Antimony-121 Mössbauer Studies of some Fluoroantimonates(III)

By **Jack G. Ballard** and **Thomas Birchall,*** Department of Chemistry, McMaster University, 1280 Main St. W., Hamilton, Ontario L8S 4M1, Canada
Robert Fourcade and **Guy Mascherpa,** Laboratoire des Acides Minéraux, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier, Cedex, France

Antimony-121 Mössbauer spectra have been recorded at liquid-helium temperatures for a number of complex anions derived from SbF_3: $M_2[SbF_5]$ (M = Na, K, or N_2H_6); $M[SbClF_3]$ (M = K or NH_4); $Na[SbClF_3]\cdot H_2O$; $M[Sb_3F_{10}]$ (M = Na, Tl, or NH_4); $M[Sb_4F_{13}]$ (M = K or Cs); and $[NH_4]_4[Sb_5F_{19}]$. The data are consistent with the known stereochemistry of these compounds in which the antimony 5*s* electron pair is stereochemically active in a distorted AX_6E environment with the 3 : 3 : 1 arrangement or monocapped octahedron, the lone pair being in the 1 position.

ANTIMONY(III) forms a number of anionic complexes with fluorine.[1] Structural information from *X*-ray crystallographic studies has been reported for a number of these fluoroantimonates(III).[2-10] Antimony-121 Mössbauer data have been presented for salts of $[Sb_2F_7]^-$, $[SbF_4]^-$, and $[SbF_5]^{2-}$,[11,12] and attempts made to interpret these results in terms of the known structures. We now report data on some further fluoride complexes of Sb^{III} all of which clearly show stereochemical activity of the 5*s* electron pair.

EXPERIMENTAL

Mössbauer spectra were recorded on apparatus previously described.[13] The source was 0.5 mCi $Ba^{121m}Sn(Sb)O_3$, which was maintained at room temperature while the samples were cooled to liquid-helium temperature. The window of the single-channel analyzer was set on the escape peak of the 37 keV γ-ray. The samples contained 10 mg Sb cm^{-2} and all the isomer shifts were measured with respect to InSb at 4 K. Each spectrum was calibrated by means of a He–Ne laser interferometer system and periodically checked against a standard spectrum of iron foil. About 100 000 counts per folded channel were accumulated and the data were computer fitted using the program described by Shenoy *et al.*[14] which uses a fast transmission-integral routine developed by Cranshaw.[15] Both stages of the fitting procedure were used and the ' thin ' approximation was shown to be adequate, although the isomer shifts and quadrupole-coupling constants differed significantly in a number of instances from the values obtained by the older fitting procedure.[11] Shenoy and Friedt[16] demonstrated the superiority of the transmission-integral method over older procedures and we therefore believe that the data presented in Table 2 are the most reliable that can be obtained from our spectra. In addition to the usual χ^2, the misfit criterion of Ruby[17] was also applied to the fitting of the data points to estimate goodness of fit.

Preparation of Salts.—$[NH_4]_4[Sb_5F_{19}]$. This was prepared by dissolving SbF_3 and $[NH_4]_2[CO_3]$ in the proportion Sb: $[NH_4]^+ = 5 : 4$ in an excess of dilute hydrofluoric acid. The solution was evaporated to dryness at room temperature to give elongated prismatic needles.

$M[Sb_4F_{13}]$. These salts were prepared by dissolving Sb_2O_3 and $M_2[CO_3]$ or $M[HCO_3]$ in an excess of 50% aqueous HF in a Teflon beaker; evaporation at 80 °C produced short prisms.

