

Synthesis and Characterisation of Alkali Metal and Thallium Polyfluoroantimonates, $\text{ASb}_n\text{F}_{5n+1}$ ($n = 2, 3$)

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Reactions of AF ($A = \text{K, Rb, Tl}$) with excess liquid SbF_5 in anhydrous HF (or SO_2) at room temperature give products having the composition $\text{ASb}_2\text{F}_{11}$. The reaction between CsF and a small excess of SbF_5 in anhydrous HF (0.76 mmol of CsF + 4.19 mmol of SbF_5 in 4 mL of aHF) yields $\text{CsSb}_2\text{F}_{11}$, whereas the reaction with a large excess of SbF_5 (0.79 mmol of CsF + 23 mmol of SbF_5 in 10 mL of aHF) yields the salt $\text{CsSb}_3\text{F}_{16}$. Efforts to prepare similar compounds using the monofluorides of Li and Na led only to the already known ASbF_6 compounds. Reactions of AF ($A = \text{Na, K, Rb, Cs}$) with liquid SbF_5 at 85 °C in the absence of solvents yield the products NaSbF_6 , $\text{ASb}_2\text{F}_{11}$ ($A = \text{K, Rb}$) and $\text{CsSb}_3\text{F}_{16}$, respectively. A single-crystal X-ray diffraction study on the salt $\text{KSb}_2\text{F}_{11}$ [orthorhombic, at 250 K, $Pbca$, with $a = 1141.65(8)$, $b = 1279.96(9)$, $c = 3948.5(3)$ pm, $V = 5.7699(7)$ nm³ and $Z = 24$] has shown it to be isostructural with $\text{AgSb}_2\text{F}_{11}$. $\text{CsSb}_2\text{F}_{11}$, on

the other hand, is monoclinic at 250 K [$P2_1/n$, with $a = 774.10(14)$, $b = 1425.41(17)$ pm, $c = 951.30(15)$ pm, $\beta = 113.226(6)^\circ$, $V = 0.9646(3)$ nm³ and $Z = 4$]. $\text{RbSb}_2\text{F}_{11}$ and $\text{TlSb}_2\text{F}_{11}$ belong to yet a third structural type. Crystals of $\text{CsSb}_3\text{F}_{16}$ are orthorhombic at 200 K [$Pca2_1$, with $a = 2207(3)$, $b = 772.6(11)$, $c = 1605(3)$ pm, $V = 2.737(8)$ nm³ and $Z = 8$]. The vibrational spectra of $\text{Sb}_2\text{F}_{11}^-$ salts are consistent with the above crystallographic assignments, showing that $\text{Sb}_2\text{F}_{11}^-$ anions deviate strongly from D_{4h} symmetry in having no symmetry at all (point group C_1). The vibrational spectra of $\text{CsSb}_3\text{F}_{16}$ confirm the presence of $\text{Sb}_3\text{F}_{16}^-$ anions, which adopt a *cis*-fluorine-bridged geometry consistent with the crystal structure.

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Introduction

Compounds of the type ASbF_6 ($A =$ monovalent cation) are well known and established.^[1] In contrast to ASbF_6 salts, reports concerning the formation of $\text{ASb}_2\text{F}_{11}$ and $\text{ASb}_3\text{F}_{16}$ compounds are scarce. $\text{CsSb}_2\text{F}_{11}$ has been prepared from CsF and SbF_5 in SO_2 solution and investigated by ¹⁹F NMR spectroscopy.^[2] Its (incomplete) vibrational spectrum was also reported.^[3,4] The salt $\text{AgSb}_2\text{F}_{11}$ has been studied and its synthesis, crystal-structure determination and vibrational spectra have been published recently.^[5] In the case of the $\text{Sb}_3\text{F}_{16}^-$ salts of alkali metal fluorides only the caesium compound has been reported to exist.^[6]

The tendency of alkali metal fluorides to form stable, complex fluoro or oxofluoro anion salts with covalent metal fluorides or oxofluorides decreases from Cs^+ to Li^+ .^[7] However, the cut-off limit for salt formation in the view of the size (volume) of the A^+ cation appears to vary somewhat from one system to another.^[7] The aim of this work was a

systematic investigation of reactions between monofluorides of alkali metals (including thallium) and antimony pentafluoride [with and without the presence of solvents such as SO_2 and anhydrous HF (aHF)] to find out how the size of the cations influences the composition of the final products. In other words, which compounds with general formula $\text{ASb}_n\text{F}_{5n+1}$ ($n = 1, 2, 3$) should exist for a specific cation.

Results and Discussion

Syntheses

Reactions of AF ($A = \text{K, Rb, Tl}$) with an excess of SbF_5 in anhydrous HF or SO_2 at room temperature yield products having the composition $\text{ASb}_2\text{F}_{11}$ [Equation (1)].



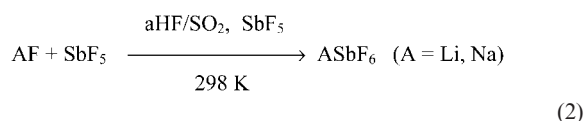
The reaction between CsF and a small excess of SbF_5 in anhydrous HF (0.76 mmol of CsF + 4.19 mmol of SbF_5 in 4 mL of aHF) yields $\text{CsSb}_2\text{F}_{11}$ whilst, in contrast, the reaction with a large excess of SbF_5 (0.79 mmol of CsF + 23 mmol of SbF_5 in 10 mL of aHF) yields $\text{CsSb}_3\text{F}_{16}$.

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The course of the reaction between KF and SbF₅ (the starting molar ratio KF/SbF₅ being 1:2) in SO₂ is in agreement with previous findings for Cs salts.^[2] KSb₂F₁₁ is similar to CsSb₂F₁₁ in being relatively soluble in SO₂.

Efforts to prepare similar compounds starting from the monofluorides of Li and Na led only to already known ASbF₆^[1] compounds [Equation (2)].



The reaction between NaF and SbF₅ in SO₂ yields only NaSbF₆ which, like the corresponding CsSbF₆, is rather insoluble^[2] in SO₂ (see Experimental Section).

The previously reported vibrational spectra of products obtained by heating equimolar mixtures of SbF₅ and the corresponding alkali metal fluoride under F₂ at 280 °C exhibited no evidence at all for the presence of polyfluoroantimonates.^[8] Our results, however, show that when the reaction mixture of a sample of alkali fluoride (AF, A = Na, K, Rb, Cs) and an excess of liquid SbF₅ is heated at 85 °C NaSbF₆, ASb₂F₁₁ (A = K, Rb) and CsSb₃F₁₆ are isolated as the final products.

Crystal Structures

Single crystals of ASb₂F₁₁ (A = K, Cs) were prepared by slow evaporation (over two months) of the volatiles from saturated solutions of the corresponding ASb₂F₁₁ salts in aHF acidified with a large excess of SbF₅. A similar procedure using NaF yields only single crystals of NaSbF₆. These results suggest that the products of the reaction between AF (A = Li, Na) and an excess of SbF₅ [Equation (2)] are not the result of kinetic control.

