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Synthesis and Crystal and Molecular Structure of Cesium Hexakis(fluorosulfato)antimonate(V) and Its Role in the HSO_3F–$Sb(SO_3F)_5$ Conjugate Superacid System

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In this communication we report the synthesis and molecular structure determination of cesium hexakis(fluorosulfato)antimonate(V), $Cs[Sb(SO_3F)_6]$. The highly symmetrical $[Sb(SO_3F)_6]^-$ ion is so far the only known binary fluorosulfate derivative of pentavalent antimony. Its existence and reasonable thermal stability suggest its use as a very weakly nucleophilic anion in synthesis and its existence as a conjugate base ion in a novel superacid system.

Superacids[1,2] are employed both in industrial applications and in academic research as reaction media to generate a wide range of highly reactive organic[2] and inorganic[1,3] cations. In solution they stabilize these otherwise short-lived species by virtue of their high acidities or acidium ion concentrations and the low nucleophilicity of the conjugate base ions. Among simple Brønsted superacids, fluorosulfuric acid, HSO_3F,[2,4] and anhydrous HF[5] have emerged as the strongest proton donors, reflected in their identical Hammet function values of $-H_o = 15.1$. Of the conjugate superacids, the equivalent to the very strong HF–SbF_5[6] system ($-H_o > 21$) HSO_3F-$Sb(SO_3F)_5$ is unknown. In the hypothetical proton-transfer equilibrium

$$2HSO_3F + Sb(SO_3F)_5(solv) \rightleftharpoons H_2SO_3F^+ + [Sb(SO_3F)_6]^-(solv) \quad (1)$$

both the Lewis acid $Sb(SO_3F)_5$ and the conjugate base ion have been considered unobtainable so far.

Extensive early work on the system HSO_3F–nSO_3–SbF_5[4,7] has shown that acidity increases with increasing *n*, but *n* is limited to maximal 3. This implies that the strongest Lewis acid and the species with highest SO_3F^- content generated *in situ* is $SbF_2(SO_3F)_3$, with the conjugate base ion $[SbF_2(SO_3F)_4]^-$, as evident from the reported ^{19}F-NMR spectra.[7] Among isolable compounds, $SbF_3(SO_3F)_2$ and $[SbF_3(SO_3F)_3]^-$ [8] have the highest fluorosulfate contents. It is generally accepted[7,8] that binary antimony(V) fluorosulfate species will be thermally unstable and convert with SO_3 elimination to antimony(V) fluoride–fluorosulfate derivatives, in HSO_3F solution as well as in isolable compounds. The facile synthesis of cesium hexakis(fluorosulfato)antimonate(V), $Cs[Sb(SO_3F)_6]$, and its thermal stability (dec pt 149 °C) reported here question these earlier assumptions.[7,8]

The synthesis of $Cs[Sb(SO_3F)_6]$ is accomplished by the reaction of an equimolar mixture of $CsSO_3F$ and antimony with an excess of bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, in HSO_3F according to

$$2CsSO_3F + 2Sb + 5S_2O_6F_2 \xrightarrow[HSO_3F]{25\ °C,\ 12\ h} 2Cs[Sb(SO_3F)_6] \quad (2)$$

The salt is isolated in quantitative yield and in the form of crystalline cubes by slow evaporation of the volatiles. The method of synthesis is identical to the one used for two sets of Cs salts of the type $Cs_n[M(SO_3F)_m]$, $n = 1$ or 2, M = Nb or Ta, and $m = 6$ or 7;[9] however, none of these salts are sufficiently crystalline for structural analysis. It is hoped that $Sb(SO_3F)_5$ can be made in an analogous, equally simple manner according to the general route

$$2M + 5S_2O_6F_2 \xrightarrow{HSO_3F} 2M(SO_3F)_5(solv) \quad (3)$$

$$M = Nb,^9\ Ta,^9\ Sb$$

and initial attempts look promising. Either the *in situ* generation of $Sb(SO_3F)_5$ or its isolation would permit a solution study by ^{19}F-NMR and electrical-conductivity measurements as reported for $Ta(SO_3F)_5$ and $Nb(SO_3F)_5$.[9]