$M[Sb_3F_{10}]$. The sodium salt was obtained from the SbF_3–NaF–H_2O system at a composition between that of $Na[SbF_4]$ and SbF_3. The salts $Tl[Sb_3F_{10}]$ and $[NH_4]$-$[Sb_3F_{10}]$ were obtained from the stoicheiometric mixture of Sb_2O_3 and $Tl_2[CO_3]$ or $Na_2[CO_3]$ in HF(aq). The thallium salt was obtained by crystallization at 80 °C while the ammonium salt was obtained at room temperature.[18]

$[N_2H_6][SbF_5]$. Antimony(III) oxide was dissolved in an excess of concentrated HF at 70 °C and an aqueous hydrazine solution was slowly added. On cooling to room temperature large colourless plates formed.

$M[SbClF_3]$. All of these salts were prepared by simultaneous dissolution in water of the stoicheiometric amounts of SbF_3 and the metal chloride followed by crystallization under low pressure at room temperature. These compounds were characterized by analysis (Table 1), i.r. and Raman spectroscopy, and *X*-ray crystallography.[18-22]

RESULTS AND DISCUSSION

Antimony trifluoride forms adducts with alkali-metal fluorides to give fluoroantimonate(III) salts with a

---

[1] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972.

[2] A. Byström and A. Westgron, *Arkiv. Kemi Miner.*, 1943, **B17**, 1.

[3] A. Byström and K. A. Wilhelmi, *Arkiv. Kemi*, 1951, **3**, 373.

[4] A. Byström and K. A. Wilhelmi, *Arkiv. Kemi*, 1951, **3**, 461.

[5] A. Byström, S. Bäcklund, and K. A. Wilhelmi, *Arkiv. Kemi*, 1952, **4**, 175.

[6] A. Byström, S. Backlund, and K. A. Wilhelmi, *Arkiv. Kemi*, 1953, **6**, 77.

[7] S. H. Mastin and R. R. Ryan, *Inorg. Chem.*, 1971, **10**, 1757.

[8] R. R. Ryan, S. H. Mastin, and A. C. Larson, *Inorg. Chem.*, 1971, **10**, 2793.

[9] R. R. Ryan and D. T. Cromer, *Inorg. Chem.*, 1972, **11**, 2322.

[10] R. Fourcade, G. Mascherpa, E. Philippot, and M. Maurin, *Rev. Chim. Minérale*, 1974, **11**, 481.

[11] T. Birchall and B. Della Valle, *Canad. J. Chem.*, 1971, **49**, 2808.

[12] J. D. Donaldson, J. T. Southern, and M. J. Tricker, *J.C.S. Dalton*, 1972, 2637.

[13] T. Birchall and A. F. Reid, *J. Solid-State Chem.*, 1975, **13**, 351.

[14] G. K. Shenoy, J. M. Friedt, H. Maletta, and S. L. Ruby, *Mössbauer Effect Methodology*, 1974, **9**, 277.

[15] T. E. Cranshaw, *J. Phys.* (*E*), 1974, **7**, 1.

[16] G. K. Shenoy and J. M. Friedt, *Nuclear Instr. Methods*, 1974, **116**, 573.

[17] S. L. Ruby, *Mössbauer Effect Methodology*, 1973, **8**, 263.

[18] B. Ducourant, B. Bonnet, R. Fourcade, and G. Mascherpa, *Bull. Soc. chim. France*, 1975, **7**—**8**, 1471.

[19] R. Fourcade, Ph.D. Thesis, Université des Sciences et Techniques du Languedoc, Montpellier, 1975.

[20] B. Ducourant, R. Fourcade, E. Philippot, and G. Mascherpa, *Rev. Chim. Minérale*, 1975, **12**, 553.

[21] R. Fourcade, G. Mascherpa, and E. Philippot, *Acta Cryst.*, 1975, **B31**, 2322.