The crystal structures of ASb₂F₁₁ compounds can be divided into three groups. The first group corresponds to ASb₂F₁₁ compounds having similarly sized cations (A = K⁺, H₃O⁺, Ag⁺). Crystals of KSb₂F₁₁ are orthorhombic at 250 K (see Experimental Section) and are isostructural to AgSb₂F₁₁^[5] and also structurally related to H₃OSb₂F₁₁.^[9] The complex structure of KSb₂F₁₁ reveals three crystallographically nonequivalent Sb₂F₁₁[−] anions that are highly distorted from ideal D_{4h} symmetry (Figure 1). Distortions of Sb₂F₁₁ units are usually expressed in terms of the bridge angle α (bending of F₅Sb–F–SbF₅ about bridging fluorine) and the torsion angle ψ (torsion of two planar SbF_{4,eq} groups from eclipsed to staggered conformation). In KSb₂F₁₁ three different bridge (149.2°, 150.4° and 146.1°) and three corresponding dihedral (20.2°, 21.2° and 32.6°) angles for three crystallographically nonequivalent Sb₂F₁₁ units were identified. The bridging and dihedral angles found in KSb₂F₁₁ are close to the values found for the anion in the isostructural AgSb₂F₁₁ (α = 148.3°, 151.8° and 143.5°; ψ = 22.5°, 18.0° and 37.1°).^[5] The Sb–F_t bonds are, as expected, shorter (181.2–186.4 pm) and show a wider

spread than the Sb–F_b bonds (202.4–204.1 pm; Table 1). The F_{eq}–Sb–F_{ax} Bond angles are slightly greater than 90°, while the F_{eq}–Sb–F_b are more acute by 3–7° (Table 2).

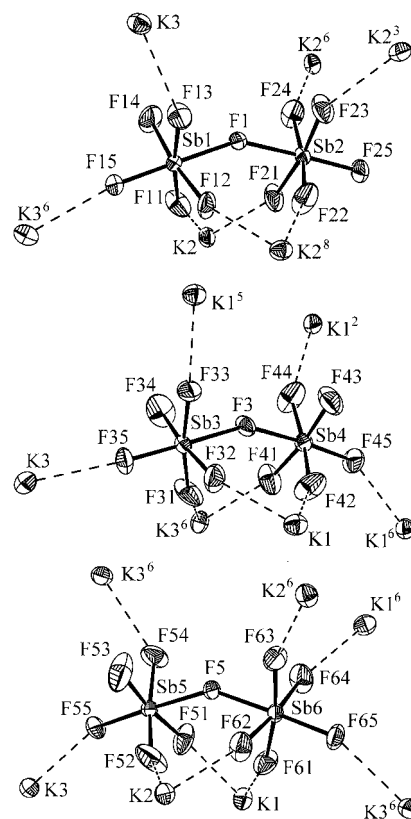


Figure 1. Three crystallographically nonequivalent Sb₂F₁₁ units and their interactions with K⁺ cations in the crystal structure of KSb₂F₁₁ (thermal ellipsoids are drawn at 40% probability level). Superscripted numbers: symmetry operations used for generation of equivalent atoms: ¹ x, y, z ; ² $x + 1/2, -y + 1/2, -z$; ³ $-x, y + 1/2, -z + 1/2$; ⁴ $-x + 1/2, -y, z + 1/2$; ⁵ $-x, -y, -z$; ⁶ $-x + 1/2, y + 1/2, z$; ⁷ $x, -y + 1/2, z + 1/2$; ⁸ $x + 1/2, y, -z + 1/2$.

There are also three crystallographically nonequivalent K⁺ cations in the crystal structure of KSb₂F₁₁. The K–F bond lengths span a wide range of values (260.1–289.8 pm). By comparison, in KSbF₆ eight fluorine atoms, which form a slightly distorted dodecahedron, surround the K atom at distances of between 261.8 and 320.4 pm.^[10] The coordination number of the potassium atoms in KSb₂F₁₁ can be written as 8 for K1 and K3 and 9 for K2.

CsSb₂F₁₁ crystallises in the monoclinic space group *P*2₁/*n* (no. 14) with the unit-cell parameters and the crystal and structure refinement data given in the Experimental Section. Selected bond lengths and angles are summarised in Tables 3 and 4, respectively. The packing diagram is depicted in Figure 2.

The structure of the Sb₂F₁₁[−] anion and its interactions with Cs⁺ cations, along with the numbering scheme adopted, are given in Figure 3. The structure of CsSb₂F₁₁ is ionic and consists of discrete Sb₂F₁₁[−] anions and

Table 1. Selected bond lengths [pm] in $\text{KSb}_2\text{F}_{11}$.

Sb1–F1	204.1(5)	Sb2–F1	202.4(5)	Sb3–F3	203.4(5)	Sb4–F3	202.8(5)
Sb1–F11	183.4(5)	Sb2–F21	184.4(6)	Sb3–F31	183.7(6)	Sb4–F41	182.9(7)
Sb1–F12	183.1(5)	Sb2–F22	184.1(6)	Sb3–F32	183.2(6)	Sb4–F42	184.0(6)
Sb1–F13	184.8(6)	Sb2–F23	185.3(6)	Sb3–F33	183.1(6)	Sb4–F43	182.7(7)
Sb1–F14	183.2(7)	Sb2–F24	184.7(6)	Sb3–F34	182.7(7)	Sb4–F44	184.0(6)
Sb1–F15	185.3(5)	Sb2–F25	183.8(5)	Sb3–F35	183.8(5)	Sb4–F45	185.1(6)
Sb5–F5	203.8(5)	Sb5–F53	181.6(7)	Sb6–F5	202.4(5)	Sb6–F63	184.4(6)
Sb5–F51	181.2(6)	Sb5–F54	182.4(6)	Sb6–F61	184.3(6)	Sb6–F64	182.9(6)
Sb5–F52	182.4(7)	Sb5–F55	184.9(5)	Sb6–F62	184.9(6)	Sb6–F65	186.4(5)
K1–F32	273.0(6)	K2–F11	269.2(6)	K3–F13	275.4(7)		
K1–F33	271.6(7)	K2–F12	266.7(6)	K3–F15	280.8(5)		
K1–F42	271.0(7)	K2–F21	274.7(6)	K3–F31	275.2(7)		
K1–F44	276.8(8)	K2–F22	267.9(7)	K3–F35	289.6(6)		
K1–F45	277.3(7)	K2–F23	291.9(6)	K3–F41	277.4(7)		
K1–F51	269.4(6)	K2–F24	278.3(6)	K3–F54	284.0(8)		
K1–F61	282.0(7)	K2–F52	288.4(8)	K3–F55	279.1(5)		
K1–F64	283.3(6)	K2–F62	260.1(6)	K3–F65	279.7(6)		
		K2–F63	289.8(6)				

Table 2. Selected bond angles [°] in $\text{KSb}_2\text{F}_{11}$.

