SO_3F)_2$ a)	
Raman $\Delta\nu$[cm^{-1}] Int.	IR ν[cm^{-1}] Int.	Raman $\Delta\nu$[cm^{-1}] Int.	IR ν[cm^{-1}] Int.	Raman $\Delta\nu$[cm^{-1}] Int.	IR $\Delta\nu$[cm^{-1}] I
1460 w,sh	1450 s,b			1461 w	1440 s,b
1426 m (p)	1420 vs	1420 m,b	1425 s,b	1424 m	1408 vs
1395 m,sh	1392 vs,sh	1398 m,sh			
1237 s (p)	1225 vs	1218 ms,sh	1230 s,sh	1242 s	1225 s
		1213 vs			1125 ms
	1135 ms,sh		1222 vs		
1069 m (p)	1060 s,sh			1078 m	1060 s,sh
1030 w,sh	1030 s			1030 w	1000 s
	965 s	960 vw,sh	975 s,b		
891 ms (p)	885 s,sh		900 ms,sh	885 s	870 vs,b
863 m	855 s	858 ms	850 s	861 s,sh	
800 vw					
750 s (p)	742 vs,b	725 s	725 s	700 s	
670 vs (p)	~670 m,sh	664 vs	650 ms,b	650 vs	
652 vs,sh	642 ms	655 vs,sh		635 s,sh	
~610 vw		611 vw,sh	610 w,sh		
590 mw (p)	590 ms	587 m	589 s	585 w	
550 m (dp)	552 ms	553 m	550 ms	556 w	
	495 mw	512 vw	495 vw,sh		
455 ms (p)		460 ms,	445 ms	442 s	
		448 m,sh			
410 w,sh		408 mw,sh		413 w,sh	
377 w		353 vw			
293 m,sh		318 ms,sh		299 m,sh	
		298 s			
268 m,b		251 m,sh		266 m,sh	
245 m,sh		247 m		251 s	
		220 w			
		178 w			
125 m					

a) see ref. 8
Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder, (p) = polarized and (dp) = depolarized

S-O stretch, indicative of a symmetry of Cs or a lower point group, for the fluorosulfate group is only found in the IR spectra of both $SbF_3(SO_3F)_2$ (8) and $AsF_3(SO_3F)_2$ at ~1140 cm^{-1}.

A model for a symmetrically bridging bidentate fluorosulfate is found in $(CH_3)_2Sn(SO_3F)_2$, where an X-ray diffraction study is reported (10). Additional complexity is introduced by the presence of covalent monodentate $-OSO_2F$ groups in $AsF_3(SO_3F)_2$, with characteristic bands at about 1460, 1240 and ~1000 cm^{-1} (ν SO), with ν SF at approximately 860 cm^{-1}. The resulting 6-coordination for As as well as for Sb (8) is not unexpected.

Obviously coincidences of bands must occur in the range below 600 cm^{-1}, where SO_3F deformation modes are expected and no clear distinction between mono- and bidentate groups is possible here. The addition of CsF or $CsSO_3F$ to $AsF_3(SO_3F)_2$. produces a much simpler Raman spectrum with stretching modes observed at approximately 1420, 1230 and 1000 cm^{-1} (ν SO), at 830 cm^{-1} (ν SF) and at 700 and 660 cm^{-1} (ν AsF). These bands in analogy to observations for the antimony compounds of the type $C\ell O_2[SbF_n(SO_3F)_{6-n}]$ (8) and to findings for $C\ell O_2[AsF_5(SO_3F)]$ (6) are attributed to covalently bonded, monodentate fluorosulfate groups in an anionic environment. It appears then, that $AsF_3(SO_3F)_2$ may act as a fluorosulfate or fluoride ion acceptor, but unfortunately no crystalline materials are obtained from the viscous liquids.