[22] B. Ducourant, R. Fourcade, E. Philippot, and G. Mascherpa, *Rev. Chim. Minérale*, 1975, **12**, 485.

variety of stoicheiometries. Byström and his co-workers examined a number of these compounds by X-ray crystallographic methods.[3-6,23] Other workers demonstrated that a variety of structures can be obtained for a given $SbF_3 : F^-$ ratio depending on the cation.[7,8,24,25] A number of these species have been investigated by ^{121}Sb Mössbauer spectroscopy [11,12] and attempts made to correlate the isomer shifts and quadrupole couplings with the available structural data. Birchall and Della Valle [11] questioned the existence of the $[Sb_4F_{13}]^-$ anion. However, Macherpa and his co-workers [18,20-25] recently isolated and reported the crystal structures of compounds containing this anion and, in addition, prepared salts containing the $[Sb_5F_{19}]^{4-}$, $[Sb_3F_{10}]^-$, and $[SbClF_3]^-$ ions. These new compounds have now been examined by Mössbauer spectroscopy and the data obtained are summarized in Table 2. Included in this Table are data for SbF_3, $M[SbF_4]$, $M[Sb_2F_7]$, and $M_2[SbF_5]$ which have already been reported [12,26] together with our data for SbF_3, $Na_2[SbF_5]$, and $K_2[SbF_5]$. Although Birchall and Della Valle [11] first reported antimony Mössbauer data for compounds of this type, their data have not been included in Table 2 because their measurements were made at 77 K on samples which were relatively thick (*ca.* 25 mg Sb cm^{-2}).

TABLE 1

Analytical data (%) for the fluoroantimonate(III) salts *

Salt	Sb	F	M
$K[Sb_4F_{13}]$	62.6 (63.0)	31.8 (32.0)	4.9 (5.05)
$Cs[Sb_4F_{13}]$	56.3 (56.2)	28.3 (28.5)	15.3 (15.35)
$Na[Sb_3F_{10}]$	65.1 (63.15)	33.2 (32.85)	3.0 (3.95)
$Tl[Sb_3F_{10}]$	(48.1)	24.9 (25.0)	
$[NH_4][Sb_3F_{10}]$	63.7 (63.7)	33.1 (33.15)	3.2 (3.15)
$[NH_4]_4[Sb_5F_{19}]$	58.2 (58.45)	34.8 (34.65)	6.8 (6.90)
$[N_2H_6][SbF_5]$	49.0 (48.55)	37.5 (37.9)	
$Na[SbClF_3]\cdot H_2O$	47.5 (47.7)	(22.35)	8.9 (9.00)
$K[SbClF_3]$	49.0 (48.05)		15.3 (15.45)
$[NH_4][SbClF_3]$	52.9 (52.4)		7.9 (7.75)

* Calculated values are given in parentheses.

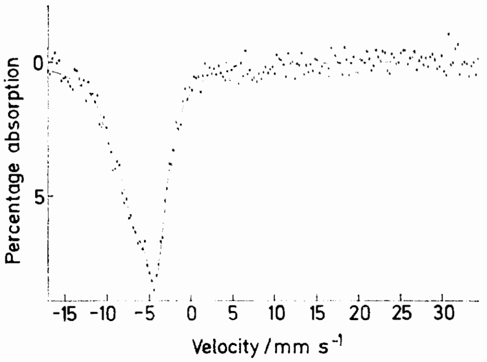

FIGURE 1 ^{121}Sb Mössbauer spectrum of $Na[SbClF_3]\cdot H_2O$ at 4 K

Fluoro-anions of Sb^{III} are now known for the following $SbF_3 : MF$ ratios: 4 : 1 ($[Sb_4F_{13}]^-$); 3 : 1 ($[Sb_3F_{10}]^-$); 2 : 1 ($[Sb_2F_7]^-$); 5 : 4 ($[Sb_5F_{19}]^{4-}$); 1 : 1 ($[SbF_4]^-$); and 1 : 2 ($[SbF_5]^{2-}$), and this is the order that the data are presented in Table 2. Examination of these data reveals an increase in isomer shift from $K[Sb_4F_{13}]$, which has a very negative shift, through to $K_2[SbF_5]$, which has the most positive shift. Within this series there are exceptions to this trend and these are discussed below. The $\delta r/r$ term in the isomer-shift expression is negative for ^{121}Sb which means that the antimony atoms in $K_2[SbF_5]$ have the lowest *s*-electron density.