F11–Sb1–F1	85.5(2)	F21–Sb2–F1	84.6(3)	F31–Sb3–F3	85.6(3)
F12–Sb1–F1	85.7(2)	F22–Sb2–F1	85.7(3)	F32–Sb3–F3	86.0(3)
F13–Sb1–F1	85.0(3)	F23–Sb2–F1	85.6(3)	F33–Sb3–F3	82.7(3)
F14–Sb1–F1	86.5(3)	F24–Sb2–F1	86.1(2)	F34–Sb3–F3	86.4(3)
F11–Sb1–F15	94.3(3)	F21–Sb2–F25	94.6(3)	F31–Sb3–F35	95.0(3)
F12–Sb1–F15	93.3(2)	F22–Sb2–F25	93.0(3)	F32–Sb3–F35	94.4(3)
F13–Sb1–F15	95.3(3)	F23–Sb2–F25	95.2(3)	F33–Sb3–F35	96.7(3)
F14–Sb1–F15	94.5(3)	F24–Sb2–F25	95.1(3)	F34–Sb3–F35	93.2(3)
		Sb1–F1–Sb2	149.2(3)		
F41–Sb4–F3	85.4(3)	F51–Sb5–F5	85.7(3)	F61–Sb6–F5	84.9(2)
F42–Sb4–F3	85.2(3)	F52–Sb5–F5	84.4(3)	F62–Sb6–F5	86.3(2)
F43–Sb4–F3	85.1(3)	F53–Sb5–F5	86.7(3)	F63–Sb6–F5	86.1(2)
F44–Sb4–F3	86.6(3)	F54–Sb5–F5	86.2(3)	F64–Sb6–F5	87.1(3)
F41–Sb4–F45	91.2(3)	F51–Sb5–F55	92.3(3)	F61–Sb6–F65	93.4(3)
F42–Sb4–F45	92.6(3)	F52–Sb5–F55	94.3(3)	F62–Sb6–F65	92.9(3)
F43–Sb4–F45	98.3(3)	F53–Sb5–F55	95.3(3)	F63–Sb6–F65	95.6(3)
F44–Sb4–F45	95.7(3)	F54–Sb5–F55	95.2(3)	F64–Sb6–F65	93.7(3)
Sb3–F3–Sb4	150.4(3)			Sb5–F5–Sb6	146.1(3)

Table 3. Selected bond lengths [pm] in $\text{CsSb}_2\text{F}_{11}$.

Sb1–F1	203.9(3)	Sb2–F1	203.9(3)	Cs1–F11	307.0(4)	Cs1–F21	315.8(4)
Sb1–F11	183.8(4)	Sb2–F21	185.8(4)	Cs1–F12	349.8(4)	Cs1–F21	355.2(4)
Sb1–F12	185.6(3)	Sb2–F22	184.9(4)	Cs1–F12	352.9(4)	Cs1–F22	339.6(4)
Sb1–F13	185.3(3)	Sb2–F23	184.6(4)	Cs1–F13	309.9(4)	Cs1–F23	345.1(4)
Sb1–F14	185.4(4)	Sb2–F24	185.4(4)	Cs1–F14	305.9(4)	Cs2–F24	323.0(4)
Sb1–F15	183.7(4)	Sb2–F25	184.9(3)	Cs1–F15	316.5(4)	Cs2–F25	310.1(3)

Table 4. Selected bond angles [°] in $\text{CsSb}_2\text{F}_{11}$.

F11–Sb1–F1	86.0(2)	F21–Sb2–F1	85.7(1)
F12–Sb1–F1	83.5(2)	F22–Sb2–F1	85.2(1)
F13–Sb1–F1	85.3(2)	F23–Sb2–F1	85.4(2)
F14–Sb1–F1	84.8(2)	F24–Sb2–F1	85.2(2)
F11–Sb1–F15	94.9(2)	F21–Sb2–F25	95.5(2)
F12–Sb1–F15	96.5(2)	F22–Sb2–F25	93.8(2)
F13–Sb1–F15	93.8(2)	F23–Sb2–F25	93.4(2)
F14–Sb1–F15	95.2(2)	F24–Sb2–F25	95.9(2)
		Sb1–F1–Sb2	146.0(2)

Cs^+ cations in a simple packing arrangement. As in the case of $\text{KSb}_2\text{F}_{11}$, the $\text{Sb}_2\text{F}_{11}^-$ anion in $\text{CsSb}_2\text{F}_{11}$ is highly distorted from ideal D_{4h} symmetry ($\alpha = 146.0^\circ$, $\psi = 33.9^\circ$; Figure 3). The Sb–F bond lengths (Table 3) and F–Sb–F bond angles (Table 4) in $\text{CsSb}_2\text{F}_{11}$ are comparable to those found for $\text{KSb}_2\text{F}_{11}$ (Tables 1 and 2).

Taking the coordination number as the number of nearest neighbour atoms^[9] then Cs is surrounded by 12 fluorine atoms at distances of between 307.0(4) and 355.2(4) pm. In

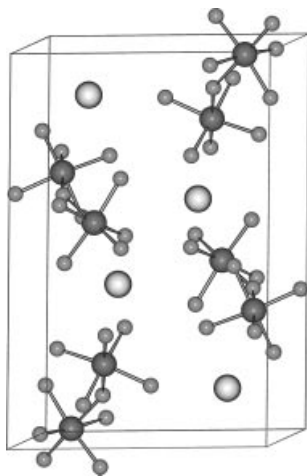
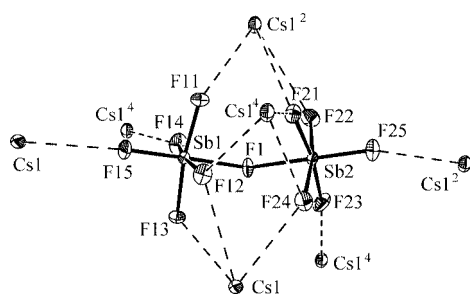
Figure 2. Packing diagram of CsSb₂F₁₁.

Figure 3. Sb₂F₁₁ unit and interacting Cs⁺ cations in CsSb₂F₁₁ (thermal ellipsoids are drawn at 40% probability level). Super-scripted numbers: symmetry operations used for generation of equivalent atoms: ¹ *x*, *y*, *z*; ² $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; ³ $-x$, $-y$, $-z$; ⁴ $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$.

CsSbF₆ twelve fluorine atoms again surround the Cs atom with six close contacts (311.6 pm) and six long contacts (338.3) pm.^[11]

The X-ray powder-diffraction photographs indicate that RbSb₂F₁₁ and TlSb₂F₁₁ are isostructural and different from KSb₂F₁₁ or CsSb₂F₁₁. Their isostructurality is consistent with the close similarity shown by the ionic radii of Rb and Tl (Shannon: Rb = 175 pm, Tl = 173 pm for C.N. = 8;^[12] Goldschmidt: Rb = Tl = 149 nm^[13]) or their volumes [*V*(Rb⁺) = *V*(Tl⁺) = 0.014 nm³].^[14]

Table 5. Selected bond lengths [pm] in CsSb₃F₁₆.

