Notes

stereochemical rigidity of CF₃SF₃ at ambient temperature. The fact that J_{F_eSC} is slightly larger than J_{F_aSC} may be a reflection of the fact that the equatorial plane of a trigonal bipyramid features more sulfur 3s character than the axes. The differences in the axial and equatorial F–S–C couplings may be useful for the stereochemical assay of fluorosulfuranes.

Registry No. CF₃SSCF₃, 372-64-5; F₂, 7782-41-4; CF₃SF₃, 374-10-7.

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Preparation and Raman Spectra of Tribromosulfur(IV) Hexafluoroarsenate(V) and Hexafluoroantimonate(V), (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻

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Sulfur tetrachloride is stable only in the solid phase (mp –30 °C), binary sulfur bromides are less stable than their corresponding chlorides, and at the present there is no evidence for sulfur tetrabromide.[1-3] However, OSBr₂,[2,4] has been well characterized and a number of salts with cations of the type R₂SBr⁺ are known.[5] The cations SF₃⁺[6] and SCl₃⁺[7] with weakly basic anions such as AsF₆⁻ and SbF₆⁻ are well established. We now report the preparation and characterization by Raman spectroscopy of (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻.

Experimental Section

Apparatus. Except where stated, apparatus and materials are the same as those described in ref 8. Raman spectra were obtained with exciting wavelengths 5145 Å (green) and 6471 Å (red).

Reagents. Reagent grade sulfur (B. D. H. Chemicals) was evacuated to dryness. Bromine (Matheson Gas Co.) was stored over tetraphosphorus decaoxide (P₄O₁₀) in a glass vessel until ready for use. Sulfur dioxide (Matheson Gas Co.) was stored over calcium hydride in a glass vessel. Antimony pentafluoride (Ozark-Mahoning) was twice distilled before use.

Spectra. All solid Raman samples were loaded into dry melting point capillaries in a drybox and flame sealed immediately on removing from the drybox. Solution samples were prepared in 5-mm o.d. glass tubing using either sulfur dioxide or arsenic trifluoride as the solvent and then sealed. Solution Raman spectra were obtained at room temperature with the 6471-Å (red) line and at a temperature just low enough to prevent bubbling with the 5145-Å (green) line, using an evacuated condenser type low temperature cell.

Reactions. All reactions were carried out in a one-piece glass apparatus, consisting of two arms linked by a tube incorporating a sintered-glass filter disk. One arm was fitted with a Teflon "Rotaflo" or a Whitey 1KS4 valve. Typically sulfur was loaded into one arm of the apparatus, which was then evacuated, and the solvent (SO₂ or AsF₃), bromine, and then AsF₅ or SbF₅ were condensed in separately at –196 °C (with thermal cycling to room temperature between each addition).

Preparation of (SBr₃)⁺(AsF₆)⁻. In a typical reaction, S₈ (0.703 mmol) and Br₂ (26.65 mmol) were allowed to react with AsF₅ (10.65 mmol) in sulfur dioxide (5.95 g) solution. The product was a saturated purple solution with a copious yellow precipitate. The soluble product was isolated by repeated washings through the frit. The volatiles were identified as a mixture of SO₂, some AsF₅ containing traces of AsF₃ from infrared spectra. A light yellow insoluble solid (0.02 g) and a bright yellow soluble solid (2.405 g or 5.22 mmol assuming (SBr₃)⁺(AsF₆)⁻) were isolated following removal of the volatiles with brief pumping. A chemical analysis of the product was not obtained since it gave off bromine on standing in a sealed glass sample tube in an atmosphere of dry nitrogen.

Raman spectra were obtained from the yellow soluble product in the solid state and in both arsenic trifluoride and sulfur dioxide solutions using both exciting wavelengths.

Preparation of (SBr₃)⁺(SbF₆)⁻. In a typical reaction S₈ (0.86 mmol) and Br₂ (11.06 mmol) were allowed to react with SbF₅ (11.63 mmol) in sulfur dioxide (5.76 g) solution. The product was a saturated purple solution with a copious yellow precipitate. The soluble product was separated by repeated washings through the frit. The volatiles were removed leaving 0.828 g of an insoluble white solid and 3.302 g or 6.50 mmol (assuming (SBr₃)⁺(SbF₆)⁻) of soluble yellow crystalline solid.