As for $SbF_3(SO_3F)_2$ (8), we were unable to obtain low temperature infrared spectra of $AsF_3(SO_3F)_2$ by using the condensation technique (8). The spectra obtained are attributed to $S_2O_5F_2$ and to $(SO_3)_3$ as the main components, presumably formed by decomposition of $AsF_3(SO_3F)_2$ in vacuo.

The vibrational spectrum of $2AsF_3 \cdot 3SO_3$, reported here for the first time, clearly identifies the compound as a fluorosulfate as had been suggested (2). The band positions at 1400 to 1420, 1215 and 960 to 980 cm^{-1} are typical for a SO_3 stretching vibrations of a monodentate fluorosulfate group with ν SF at ~855 cm^{-1}. It appears however that the positions of the SO stretching modes are shifted to lower wave numbers, when compared to the positions found for $AsF_3(SO_3F)_2$ This may be attributed to weak intermolecular association via dominantly monodentate fluorosulfate groups. The fluorosulfate bridges, judging by the vibrational spectra, are not symmetrical, as e.g. found for $(CH_3)_2Sn(SO_3F)_2$ (10) and postulated for $SbF_3(SO_3F)_2$ and $AsF_3(SO_3F)_2$, but rather an unsymmetrical or 'anisobidentate'. It can be argued, that As (V) is a stronger acceptor than As (III) with the ligand in both cases F or SO_3F.

It is interesting to note, that the presence of intermolecular association for AsF_3 had been deduced from state dependant frequency shifts for AsF_3 (11)

(12). These shifts, most notable when comparing vibrational spectra of $AsF_{3(g)}$ and $AsF_{3\ (\ell)}$, are rather small, suggesting weak association. To suggest fluorosulfate rather than fluoride bridging is in keeping with earlier observations by us on comparable antimony (8) and tin (IV) fluoride-fluorosulfates (13), but the positions of ν AsF between 725 and 650 cm^{-1} in the liquid samples are compar to ν AsF in AsF_3 (ℓ) (11) (12) and additional weak fluorine bridging cannot be ruled out.

An alternative explanation for the observed frequency lowering would be the presence of fluorosulfate arsenic (III) anions, however the specific electrical conductivity of distilled $2AsF_3.3SO_3$ is with 1.67×10^{-5} $ohm^{-1}cm^{-1}$ at 25°C even lower than found for $AsF_3(SO_3F)_2$. It appears, while some ionic dissociation may occur for both compounds and may contribute to the rapid fluorosulfate and fluoride exchange, the ions formed should only be present in small concentrations and should not affect the vibrational spectra appreciably.

While $2AsF_3 \cdot 3SO_3$ is the only well defined compound in the AsF_3-SO_3 system, obtained by distillation, AsF_3 and SO_3 may be reacted over a wide range of molar ratios. We have studied the Raman spectra of those mixtures ranging in AsF_3/SO_3 from 5.0 to 0.35. While the bands attributed to SO_3F-stretching modes remain relatively unchanged, both positional and intensity changes are noted in the AsF stretching range. The band at 725 cm^{-1} will decrease in intensity on SO_3 addition relative to a broad band at 670 cm^{-1}, but will not disappear even at a SO_3 to AsF_3 ratio 3:1. On the other hand an excess of AsF_3 results in a very intense broad band at 702 cm^{-1} with a weaker, even broader band at 640 cm^{-1}. Both these bands are of almost equal intensity for $2AsF_3 \cdot 3SO_3$. While a detailed assignment, due to the rather broad band is not possible, the presence of complex equilibria involving all species of the type $AsF_n(SO_3F)_{3-n}$ with n ranging from 0 to 3 is not only consistent with our Raman spectra but also with the results of an earlier ^{19}F nmr study by Gillespie and Oubridge (3), on similar mixtures .