Sb1–F11	186(6)	Sb3–F34	185(4)	Sb6–F61	186(2)	Cs1–F45	309(11)
Sb1–F12	186(7)	Sb3–F35	185(2)	Sb6–F62	187(4)	Cs1–F52	320.3(12)
Sb1–F13	187(9)	Sb3–F36	207(2)	Sb6–F63	182(2)	Cs1–F63	337(2)
Sb1–F14	185(6)	Sb4–F41	183(8)	Sb6–F64	183(2)	Cs2–F12	312(2)
Sb1–F15	183.7(18)	Sb4–F42	184(6)	Sb6–F65	185.0(12)	Cs2–F15	304(12)
Sb1–F16	208.9(15)	Sb4–F43	183(11)	Sb6–F66	209.5(9)	Cs2–F22	326.8(11)
Sb2–F16	199(11)	Sb4–F44	184(8)			Cs2–F34	344(3)
Sb2–F21	186(12)	Sb4–F45	186(2)	Cs1–F11	344(5)	Cs2–F35	307(3)
Sb2–F22	183.8(10)	Sb4–F46	208(2)	Cs1–F13	351(5)	Cs2–F41	341(8)
Sb2–F23	184(8)	Sb5–F46	196(8)	Cs1–F14	330(13)	Cs2–F42	350(20)
Sb2–F24	180(9)	Sb5–F51	182(10)	Cs1–F21	310(20)	Cs2–F43	366(3)
Sb2–F36	199.6(17)	Sb5–F52	184.6(11)	Cs1–F31	337(8)	Cs2–F51	320(20)
Sb3–F31	185(6)	Sb5–F53	181(4)	Cs1–F32	329(5)	Cs2–F61	353(5)
Sb3–F32	184(3)	Sb5–F46	196(8)	Cs1–F33	322(4)	Cs2–F62	329(7)
Sb3–F33	185(3)	Sb5–F66	196.4(9)	Cs1–F44	311(3)	Cs2–F64	328.6(18)

Examples of crystal structures of Sb₃F₁₆[−] salts are rare. The Sb₃F₁₆[−] anion adopts a *cis*-fluorine-bridged geometry in the crystal structures of [OsO₃F][Sb₃F₁₆],^[15] [OCNCO][Sb₃F₁₆],^[16] [XeN(SO₂F)₂][Sb₃F₁₆]^[17] and [Cl₃][Sb₃F₁₆],^[18] whereas a *trans*-fluorine-bridged Sb₃F₁₆[−] anion has been reported in the crystal structure of [Br₂][Sb₃F₁₆].^[19] CsSb₃F₁₆ crystallises in the orthorhombic space group *Pca*2₁ (no. 29). The unit-cell parameters and the crystal and structure refinement data are given in the Experimental Section. Selected bond lengths and angles are summarised in Tables 5 and 6, respectively. The packing diagram is depicted in Figure 4.

Table 6. Selected bond angles [°] in CsSb₃F₁₆.

F11–Sb1–F16	85(6)	F22–Sb2–F36	171.2(6)
F12–Sb1–F16	84(2)	F23–Sb2–F36	86(4)
F13–Sb1–F16	83(6)	F24–Sb2–F36	91(2)
F14–Sb1–F16	85(3)	F36–Sb3–F35	179.4(6)
F15–Sb1–F16	177.1(5)	F36–Sb3–F31	88(7)
F16–Sb2–F24	173.4(6)	F36–Sb3–F32	84(2)
F16–Sb2–F21	85(5)	F36–Sb3–F33	83(7)
F16–Sb2–F22	89.1(22)	F36–Sb3–F34	84(2)
F16–Sb2–F23	84(6)		
F16–Sb2–F36	82(2)	Sb1–F16–Sb2	151.9(7)
F21–Sb2–F36	86(3)	Sb2–F36–Sb3	152.6(11)
F41–Sb4–F46	86(6)	F52–Sb5–F66	172.8(4)
F42–Sb4–F46	84(4)	F53–Sb5–F66	86(4)
F43–Sb4–F46	83(5)	F54–Sb5–F66	89.0(14)
F44–Sb4–F46	87(3)	F66–Sb6–F65	177.8(6)
F45–Sb4–F46	178.8(6)	F66–Sb6–F61	82.4(13)
F46–Sb4–F54	172.3(6)	F66–Sb6–F62	85(7)
F46–Sb5–F51	85(6)	F66–Sb6–F63	86.6(9)
F46–Sb5–F52	89.8(12)	F66–Sb6–F64	84(7)
F46–Sb5–F53	84(7)		
F46–Sb5–F66	83.3(11)	Sb4–F46–Sb5	156.3(8)
F51–Sb5–F66	83(4)	Sb5–F66–Sb6	155.5(5)

The crystal structure of CsSb₃F₁₆ reveals two crystallographically nonequivalent Sb₃F₁₆[−] anions adopting a *cis*-fluorine-bridged geometry. The structure of the Sb₃F₁₆[−] anions and their interactions with Cs⁺ cations, along with the numbering scheme adopted, are given in Figure 5. The Sb–F_{*i*} bond lengths (Table 5) in CsSb₃F₁₆ are comparable to those found for KSb₂F₁₁ and CsSb₂F₁₁ (Tables 1 and 3).

The corresponding pairs of Sb–F_{*b*} bond lengths in the F₅Sb–F_{*b*}–SbF₅ units of KSb₂F₁₁ [Sb1–F1 = 204.1(5), F1–

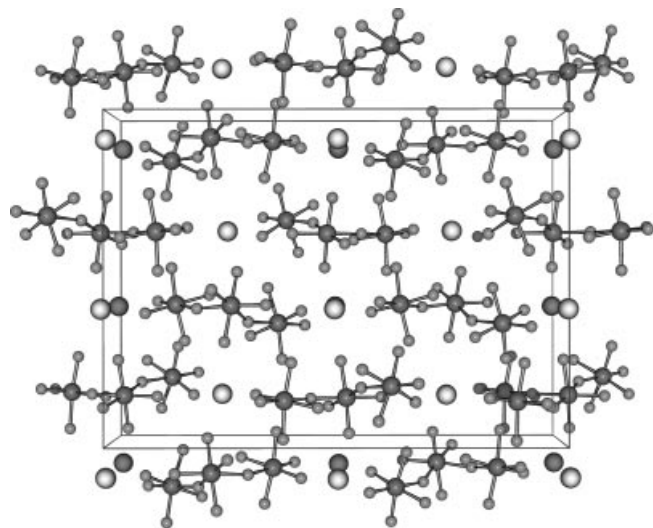
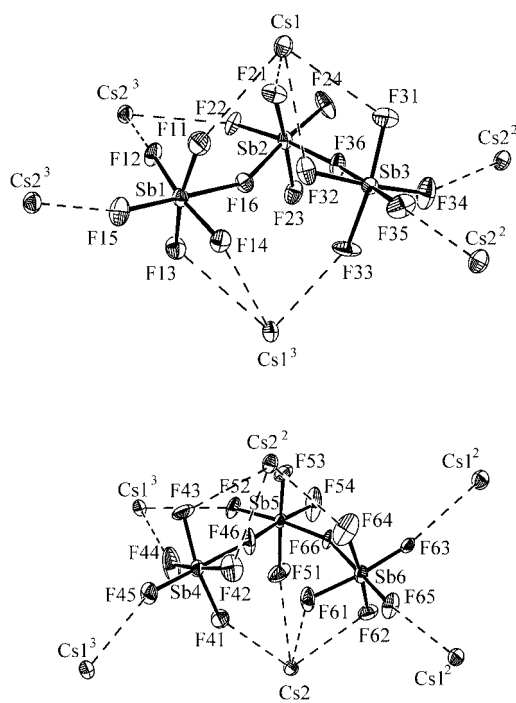
Figure 4. Packing diagram for $\text{CsSb}_3\text{F}_{16}$.