TABLE 2

Antimony-121 Mössbauer data for some antimony(III)-fluorine systems

Compound	I.s.[a]	eQV_{zz} [b]	Ta[c]	χ^2/degrees of freedom	M[d]	Ref.
	mm s^{-1}					
SbF_3	−6.0	19.6				26
	−6.29	19.1	0.75	1.25	0.23	*e*
$K[Sb_4F_{13}]$	−6.32	17.7	0.30	0.97	0.19	*e*
$Cs[Sb_4F_{13}]$	−5.83	16.3	0.28	1.10	0.36	*e*
$Na[Sb_3F_{10}]$	−6.56	19.1	0.46	1.02	0.01	*e*
$Tl[Sb_3F_{10}]$	−6.30	19.3	0.51	0.98	0.08	*e*
$[NH_4][Sb_3F_{10}]$	−6.26	18.5	0.65	1.11	0.11	*e*
$K[Sb_2F_7]$	−4.82	16.7				12
$Cs[Sb_2F_7]$	−5.50	18.6				12
$[NH_4][Sb_5F_{19}]$	−5.93	18.5	0.62	1.11	0.10	*e*
$Na[SbF_4]$	−5.48	18.6				12
$K[SbF_4]$	−5.48	18.6				12
$[NH_4][SbF_4]$	−5.6	14.2				12
$Na_2[SbF_5]$	−4.75	−8.3				12
	−5.30	15.4	0.48	0.87	0.47	*e*
$K_2[SbF_5]$	−4.09	14.3				12
	−4.48	15.7	0.65	1.14	0.22	*e*
$[N_2H_6][SbF_5]$	−6.41	18.4	0.50	0.77	0.38	*e*
$Na[SbClF_3]\cdot H_2O$	−6.29	16.5	0.80	1.17	0.07	*e*
$K[SbClF_3]$	−5.78	19.2	1.05	1.90	0.38	*e*
$[NH_4][SbClF_3]$	−5.89	20.1	0.30	0.95	0.34	*e*
InSb	0.0[f]			1.00	0.05	*e*

[a] ±0.1 mm s^{-1}. [b] ±0.5 mm s^{-1} (quadrupole couplings refer to the ground state). [c] Thickness. [d] Misfit (see ref. 17). [e] This work. [f] −8.50 mm s^{-1} from $Ba^{121}Sn(Sb)O_3$.

Previous interpretations of isomer-shift data for fluoroantimonates(III) [11,12] have been based on the assumption that, apart from SbF_3, the antimony in these salts is six-co-ordinate or lower, the geometry being described as AX_5E or AX_4E according to the Gillespie V.S.E.P.R. theory.[27] Edwards [28] showed that the antimony environment in SbF_3 consists of six fluorines, three short and three much longer although still considerably shorter than the sum of the van der Waals radii, and a lone pair of electrons. The environment in SbF_3 is then described as AX_6E, a monocapped octahedron (**3.3.1.**). Recently Fourcade [19] re-examined the previously published crystallographic data for fluoroantimonate(III) salts and in addition obtained crystallographic results for some new salts. He presented extremely good evidence to indicate that the AX_6E monocapped-octahedral (**3.3.1**) configuration is the predominant geometry in these fluoro-anions. These structures are summarized in Figure 2 where the basic geometry

---

[23] A. Byström and K. A. Wilhelmi, *Arkiv. Kemi*, 1951, **3**, 17.

[24] M. Merhain, B. Ducourant, R. Fourcade, and G. Mascherpa, *Bull. Soc. chim. France*, 1974, **5—6**, 757.