CONCLUSION

Both As (V) and As (III) form a number of strongly associated fluoride-fluorosulfates of the general compositions $AsF_n(SO_3F)_{5-n}$ where n may range from ~2 to 4; and $AsF_n(SO_3F)_{3-n}$ with n ranging from 0 to 3. While there appears to be a difference in the extent of intermolecular association as reflected in the Raman spectra, and also a difference in the thermal stability with As (V) compounds of decomposing more readily, both series are similar in appearance (viscous colorless and moisture sensitive liquids). Ligand rearrangement within a series or between both series is possible and reflected in the ^{19}F nmr spectra consisting of single lines only.

While in the As (V) system $AsF_3(SO_3F)_2$ has a well defined stoichiometry, the earlier reported compound of the composition $2AsF_3 \cdot 3SO_3$ is readily isolated. This compound may be regarded as a 1:1 complex of $AsF(SO_3F)_2$ and $AsF_2(SO_3F)$, consistent with the ^{19}F nmr -3 line spectrum (2) (3) and the vibrational spectrum, and it appears that this complex has a greater thermal stability than either $AsF(SO_3F)_2$ or $AsF_2(SO_3F)$, perhaps by virtue of a dimeric cyclic structure with anisobidentate fluorosulfate bridges.

EXPERIMENTAL

All reagents used are obtained from commercial sources. AsF_5 and AsF_3 (both from Ozark-Mahoring) are distilled before use. Stabilized SO_3 (Allied Chemicals) is used to prepare oleums, from which SO_3 can be distilled off when required. Bis(fluorosulfuryl)peroxide is synthesized in a flow reaction between F_2 and SO_3 using a catalytic AgF_2 reactor (14), and the original method (1) is used to obtain $2AsF_3 \cdot 3SO_3$. IR spectra are obtained on a Perkin Elmer 457 grating spectrophotometer with the samples as thin films between BaF_2 and $AgC\ell$ windows. Our low temperature IR equipment (15) and our apparatus to measure electrical conductances (16) have been described earlier.

Raman spectra are obtained using a Spex Ramalog 5 spectrometer, equipped with an argon ion laser with the line at 514.5 nm used for excitation. ^{19}F nmr spectra are obtained on a XL-100 spectrometer (Varian Associates). ^{19}F chemical shifts are reported with respect to $CFC\ell_3$ as external standard, with shifts to lower fields considered positive.

Hygroscopic materials are stored and handled in a 'Dri-Lab' Model No. HE-43-2 (Vacuum Atmosphere Corp.) filled with dry N_2 and equipped with a 'Dri-Train' Model No. HE-Q3B. Volatile reagents are manipulated in a Pyrex vacuum line fitted with Kontes Teflon stem stopcocks. All reactions are carried out in Pyrex reactioı vials of about 50 ml capacity fitted with a Kontes Teflon stem stopcock. Calibrated storage vials are used to make additions of stochiometric quantities of AsF_3 or $S_2O_6F_2$.

To prepare $AsF_3(SO_3F)_2$, 1.5026 g (11.39 mmol) of AsF_3 are combined with 2.50 g (12.63 mmol) of $S_2O_6F_2$ into a pyrex reaction vial by distillation in vacuo. The reaction mixture is then allowed to warm from -78°C to room temperature overnight, and subsequently heated to 60°C for several hours to complete the reaction.

Removal of all volatiles in vacuo, with some slight loss of reaction product, yields a viscous, colorless material of the composition $AsF_3(SO_3F)_2$. Both ^{19}F nmr and Raman spectra provide good evidence for the absence of any $S_2O_6F_2$ in the sample. The rather intense Raman band at 800 cm^{-1} (ν 0-0) is a very good check. Elemental analysis is performed by Microanalytical Laboratories (formerly A. Bernhardt), Elbach, West Germany.

Calculated for $AsF_3(SO_3F)$: As, 22.70; S, 19.43 and F, 28.78. Found : A, 22.33; S,

The As (III) content in samples is determined volumetrically by oxidation with an aqueous solution of $KBrO_3$ (17), while As (V) contents was determined by an iodometric titration in an acidic aqueous solution (17).

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