Figure 5. Two crystallographically nonequivalent Sb_3F_{16} units and their interactions with Cs^+ cations in the crystal structure of $\text{CsSb}_3\text{F}_{16}$ (thermal ellipsoids are drawn at 40% probability level). Superscripted numbers: symmetry operations used for generation of equivalent atoms: ¹ x, y, z ; ² $-x, -y, z + 1/2$; ³ $-x + 1/2, y, z + 1/2$; ⁴ $x + 1/2, -y, z$.

$\text{Sb1} = 202.4(5)$; $\text{Sb3-F3} = 203.4(5)$; $\text{F3-Sb4} = 202.8(5)$; $\text{Sb5-F5} = 203.8(5)$, $\text{F5-Sb6} = 202.4(5)$ pm] and $\text{CsSb}_2\text{F}_{11}$ [$\text{Sb1-F1} = 203.9(3)$, $\text{F1-Sb2} = 203.9(3)$ pm] are much closer than the corresponding pairs of Sb-F_b bond lengths in the $\text{F}_5\text{Sb-F}_b\text{-SbF}_4\text{-F}_b\text{-SbF}_5$ units of $\text{CsSb}_3\text{F}_{16}$. The Sb-F_b bond lengths (Sb2-F16 , Sb2-F36 and Sb5-F46 , Sb5-F66) between F_b and the central Sb atom are much shorter [196(8)–199.6(17) pm] than the corresponding bond lengths between F_b and the terminal Sb atoms (F16-Sb1 , F36-Sb3

and F46-Sb4 , F66-Sb6), which are in the range 207(2)–209.5(9) pm.

There are also two crystallographically nonequivalent Cs^+ cations in the crystal structure of $\text{CsSb}_3\text{F}_{16}$. On a similar basis to the assignment of the coordination number made in the case of $\text{CsSb}_2\text{F}_{11}$, these cations are surrounded by 12 fluorine atoms at distances of between 304(12) and 366(5) pm.

Vibrational Spectra

The Raman and IR spectra of $\text{ASb}_2\text{F}_{11}$ ($A = \text{K, Rb, Cs, Tl}$) and $\text{CsSb}_3\text{F}_{16}$ are shown in Figures 6 and 7, respectively, with additional details given in Tables 7 and 8.

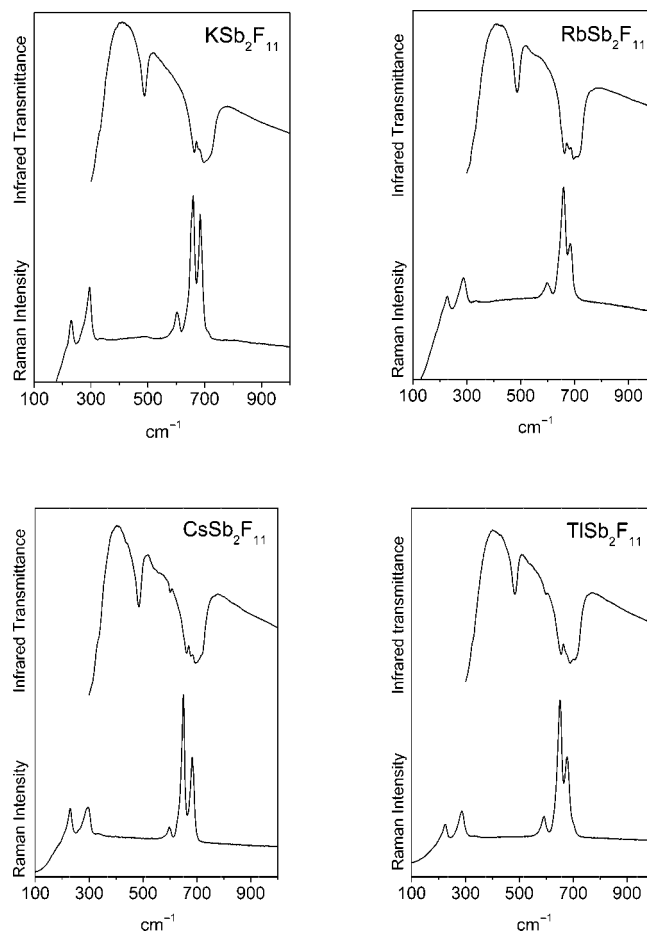
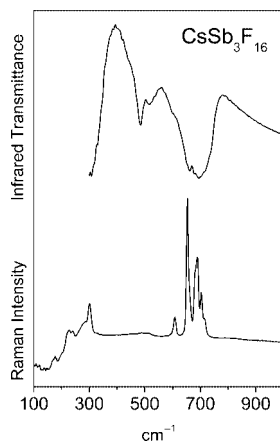


Figure 6. Infrared and Raman spectra of $\text{ASb}_2\text{F}_{11}$ ($A = \text{K, Rb, Cs, Tl}$).

The IR spectra (Figure 6, Table 7) were taken for powdered samples obtained from the synthesis [Equation (1)] and also for powdered samples obtained by grinding selected single crystals of $\text{ASb}_2\text{F}_{11}$ ($A = \text{K, Cs}$). They were found to be identical. Raman spectra taken for powdered samples obtained from the synthesis [Equation (1)] and Raman spectra taken for single crystals of $\text{ASb}_2\text{F}_{11}$ ($A = \text{K, Cs}$) were also identical. Small differences in the observed wavenumbers and relative intensities of some of the Raman and infrared bands of these salts arise as a consequence of

Figure 7. Infrared and Raman spectra of CsSb₃F₁₆.

the fact that some bands are broad, which makes the precise estimation of particular band positions difficult. A further factor contributing to these small differences are the crystal effects.