[25] N. Habibi, B. Ducourant, R. Fourcade, and G. Mascherpa, *Bull. Soc. chim. France*, 1974, **11**, 2320.

[26] S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. L. Synder, *Phys. Rev.*, 1967, **159**, 239.

[27] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand Reinhold, London, 1972.

[28] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751.

about each antimony is shown with all of the significant interactions included. Of the structures represented, only the $[SbF_5]^{2-}$ salts and one antimony site in the $K[Sb_2F_7]$ salt do not have the AX_6E geometry. The $[SbF_5]^{2-}$ salts have five fluorines and a lone pair making up the expected distorted-octahedral arrangement, while the Sb^1 site in $K[Sb_2F_7]$ has only four fluorines and a lone pair, with a distorted AX_4E structure.

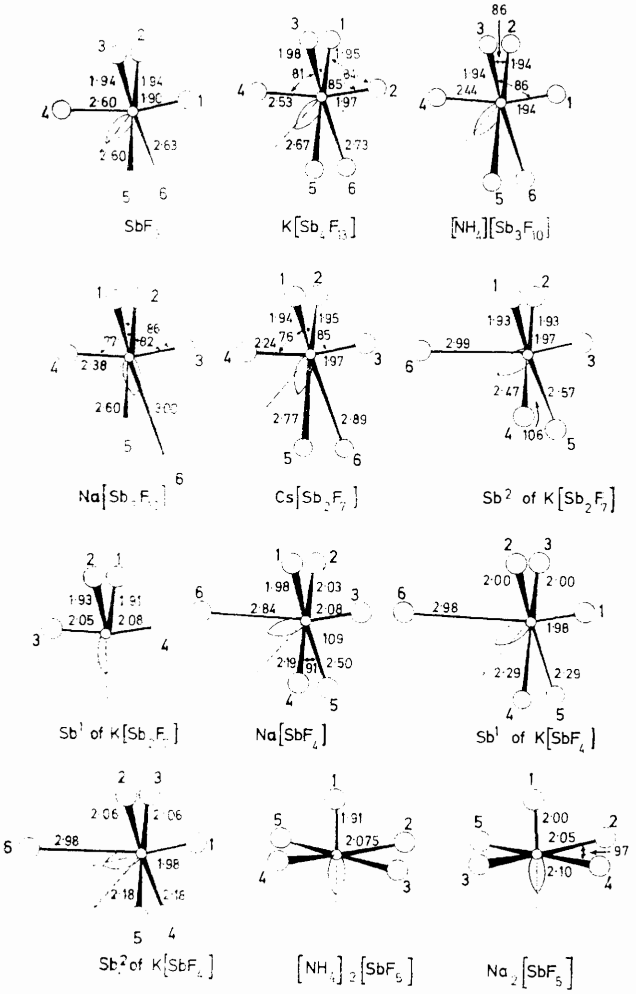

Figure 2 Structural representations of the antimony environments in SbF_3 and the fluoroantimonate(III) salts

Comparing the isomer shifts for structurally related compounds, one notes a general increase to more positive values as the ratio of $SbF_3 : F^-$ approaches 1 : 1. This means that the *s*-electron density at antimony decreases as the negative charge per antimony atom approaches one. Presumably this increase in negative charge per antimony brings about an expansion of the orbital wavefunctions and results in the observed decrease in *s*-electron density. As the negative charge per Sb increases one also notes that one Sb–F bond becomes quite long under the influence of the lone-pair orbital. At $[SbF_5]^{2-}$ this lone pair has expanded to such a degree that one fluorine is pushed off completely, the 5*s* electrons are now shared almost equally between five fluorines, rather than with six, and the $M_2[SbF_5]$ salts have the lowest *s*-electron density at the antimony nucleus.