Neither the existence nor the thermal stability of the $[Sb(SO_3F)_6]^-$ ion should have been surprising. Over 20 years ago we reported the synthesis of the isoelectronic anion $[Sn(SO_3F)_6]^{2-}$ stabilized by K^+, Cs^+, NO^+, and ClO_2^+.[10] The Cs^+ salt is thermally stable to 250 °C, which is possibly due to its higher lattice energy. In the meantime, a number of salts (in addition to those already mentioned) of the type $Cs_2[M(SO_3F)_6]$ has been obtained by us,[11] but none of these have been structurally characterized. The vibrational spectra of the anions show strong similarities to the IR and Raman spectra of $Cs[Sb(SO_3F)_6]$ that are reported as supplementary material. The binary fluorosulfates of the type $M(SO_3F)_4$[11] are, where obtainable, insufficiently soluble in HSO_3F to permit solution studies.[11] An exception is $Pt(SO_3F)_4$, which in HSO_3F solution gives rise to a strong, diprotic conjugate superacid system.[12]

These structurally related precedents and the ease of synthesis following previously established routes[9−12] noted here raise the question as to why the synthesis of $Cs[Sb(SO_3F)_6]$ was not attempted previously. Besides the assumed thermal instability of binary antimony(V) fluorosulfate species[7,8] already discussed, there were practical problems arising from previous reports of antimony fluorosulfates with antimony in oxidation states lower than +5. The interaction of Sb with HSO_3F is reported to produce a white solid of the composition $Sb(SO_3F)$.[13] Oxidation of Sb by $S_2O_6F_2$ is claimed by the same authors to lead to white,

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seemingly polymeric $Sb(SO_3F)_3$.[13] Copious amounts of a white solid obtained by us in initial attempts to oxidize Sb in HSO_3F as solvent seemed to interfere in the early stages of the oxidation process of Sb to Sb(V) fluorosulfates.

Immediately preceding this study, we were able to resolve this issue with the following observations: (i) $Sb(SO_3F)$ does not appear to exist. The white solid described[13] is identified by us as a mixture of S_8 and Sb(III) fluoride–fluorosulfates. (ii) We have been able to separate this mixture, have subsequently isolated the three polymeric compounds $[SbF_2(SO_3F)]_x$, $[SbF(SO_3F)_2]_x$, and $[Sb(SO_3F)_3]_x$, and have determined their molecular structures.[14] Formation of these byproducts and of S_8 is avoided by allowing a solution of $S_2O_6F_2$ in HSO_3F to react with antimony. (iii) The molecular structure of $[Sb(SO_3F)_3]_x$,[14] which is a likely intermediate in the oxidation of Sb by $S_2O_6F_2$, shows that the SO_3F groups function as asymmetric tridentate bridges. The primary coordination polyhedron, trigonal pyramidal SbO_3, is linked by intermediate (d(Sb–O) $\sim 2.6 \pm 0.5$ Å) and secondary[15] bridge bonds (d(Sb–O) $\sim 2.9 \pm 1$ Å) to give a polymer that is nevertheless reasonably soluble in HSO_3F, to permit further oxidation at 25 °C.

The molecular structure of $Cs[Sb(SO_3F)_6]$[16] is less complex than that of $[Sb(SO_3F)_3]_x$.[14] The Cs^+ ion is 12-coordinate, which is not uncommon. All O atoms not bonded to Sb are coordinated to Cs^+ *via* two long contacts of 3.241(3) and 3.413(4) Å, respectively. An ORTEP drawing of the anion is shown in Figure 1, and selected bond parameters are given in the figure caption. The anion has S_6 symmetry. The six monodentate fluorosulfate groups are all symmetry related and efficiently packed.

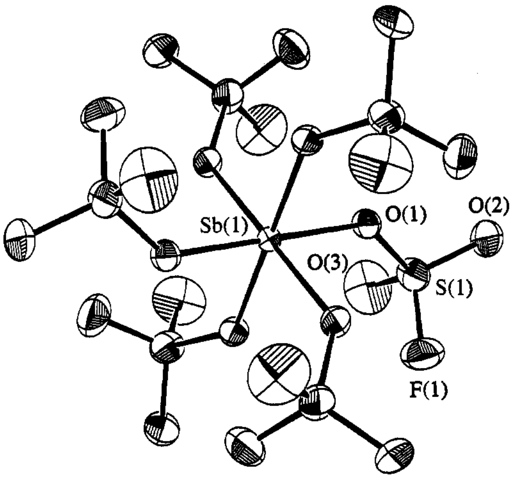

Figure 1. Perspective view of the $[Sb(SO_3F)_6]^-$ anion, showing 33% probability thermal ellipsoids. Pertinent geometrical parameters: Sb(1)–O(1) = 1.955(2) Å, S(1)–F(1) = 1.486(3) Å, S(1)–O(1) = 1.516(2) Å, S(1)–O(2) = 1.396(3) Å, S(1)–O(3) = 1.409(4) Å, *trans* O–Sb–O = 180°, *cis* O–Sb–O = 92.15(9) or 87.85(9)°.