Sb₂F₁₁[−] anions deviate strongly from ideal *D*_{4h} symmetry and, in fact, possess no symmetry at all (point group *C*₁). A partial assignment of the spectra of the Sb₂F₁₁[−] anions was made on the basis of comparison with [M(CO)₄-(Sb₂F₁₁)₂] (M = Pd, Pt),^[20] which contain two crystallographically nonequivalent and highly distorted Sb₂F₁₁[−] anions (Table 7, Figure 6). The bands in the regions 592–698 cm^{−1} and 702–719 cm^{−1} are assigned to Sb–F_{eq} and Sb–F_{ax} stretches, respectively, meanwhile bands around 500 cm^{−1} are typical for Sb–F–Sb bridging. Bands below 300 cm^{−1} were assigned to bending deformations.

Table 8. Vibrational spectra of CsSb₃F₁₆.

IR ^[a]	Ra	Assignments ^[b]
738(sh)		v(SbF _l)
719(sh)	715(sh)	v(SbF _l)
706(s)	704(35)	v(SbF _l)
694(vs)	689(60)	v(SbF _l)
678(s)	680(sh)	v(SbF _l)
662(vs)	661(sh)	v(SbF _l)
650(sh)	653(100)	v(SbF _l)
601(mw)	607(20)	v(SbF _l)
568(w)		
539(mw)		
517(m)	517(1)	v(SbFSb)
486(ms)	489(1)	v(SbFSb)
456(sh)		v(SbFSb)
419(mw)		
	329(1)	δ(FSbF)
	300(20)	δ(FSbF)
	285(sh)	δ(FSbF)
	240(5)	δ(FSbF)
	228(7)	δ(FSbF)
	177(5)	lattice vibrations

[a] Intensities are given in parentheses; w = weak, mw = medium weak, m = medium, ms = medium strong, s = strong, vs. = very strong, sh = shoulder. [b] v = Stretching mode, δ = deformation mode.

The vibrational spectrum of CsSb₃F₁₆ is similar but not identical to that for CsSb₂F₁₁. The Sb₃F₁₆[−] anion in CsSb₃F₁₆ exhibits very complex Raman and infrared spectra (Figure 7, Table 8). Reported vibrational data for the Sb₃F₁₆[−] anion are scarce. [OsO₃F][Sb₃F₁₆],^[15] [ClCO][Sb₃F₁₆],^[22] [OCNCO][Sb₃F₁₆],^[16] [XeN(SO₂F)₂][Sb₃F₁₆],^[17] [ReF₆][Sb₃F₁₆]^[23] and [PF₄][Sb₃F₁₆]^[24] have

Table 7. Vibrational spectra of undecafluorodiantimonates of monovalent cations.

KSb ₂ F ₁₁		RbSb ₂ F ₁₁		CsSb ₂ F ₁₁		TlSb ₂ F ₁₁		Pd(CO) ₄ (Sb ₂ F ₁₁) ₂ ^[a]		Assignments ^[b]
IR ^[c]	Raman	IR	Raman	IR ^[d]	Raman ^[e]	IR	Raman	IR	Raman	
711(sh)	713(sh)	713(s)		719(sh)		707(s)	703(sh)	718(sh)	714(w)	v (SbF _{ax})
698(vs)		696(vs)		702(s)		689(vs)		708(vs)	709(sh)	v(SbF _{ax})
	684(85)		684(50)	693(vs)	688(sh)		678(60)	690 (vs)		v(SbF _{4eq})
					683(60)				686(m)	v(SbF _{4eq})
678(s)		681(s)		677(s)		674(sh)		675(s)	668(s)	v(SbF _{4eq})
664(vs)	660(100)	662(vs)	659(100)	662(vs)	650(100)	655(s)	651(100)	662(s)	656(s)	v(SbF _{4eq})
	654(sh)							648(sh)	649(s)	v(SbF _{4eq})
	603(20)		599(15)	601(m)	598(5)	599(w)	592(16)	604(vw)	598(w)	v(SbF _{4eq})
								596(w)	585(w)	v(SbF _{4eq})
488(ms)		558(sh)		556(vw)		536(vw)				
		487 (ms)		485(ms)		484(ms)		503(m)		v(SbFSb)
				436(sh)						v(SbFSb)
	339(5)		336(3)		336(3)		346(1)		349(2)	
	295(40)		288(25)		298(25)		288(20)	315(s)	305(m)	δ(SbF _{4eq})
					293(25)			305(s)		δ(SbF _{4eq})
	271(sh)								275(w)	δ(SbF _{4eq})
								267(vs)		δ(SbF _{4eq})
								250(sh)		δ(SbF _{4eq})
	231(15)		227(15)		230(10)		225(10)	228(sh)	230(m)	δ(SbF _{4eq})
								196(vw)	201(vw)	δ(SbF _{4eq})

[a] Ref.^[20] [b] v = stretching mode, δ = deformation mode. [c] Intensities are given in parentheses; vw = very weak, w = weak, m = medium, ms = medium strong, s = strong, vs. = very strong, sh = shoulder. [d] Literature data: broad band at 700 cm^{−1}, shoulder at 600 cm^{−1}, sharp and intense band at 480 cm^{−1} (ref.^[4]). [e] Literature data: 692/685(93), 654(100), 603/597(15), 521(1), 332(4), 300/291(39), 232(?) (ref.^[21]).

been characterised by Raman spectroscopy and $[\text{ClO}_2][\text{Sb}_3\text{F}_{16}]^{[25]}$ by IR spectroscopy. These data vary significantly as the nature of the cation changes. The bands attributed to the $\text{Sb}_3\text{F}_{16}^-$ anion in $\text{CsSb}_3\text{F}_{16}$ show most correspondence with those found in $[\text{ClCO}][\text{Sb}_3\text{F}_{16}]^{[22]}$ where $\text{Sb}_3\text{F}_{16}^-$ was found to exhibit a common *cis*-fluorine-bridged $\text{Sb}_3\text{F}_{16}^-$ anion consistent with the crystal structure analysis made for $\text{CsSb}_3\text{F}_{16}$.

Conclusions

Smaller cations such as Li^+ [$V(\text{Li}^+) = 0.002 \text{ nm}^3$]^[14] and Na^+ [$V(\text{Na}^+) = 0.004 \text{ nm}^3$]^[14] yield ASbF_6 compounds, whereas larger A^+ cations ($\text{A} = \text{Ag}^+, \text{H}_3\text{O}^+, \text{K}^+$) prefer to form $\text{ASb}_2\text{F}_{11}$ salts. These latter ions, with volumes $V(\text{Ag}^+) = 0.006 \text{ nm}^3$,^[5] $V(\text{H}_3\text{O}^+) = 0.008 \text{ nm}^3$ ^[5] and $V(\text{K}^+) = 0.010 \text{ nm}^3$,^[14] lead to salts which crystallise in an identical structural type. The coordination of the three crystallographically nonequivalent A^+ cations can be approximately regarded as being 5+3, (C.N. = 8), 6+3 (C.N. = 9) and 6+2 (C.N. = 8), respectively. X-ray powder diffraction patterns indicate that $\text{RbSb}_2\text{F}_{11}$ and $\text{TlSb}_2\text{F}_{11}$ are isostructural, which, as was alluded to above, is not surprising in light of their similar volumes. The larger Cs^+ cation [$V(\text{Cs}^+) = 0.019 \text{ nm}^3$]^[14] yields $\text{CsSb}_2\text{F}_{11}$, which represents the third structural type with the highest coordination number (C.N. = 12) found for the cation A^+ .