The stereochemistry about the antimony in $[Sb_4F_{13}]^-$ [20] and in SbF_3 [28] is very similar (Figure 2), but whereas in SbF_3 all fluorines are involved in symmetric Sb–F–Sb bridges, in $[Sb_4F_{13}]^-$ there is one purely terminal Sb–F bond and another fluorine is tetrahedrally co-ordinated by four antimony atoms. This tetrahedral fluorine–antimony distance, 2.51 Å, is much shorter than the value (2.87 Å) previously reported by Byström and Wilhelmi.[23] Since the *s*-electron density at antimony in SbF_3 and $K[Sb_4F_{13}]$ is the same, one must conclude that the effect of the longer Sb–F bonds in the two compounds, that is the fluorines supplying largely *p*- and *d*-electron density, is self compensating: Sb–F (4) is shortened in $K[Sb_4F_{13}]$ while Sb–F (5,6) are lengthened (Figure 2). The lower *s*-electron density for the caesium salt could be the result of a lengthening of all the Sb–F bonds as the crystal lattice expands to accommodate the larger cation. Changes in isomer shift as a result of cation–anion interactions have been noted previously for tin(II) fluoride systems.[29] The smaller quadrupole-coupling constants noted for $[Sb_4F_{13}]^-$ are possibly the result of a positive contribution by V_{zz} (lattice) to the negative V_{zz} (ion) resulting from the asymmetric distribution of cations about each antimony.

Crystallographic evidence for the $[Sb_3F_{10}]^-$ ion has been reported with sodium as the counter ion.[21] Three SbF_3 units share one F^- compared to four in the previous case and one might have expected a reduction in *s*-electron density because of the increased negative charge causing an expansion of the wavefunction. However, only the ammonium salt has a more positive shift than $K[Sb_4F_{13}]$. The sodium and thallium(I) salts have more negative shifts, *i.e.* higher *s*-electron densities. Examination of Figure 2 reveals that the Sb environment in the ammonium salt does resemble that in $[Sb_4F_{13}]^-$. The sodium salt has a very long Sb–F bond which will contribute little in the way of shielding the *s* electrons from the antimony nucleus and therefore an increase in *s*-electron density will result. The environments about the antimony in these salts are more asymmetric than in the previous cases and this is reflected in the slightly increased quadrupole-coupling constants. We attempted to fit these spectra with a program which allowed for the variation of the asymmetry parameter η. For these $[Sb_3F_{10}]^-$ ions an η value of 0.13 was obtained, but since the goodness-of-fit criteria were not better than the fits using the transmission-integral method these values have not been included in Table 2. All the other compounds studied gave η values close to zero. The isomer-shift difference between $K[Sb_2F_7]$ and $Cs[Sb_2F_7]$ is greater than can be explained on the basis of cation–anion interactions.[29] For the heptafluorodiantimonates(III) there are gross structural differences between

---

[29] J. D. Donaldson and B. J. Senior, *J. Chem. Soc.*, **1960**, 1796, 1798.

the potassium and caesium salts. The caesium salt has only one antimony site and its isomer shift is as expected. Potassium heptafluorodiantimonate(III) on the other hand has two sites, one of which has AX_6E geometry and should therefore have an isomer shift close to -5.5 mm s^{-1}. The other site has an AX_4E envionment and should have a much more positive isomer-shift value. Furthermore examination of Figure 2 indicates that eQV_{zz} for these sites should be of opposite sign. These facts would all lead to $K[Sb_2F_7]$ having the anomalous value reported. Neither of the earlier workers were able to resolve the two sites.[11,12] For the $[SbF_5]^{2-}$ series there are also large differences in Mössbauer parameters from the sodium to hydrazinium salts and discrepancies exist between our data and those previously reported.[12] These compounds are isostructural except for the sodium salt,[4,10,30] but all have the AX_5E geometry. While one might expect some variation in Mössbauer parameters due to cation–anion interaction, gross differences would not be expected. Indeed, for $Na_2[SbF_5]$ and $K_2[SbF_5]$ we find similar values for the quadrupole-coupling constants in contrast to the previous workers[12] who reported eQV_{zz} values that are of opposite sign for these two salts. The quite negative isomer-shift value that we observe for the hydrazinium salt indicates a higher *s*-electron density at the antimony nucleus than is found for the sodium or potassium salts. Presumably this is the result of a reduction of the double negative charge on the anion by a strong hydrogen-bonded interaction with the hydrazinium dication.