The internal bond lengths are at the lower ends of their respective ranges. Not surprisingly, the Sb–O distance of 1.955(2) Å is about 0.1–0.15 Å shorter than that in $[Sb(SO_3F)_3]_x$ but slightly longer than those in the recently reported anion $[Sb(OTeF_5)_6]^-$ (1.87(1)–1.92(1) Å),[17] which has Sb in an octahedral coordination environment. Very strong, tight bonding is observed within the fluorosulfate groups of the anion. Appreciable multiple-bond character is suggested for both the sulfur–oxygen and the sulfur–fluorine bonds. The S–F distance of 1.486(3) Å is unprecedented among neutral sulfur-fluorine derivatives and even shorter than those in SO_2F_2[18] (1.530(2) Å). The S–O bond distances of SO_2F_2 (1.397(2) Å) are comparable to the distances of 1.409(4) and 1.396(3) Å found for $[Sb(SO_3F)_6]^-$, even though both O atoms are weakly coordinated to cesium. They are the shortest sulfur–oxygen bonds observed in neutral or anionic sulfur–oxygen compounds. The electron causing the net ionic charge of −1 appears to contribute to enhanced S–O and S–F π-bonding within the SO_3F groups. Only for the cation OSF_3^+ are shorter S–O (1.35(1) Å) and S–F (1.44(1) Å) bond distances reported.[20]

On account of its very strong intramolecular S–O and S–F π-bonds and its symmetrical, nearly spherical shape, we suggest that $[Sb(SO_3F)_6]^-$ is a very weakly nucleophilic and poorly coordinating anion,[21] which should have an interesting chemistry. In proton-transfer equilibria in the conjugate superacid systems (see eq 1), additional stabilization of the anion in solution is expected from hydrogen bonding involving HSO_3F and the peripheral O and F atoms of the anion. It is anticipated that the conjugate superacid system $HSO_3F\text{-}Sb(SO_3F)_5$ will be more acidic than the two strongest systems presently known in HSO_3F: $HSO_3F\text{-}SbF_2(SO_3F)_3$[7] and $HSO_3F\text{-}Ta(SO_3F)_5$.[9]

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Supplementary Material Available: Text giving full experimental details of the structure analysis, tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, torsion angles, and intermolecular contacts, additional structural diagrams, text giving experimental details of the synthesis of $Cs[Sb(SO_3F)_6]$ and its characterization by ^{19}F NMR and vibrational spectroscopy, and two figures showing the FT-IR and FT-Raman spectra of $Cs[Sb(SO_3F)_6]$ (19 pages). Ordering information is given on any current masthead page.

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(16) Crystal data: $Cs[Sb(SO_3F)_6]$, colorless cube, 0.35 × 0.35 × 0.35 mm, trigonal, $a = b = 12.0317(7)$ Å, $c = 12.062(2)$ Å, $Z = 3$, space group $R\bar{3}$. Data were collected to high resolution (Rigaku AFC6S diffractometer, graphite-monochromated Mo radiation, $\lambda = 0.710\,69$ Å, $2\theta_{max} = 100°$, $T = 294$ K, $\omega{-}2\theta$ scan, scan range $(1.42 + 0.35 \tan\theta)°$ in ω, data collected $\pm h, +k, +l$ $(h + k > 0)$) in order to provide accurate structural information. Total of 3763 reflections; 3502 unique ($R_{merge} = 0.042$). The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.039$ and $R_w = 0.037$ for 1485 reflections with $I \geq 3\sigma(F^2)$. Data were corrected for absorption ($\mu = 39.15$ cm^{-1}, empirical, based on three azimuthal scans, relative transmission factors 0.74-1.00) and secondary extinction (Zachariasen isotropic type I, coefficient $1.93(3) \times 10^{-6}$). All calculations were performed using: *teXsan*: *Crystal Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1992.

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