In all crystal structures determined for $\text{ASb}_2\text{F}_{11}$ compounds the Sb_2F_{11} units are observed to have a high degree of distortion. The bridge angle α and torsion angle ψ in the Sb_2F_{11} units may have some cation-dependence, although these values are mostly influenced by long interionic contacts in the solid state.

Only the largest of the alkali metal cations (Cs^+) is capable of stabilizing the weakly fluoro-basic $\text{Sb}_3\text{F}_{16}^-$ anion.

A summary of known compounds with general formula $\text{ASb}_n\text{F}_{5n+1}$ ($\text{A} = \text{monovalent metal cation}; n = 1, 2, 3$) is shown in Table 9.

Table 9. Compounds with general formula $\text{ASb}_n\text{F}_{5n+1}$ ($\text{A} = \text{monovalent metal cation}; n = 1, 2, 3$).

SbF_6^-		$\text{Sb}_2\text{F}_{11}^-$	$\text{Sb}_3\text{F}_{16}^-$
Li^+	[a]		
Cu^+	[b]		
Na^+	[a]		
K^+	[a]	[g]	
Ag^+	[c]	[h]	
Rb^+	[d]	[g]	
In^+	[e]		
Tl^+	[f]	[g]	
Cs^+	[a]	[g]	[g]

[a] Ref.^[1] [b] Ref.^[26] [c] Ref.^[27] [d] Ref.^[28] [e] Ref.^[29] [f] Ref.^[30]
[g] This work. [h] Ref.^[5]

Experimental Section

Techniques

The infrared spectra, with a resolution of 4 cm^{-1} , of powdered samples sandwiched between AgCl windows in a leak-tight brass cell were recorded (5 scans) with a Perkin–Elmer FTIR 1710 spectrometer. Raman spectra, with a resolution of 1 cm^{-1} , were recorded (10–20 scans) with a Renishaw Raman Imaging Microscope System 1000, with the 632.8-nm exciting line of a He–Ne laser.

X-ray powder diffraction patterns were obtained using the Debye–Scherrer technique with Ni-filtered $\text{Cu-K}\alpha$ radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry-box. Intensities were estimated visually.

Reagents and Apparatus

Volatile materials were manipulated using an all-PTFE vacuum line equipped with PTFE valves. The manipulation of the non-volatile solids was accomplished under a dry argon atmosphere in a dry-box (M. Braun, Germany). The residual water in the atmosphere within the dry-box never exceeded 1 ppm. All reactions were carried out in FEP (Polytetra, Germany) reaction vessels (height: 300 mm; inner diameter: 15.5 mm; outer diameter: 18.75 mm) equipped with PTFE valves^[31] and PTFE-coated stirring bars. All reaction vessels were pretreated with F_2 prior to use.

LiF (Merck, 99.9%), NaF (Merck, 99%), KF (Ventron, 99.9%), RbF (Aldrich, 99%), CsF (Ventron, 99.9%), SO_2 (Messer Griesheim, 99.9%) and fluorine (Solvay) were used as supplied. TIF was prepared by reaction between Tl_2CO_3 (Merck, P.A.) and aqueous HF . SbF_3 (Alfa Aesar, 99%) was treated with aHF in order to remove possible traces of Sb_2O_3 . SbF_5 was prepared by fluorination of SbF_3 in a flow reaction. Its purity was checked by Raman spectroscopy. Anhydrous HF (Fluka, Purum) was treated with K_2NiF_6 for several hours prior to use.

Reactions between AF and an Excess of SbF_5

In a dry-box a sample of the fluoride AF ($\text{A} = \text{Li} - \text{Cs}, \text{Tl}$) was loaded into the FEP reaction vessel. An excess of SbF_5 and the solvent (aHF or SO_2) were condensed onto the solid fluoride salt at 77 K. The reaction mixtures were left stirring for several days at room temperature. The details of the reaction conditions are given in Table 10. Clear colourless solutions were obtained in the case of reactions between NaF or KF and SbF_5 in aHF. However, in the case of the reaction between AF ($\text{A} = \text{Li}, \text{Rb}, \text{Cs}$ and Tl) and SbF_5 in aHF, a clear, colourless liquid phase was visible above an insoluble white solid, which always formed. The reaction between KF and SbF_5 (molar ratio = 1:2) in SO_2 as solvent, yielded a clear, colourless solution. In the case of the reaction between NaF and SbF_5 (molar ratio = 1:2) in SO_2 two liquid phases were observed. In this latter case a clear, colourless solution was visible above a milky suspension.

Volatiles were slowly pumped off at room temperature over a few hours to leave behind white solids. The chemical analyses of the resulting isolated $\text{ASb}_2\text{F}_{11}$ salts ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) are given in Table 11. The Raman spectra of the products of reactions between AF ($\text{A} = \text{Li}, \text{Na}$) and SbF_5 in aHF or SO_2 showed only the bands [Li : 669(100), 569(10), 295(80); Na : 672(100), 581(10), 279(50)] that can be assigned to ASbF_6 salts.^[32]

In further experiments a sample of alkali metal fluoride (AF, $\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) was loaded into the FEP reaction vessel and an excess of liquid SbF_5 was condensed onto the solid fluoride salt at 77 K. The reaction mixture was warmed up to 85 °C. The details

Table 10. Reaction conditions for the reactions of AF (A = Li–Cs, Tl) with an excess of SbF₅ in aHF (or SO₂) at room temperature.

AF	Starting materials		SbF ₅		Solvent	<i>V</i> _{solvent} [mL]	Reaction time [d]	Final product
	[g]	[mmol]	[g]	[mmol]				
LiF	0.024	0.92	1.767	8.15	aHF	5	11	LiSbF ₆
NaF	0.036	0.87	0.815	3.76	aHF	6	11	NaSbF ₆
KF	0.054	0.92	1.560	7.20	aHF	5	7	KSb ₂ F ₁₁
RbF	0.103	0.99	1.800	8.30	aHF	5	13	RbSb ₂ F ₁₁
CsF	0.115	0.76	0.908	4.19	aHF	4	11	CsSb ₂ F ₁₁
CsF	0.120	0.79	5.00	23.00	aHF	10	3	CsSb ₃ F ₁₆
TlF	0.216	0.96	0.900	4.15	aHF	3	2	TlSb ₂ F ₁₁
NaF	0.035	0.83	0.361	1.66	SO ₂	6	1	NaSbF ₆
KF	0.055	0.95	0.411	1.90	SO ₂	6	1	KSb ₂ F ₁₁

[a] A = Alkali metal.