The quadrupole couplings (eQV_{zz}) observed for these salts are all large and positive. Since eQ for ^{121}Sb is negative, the sign of V_{zz} must also be negative. This indicates that the principal component of the electric-field gradient should be through the lone-pair orbital with an excess of electron density in this direction compared to that in the *xy* plane. This is clearly consistent with the proposed geometries of the various ions shown in Figure 2. Only for the Sb^1 site in $K[Sb_2F_7]$ should eQV_{zz} be negative. The magnitudes of the quadrupole couplings for the new compounds reported here are all *ca.* 18 mm s^{-1} and the relatively small variations are no doubt due to the minor structural changes indicated in Figure 2, some of which have been discussed above. Further detailed discussion of this parameter is not warranted, for although χ^2 is good for our computer-fitting procedure, the misfit criterion[17] indicates that some of the spectra are not as good as they appear. A value for $M < 0.1$ is taken to indicate that the data from the fitted spectrum are extremely reliable. The parameter most affected by poor data is eQV_{zz} and hence a large error has been placed on the quadrupole-coupling values.

The $[SbClF_3]^-$ salts were prepared and their structures investigated to ascertain whether the ion existed as a discrete $SbClF_3E^-$ ion, which would be expected to have a trigonal-bipyramidal structure, or as $[(SbClF_3)_x]^{x-}$ a bridged polymer which, by analogy with the $[SbF_4]^-$ ions, we would expect to have AX_6E geometry. The discrete ion would have the lone pair in an equatorial position of the trigonal bipyramid and hence be expected to have a negative eQV_{zz}. On the basis of the Mössbauer evidence (Table 2) this clearly is not the case and hence the discrete ion is ruled out. The Mössbauer parameters for these salts are very close to the data for SbF_3 and the $[Sb_4F_{13}]^-$ ion, suggesting a similar environment. This is borne out in practice[19,22] with each antimony in $K[SbClF_3]$ being co-ordinated by three fluorines at 1.94, 1.95, and 1.96 Å and three chlorines at 3.09, 3.11, and 3.16 Å (Figure 3). The F-Sb-F angles are all less than 90° (82.2, 85.6, and 87.9)° while the Cl-Sb-Cl angles are 110.4, 124.8, and 110.5° with the lone pair of electrons obviously situated between the Sb–Cl bonds. The electric-field gradient would be expected to lie along the direction of the lone pair and, as in the other fluoro-anions, a positive quadrupole splitting is obtained. Crystallographic evidence[19] indicates that $Na[SbClF_3]\cdot H_2O$ is not isostructural with the other $[SbClF_3]^-$ salts. The Mössbauer isomer shift of the sodium salt is significantly different from the other two and while one would expect a small change on going from K^+ to Na^+, the change observed here is more likely to be due to the influence of the water molecule present in the crystal. Presumably it is hydrogen-bonded to a fluorine making it less effective at withdrawing electron density from the antimony, the result being a higher *s*-electron density and a more negative isomer shift.

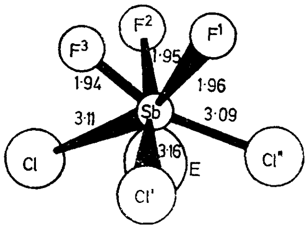

FIGURE 3 Structural representation of the antimony environment in $K[SbClF_3]$

We thank the National Research Council of Canada for assistance.

[6/198 *Received, 29th January,* 1976]

---

[30] R. Fourcade, unpublished work.