The yellow solid gave elemental analysis consistent with the formulation (SBr₃)⁺(SbF₆)⁻. Anal. Calcd for (SBr₃)⁺(SbF₆)⁻: S, 6.30; Br, 47.23; Sb, 23.99; F, 22.46. Found: S, 6.13; Br, 46.80; Sb, 24.16; F, 22.77.

Raman spectra were obtained for both solids. The spectrum of the white insoluble solid is similar to that obtained when SbF₃·SbF₅ (A)[9] was reacted with excess PF₃ in arsenic trifluoride solution for 2 days.[10] Raman spectra were also obtained from the yellow soluble product in the solid state and in arsenic trifluoride and sulfur dioxide solutions using both exciting wavelengths.

In another experiment S₈ (2.52 mmol) and Br₂ (30.6 mmol) were allowed to react with SbF₅ (34.46 mmol) in SO₂ (7.57 g) solution yielding 19.91 mmol of soluble (SBr₃)⁺(SbF₆)⁻ and 2.27 g of a reduced antimony fluoride. The products were characterized by their Raman spectra.

Results and Discussion

Preparation of (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻. Sulfur reacts with excess bromine and a slight excess of AsF₅ in arsenic trifluoride to give a bright yellow solid (SBr₃)⁺(AsF₆)⁻ according to the equation

$$\tfrac{1}{8}S_8 + 3Br_2 + 3AsF_5 \rightarrow 2(SBr_3)^+(AsF_6)^- + AsF_3$$
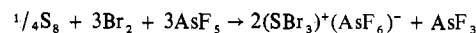
The salt was identified from Raman spectra in the solid state, in arsenic trifluoride solution, and also in sulfur dioxide solution. The solid gave some bromine on standing, in a sealed glass sample tube under an atmosphere of dry nitrogen. The (SBr₃)⁺(SbF₆)⁻ cation salt made in a similar fashion was stable and good analyses were obtained. The nature of the insoluble reduced antimony fluoride product given in the S₈/Br₂/SbF₅ reaction is presently under investigation. Elemental analysis and Raman spectroscopy were used to characterize the (SBr₃)⁺(SbF₆)⁻.

We note that the analogous reactions with iodine and sulfur lead to S₇I⁺ containing salts[11] and related species; whereas SeBr₃⁺ and TeBr₃⁺ can be made in a similar manner.[12]

Raman Spectra. Raman spectra of (SBr₃)⁺(AsF₆)⁻ and (SBr₃)⁺(SbF₆)⁻ in the solid state and in solution are given in Figure 1, and Table I lists the frequencies and assignments by comparison with the corresponding anions[6,13] and PBr₃.[14] Solvent peaks[15,16] and a weak peak at 319 cm⁻¹ observed in the solution spectra and attributed to bromine[17] are not included in Table I.

Table I. Assignments of Raman Spectra[a] of $(SBr_3)^+(AsF_6)^-$ and $(SBr_3)^+(SbF_6)^-$

| (SBr₃)⁺(AsF₆)⁻ | | (SBr₃)⁺(SbF₆)⁻ | | PBr₃[c] | (SF₃)⁺(As- | | | |
Solid	AsF₃ soln	Solid	SO₂ soln	gas	F₆)⁻[d] solid	CsAsF₆[e]	LiSbF₆[e]	Assignment
	1309[b]							$3\nu(X)$
	872.5		867.5					$2\nu(X)$
685 sh		675 sh			711			$\nu_3{}^f(MF_6)^-$
674	676	642	643.5		686	685	668	$\nu_1(MF_6)$
573					583			$\left.\right\}\nu_2(MF_6)^-$
562	560	562.5	560		562	576	558	
	436 p		434 p					$\nu(X)$
429	421 dp	421	417 dp		922			$\left.\right\}\nu_3{}^g(SBr_3)^+$
414		410.5						
391		277	280[h]		395	372	294	$\left.\right\}\nu_5(MF_6)^-$ or $\begin{matrix}\nu_4(MF_6)^-\\\nu_5(MF_6)^-\end{matrix}$
367.5					360			
375	378.5 p	379	376.5 p	381	942			$\nu_1(SBr_3)^+$
175	174 p	175	175.5 p	161	534			$\nu_2(SBr_3)^+$
128	124 dp	127.5	124 dp	116	403			$\nu_4(SBr_3)^+$