Table 11. Chemical analyses of K, Rb, and Cs polyfluoroantimonates.

Product	Chemical analyses ^[a]					
	A ^[b]	calcd. [%] Sb	F	A	found [%] Sb	F
KSb ₂ F ₁₁ ^[c]	7.95	49.53	42.51	8.5	49.5	41.8
RbSb ₂ F ₁₁ ^[c]	15.89	45.26	38.85	16.4	45.5	38.5
CsSb ₂ F ₁₁ ^[d]	–	41.6	35.7	–	41.4	35.4
CsSb ₃ F ₁₆ ^[e]	–	–	37.90	–	–	37.3
CsSb ₃ F ₁₆ ^[f]	–	45.53	37.90	–	45.0	37.7

[a] The chemical analyses are given in mass percent. [b] A = alkali metal. [c] Prepared in aHF. [d] Prepared in aHF with a small excess of SbF₅. [e] Prepared in aHF with a large excess of SbF₅. [f] Prepared at 85 °C without aHF.

of the reaction conditions are given in Table 12. On the basis of the final masses of the solidified isolated solids and comparison of their vibrational spectra with the vibrational spectra obtained for the products in AF/SbF₅/aHF system it was concluded that the final products were ASbF₆ (A = Na), ASb₂F₁₁ (A = K, Rb) and ASb₃F₁₆ (A = Cs). The chemical analysis of the latter salt is given in Table 11.

Table 12. Reaction conditions for the reactions of AF (A = Na, K, Rb, Cs) with an excess of SbF₅ at 85 °C.

AF	Starting materials		SbF ₅		Reaction time [d]	Mass balance		Final product
	[g]	[mmol]	[g]	[mmol]		calcd.	found	
NaF	0.012	0.29	0.400	1.85	5	0.075 ^[b]	0.070	NaSbF ₆
KF	0.060	1.03	5.000	23.07	9	0.507 ^[c]	0.480	KSb ₂ F ₁₁
RbF	0.091	0.87	1.600	7.38	5	0.466 ^[c]	0.461	RbSb ₂ F ₁₁
CsF	0.158	1.04	1.250	5.77	5	0.834 ^[d]	0.823	CsSb ₃ F ₁₆

[a] A = alkali metal. [b] Calculated for ASbF₆. [c] Calculated for ASb₂F₁₁. [d] Calculated for ASb₃F₁₆.

Preparation of Single Crystals of ASb₂F₁₁ (A = K, Cs) and CsSb₃F₁₆

Preparations were carried out in a double T-shaped apparatus consisting of two FEP tubes (19 mm o.d., and 6 mm o.d.). CsF or KSb₂F₁₁ (ca. 0.2 mmol of each) were loaded into the wider of the two tubes in a dry-box. SbF₅ (ca. 7 mmol) and aHF (ca. 4 mL) were then condensed onto the starting material at 77 K. The reaction mixtures were then brought up to room temperature. After one day the clear solutions that had developed were transferred into the narrower tube. The evaporation of the solvent from these solutions was carried out by maintaining a temperature gradient corresponding to about 10 K between both tubes for one month, and later increasing this further to about 50 K for an additional month. The effect of this treatment was to enable aHF and the excess of SbF₅ to be slowly evaporated from the narrower into the wider tube, leaving colourless crystals of ASb₂F₁₁ (A = K, Cs). A similar procedure was adopted with NaF but this yielded only single crystals of NaSbF₆. Crystals were selected from the compounds in a dry-box and these were then placed inside 0.3-mm quartz capillaries, which were heat-sealed and mounted on the goniometer head of the diffractometer.

When the final product of the reaction between CsF and liquid SbF₅ at 85 °C was checked under a microscope it was found to consist of small regular blocks. Single crystals were immersed in perfluorinated oil (ABCR, FO5960) in the dry-box, selected under the microscope and then transferred into the cold nitrogen stream of the diffractometer.

Table 13. Crystal data and structure refinement for KSb₂F₁₁, CsSb₂F₁₁ and CsSb₃F₁₆.

Empirical formula	KSb ₂ F ₁₁	CsSb ₂ F ₁₁	CsSb ₃ F ₁₆
Formula mass	507.60	585.41	802.16
Temp [K]	250	250	200
<i>a</i> [pm]	1141.65(8)	774.10(14)	2207(3)
<i>b</i> [pm]	1279.96(9)	1425.41(17)	772.6(11)
<i>c</i> [pm]	3948.5(3)	951.30(15)	1605(3)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	90	113.226(6)	90
<i>γ</i> [°]	90	90	90
<i>V</i> [nm ³]	5.7699(7)	0.9646(3)	2.737(8)
<i>Z</i>	24	4	8
<i>D</i> _{calcd.} [Mgm ^{−3}]	3.506	4.031	1.947
<i>λ</i> [pm]	71.069	71.069	71.069
<i>μ</i> [mm ^{−1}]	6.19	9.449	4.335
Space group	<i>Pbca</i> (no. 61)	<i>P2₁/n</i> (no. 14)	<i>Pca2₁</i> (no. 29)
<i>GOF</i> indicator	1.101	1.064	1.422
<i>R</i> ₁ ; <i>wR</i> ₂ [<i>I</i> > 2.00σ(<i>I</i>) ^[a]]	0.0511; 0.1213	0.0309; 0.0735	0.0609; 0.1165

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$, $GOF = [\Sigma [w(F_o^2 - F_c^2)^2 / (N_o - N_p)]]^{1/2}$, where N_o = no. of reflns. and N_p = no. of refined parameters.

Chemical Analyses

The alkali metal content (A) was determined by flame atomic emission spectrometry.^[33] The total fluoride content (F) was determined following complete decomposition of the sample with Devarda alloy in alkaline media by direct potentiometry using a fluoride ion selective electrode.^[34] The antimony content was, in turn, determined potentiometrically by redox titration with KBrO₃ after prior reduction of the antimony with alumina powder in acidic media.^[35] The results of analysis of the isolated K, Rb, and Cs polyfluoroantimonate products are given in Table 11.

X-ray Structure Determination of ASb₂F₁₁ (A = K, Cs) and CsSb₃F₁₆ Salts

Single-crystal data of ASb₂F₁₁ (A = K, Cs) and CsSb₃F₁₆ were collected using a Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer with a graphite-monochromated Mo-K_α radiation source. Data were corrected for Lorentz, polarisation and absorption effects and processed using the Rigaku CrystalClear software suite.^[36] The structures were solved by direct methods^[37] and then expanded using Fourier techniques. The salt CsSb₃F₁₆ crystallizes in an acentric space group (*Pca*2₁), so the Flack parameter^[38] was refined. The latter converged to a twin ratio of 0.75(7). Some details of the single-crystal data collection and data processing and refinement for ASb₂F₁₁ (A = K, Cs) and CsSb₃F₁₆ are given in Table 13.

Further details of the crystal-structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-415752 (KSb₂F₁₁), -415751 (CsSb₂F₁₁) and -415750 (CsSb₃F₁₆).

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