[a] Solvent peaks and Br_2 stretch omitted. These are, however, marked in Figure 1. [b] Frequencies (in cm^{-1}) accurate to ca. ±2 cm^{-1}. [c] See ref 14. [d] See ref 6. [e] See ref 13. [f] Tentative assignment assuming O_h and C_{3v} symmetry for $(MF_6)^-$ (M = As or Sb) and $(SBr_3)^+$. [g] Corresponds to $\nu_3(PBr_3)$ or $\nu_3(SF_3)^+$ in appropriate column. [h] Could be an impurity.
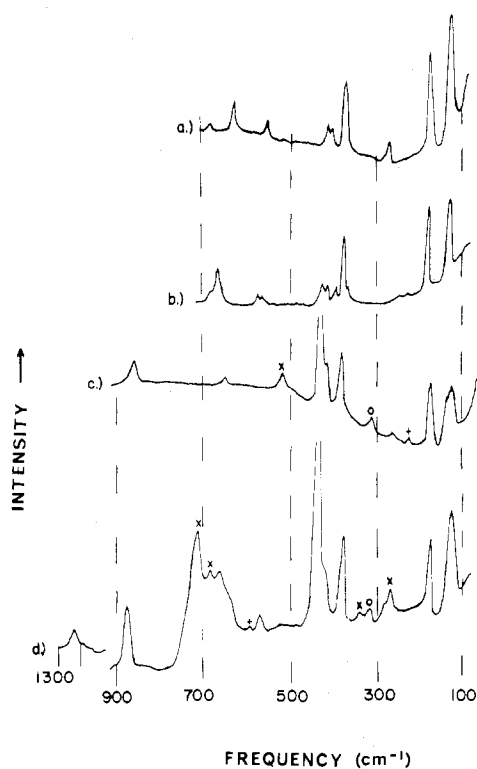

Figure 1. Raman spectra of the $(SBr_3)^+$ cation: (a) solid $(SBr_3)^+(SbF_6)^-$ (6471-Å line); (b) solid $(SBr_3)^+(AsF_6)^-$ (5145-Å line); (c) $(SBr_3)^+(SbF_6)^-$ in SO_2 solution (5145-Å line); (d) $(SBr_3)^+(AsF_6)^-$ in AsF_3 solution (5145-Å line). Slit width 8 cm^{-1} except in (b), which was at 4 cm^{-1}. × indicates solvent peaks. O indicates the Br_2 peak. + indicates impurities.

The spectra support an essentially ionic formulation for the two salts. The peaks attributed to SBr_3^+ are similar in solution and in the solid state, except ν_3 (SBr_3^+), the antisymmetric stretching mode, (e), is split in the solid state. The four Raman active bands (two polarized and two depolarized) expected for SBr_3^+ are observed, and as expected,[6,18] they are at higher frequencies than the corresponding bands for the isoelectronic molecule PBr_3 except for ν_1 (SBr_3^+) which is not significantly different from ν_1 (PBr_3).

The peaks designated $\nu(X)$ in Table I were observed in solution spectra and varied in intensity from sample to sample. The most intense was observed for $(SBr_3)^+(AsF_6)^-$ made in situ in arsenic trifluoride and $(SBr_3)^+(SbF_6)^-$ in dilute sulfur dioxide or arsenic trifluoride solution with the 5145-Å (green) exciting wavelength. The intensity decreased, and the peak

broadened in the order $436 > 872 > 1309$ cm^{-1} and therefore is likely a resonance Raman spectrum. It was least intense for $(SBr_3)^+(SbF_6)^-$ in sulfur dioxide solution using the 6471-Å (red) exciting frequency and no overtones were observed. We are presently attempting to determine the nature of this species.

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Polarized Crystal Electronic Spectrum of Bis(ethylammonium) Tetrachlorocuprate(II) and an Application of the Angular Overlap Model to the Bonding in Chlorocuprate Complexes

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The chlorocuprates exhibit a wide variety of stereochemistries and it is probably for this reason that they have often