An Antimony-121 Mössbauer Study of Some Complexes of Antimony Trifluoride with Chloride, Bromide, and Oxalate Anions

By **Thomas Birchall**,* Department of Chemistry, McMaster University, 1280 Main St. W., Hamilton, Ontario, Canada L8S 4M1
Bernard Ducourant, 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 some complex salts derived from SbF_3: $Cs[SbClF_3]$, $M[SbBrF_3]$ ($M = [NH_4]^+$, Rb^+, or Cs^+), $Na[SbBrF_3]\cdot H_2O$, $M_2[C_2O_4(SbF_3)_2]$ ($M = Na^+$ or K^+), $Rb_2[C_2O_4(SbF_3)_2]\cdot 6H_2O$, and $Cs_2[C_2O_4(SbF_3)_2]\cdot 4H_2O$. The Mössbauer data indicate that in each case the antimony lone pair of electrons is stereochemically active.

ANTIMONY-121 Mössbauer data have been reported for a variety of fluoroantimonates(III) and structural interpretations placed upon these data.[1-3] Antimony(III) fluoride also forms adducts with alkali-metal chlorides and Mössbauer data for the $[NH_4]^+$, Na^+, and K^+ salts have been presented.[3] In all the above cases the spectra clearly show that the lone pair of the antimony is stereochemically active. In continuing these structural investigations we now report data for some SbF_3 adducts with alkali-metal chlorides, bromides, and oxalates.

EXPERIMENTAL

The Mössbauer spectra were recorded and calibrated as described previously.[3] About 60 000 counts per folded channel were accumulated and the spectra were computer-fitted using the program described by Shenoy *et al.*[4] which uses a fast transmission-integral routine developed by Cranshaw.[5] Both stages of the fitting procedure were used and the thin approximation was shown to be adequate in each case. Samples (containing 8 mg of Sb per cm^2) were cooled to 4 K and were referenced against InSb at the same temperature.

Preparation of Salts.—The mixed-halide salts were prepared by simultaneous dissolution in water of the stoicheiometric amounts of SbF_3 and the metal halide followed by slow evaporation of the solvent at 20 °C until crystallization occurred. These salts were characterized by analysis, i.r. and Raman spectroscopy, and *X*-ray crystallography.[6,7] The oxalate salts were prepared in a similar manner.[8]

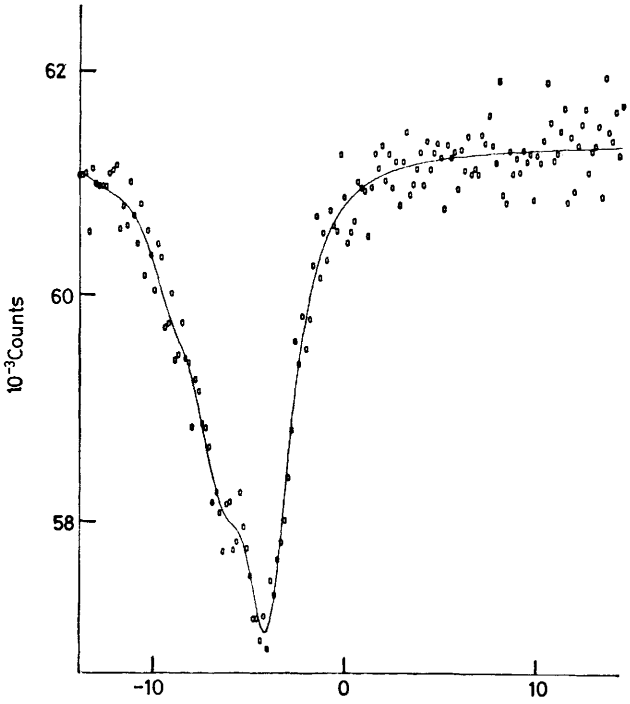
Antimony-121 Mössbauer data for some complexes of SbF_3 with Cl^-, Br^-, and $[C_2O_4]^{2-}$

Compound	i.s.	eQ_gV_{zz}	Γ	Ta [4,5]	χ^2/Degrees of freedom
	mm s^{-1}				
SbF_3	−6.29	19.1		0.75	1.25 *
$Na[SbClF_3]\cdot H_2O$	−6.29	16.5		0.80	1.17 *
$K[SbClF_3]$	−5.78	19.2		1.05	1.90 *
$[NH_4][SbClF_3]$	−5.89	20.1		0.30	0.95 *
$Cs[SbClF_3]$	−6.18	17.4	1.25	0.35	1.05
$Na[SbBrF_3]\cdot H_2O$	−6.49	15.7	1.22	0.39	1.09
$[NH_4][SbBrF_3]$	−6.18	18.3	1.58	0.55	1.14
$Rb[SbBrF_3]$	−5.83	17.4	1.59	0.49	0.95
$Cs[SbBrF_3]$	−6.01	17.9	1.21	0.32	0.98
$Na_2[C_2O_4(SbF_3)_2]$	−6.44	15.7	1.12	0.26	1.01
$K_2[C_2O_4(SbF_3)_2]$	−5.64	17.5	1.40	0.41	1.07
$Rb_2[C_2O_4(SbF_3)_2]\cdot 6H_2O$	−6.29	18.1	1.31	0.42	0.96
$Cs_2[C_2O_4(SbF_3)_2]\cdot 4H_2O$	−6.60	15.9	1.51	0.42	0.94

* Ref. 1.

RESULTS AND DISCUSSION

The Mössbauer data are presented in the Table together with some previously reported data for $M[SbClF_3]$ salts. The Figure shows a representative spectrum. All the compounds have quite negative isomer shifts, $\delta r/r$ is negative for ^{121}Sb, and large positive quadrupole coupling constants which are typical of antimony(III) halide systems where the lone pair is stereochemically active.[1-3]



Antimony-121 Mössbauer spectrum of $Cs[SbBrF_3]$ at 4 K

We have previously noted[3] that the K^+ and $[NH_4]^+$ salts of $[SbClF_3]^-$ have rather similar Mössbauer parameters and these complexes indeed are isostructural but different from the sodium salt. The hydrated sodium salt has a more negative isomer shift, indicating a higher *s*-electron density at the antimony, and the antimony is in a less distorted environment. It was proposed that these differences were attributable to hydrogen bonding between the water molecule present in the crystal and the fluorines bonded to antimony.[3] Recently, Ducourant *et al.*[9] have shown by *X*-ray crystallography that such hydrogen bonding does indeed occur, but it is clear from their data that this is not the only reason for the more negative isomer shift and smaller quadrupole coupling constant. The geometry about the antimony is also different, being 3, 2 + 2, 1 rather than the 3,3,1 found for the potassium salt.[10] In $K[SbClF_3]$ there are three Sb–F bonds (average length 1.946 Å) and three Sb–Cl bonds (average length 3.118 Å) whereas in $Na[SbClF_3]\cdot H_2O$ the Sb–F distances (average 1.969 Å) are slightly longer. Completing the co-ordination are two shorter Sb–Cl bonds (2.830 and 2.999 Å) and two much longer Sb–Cl interactions (3.421 and 3.547 Å). The difference in the Mössbauer parameters are then a combination of a change in co-ordination number and the effect of hydrogen bonding. The isomer shift of the caesium salt is slightly more positive than that of $Na[SbClF_3]\cdot H_2O$, with a similar quadrupole coupling constant, implying that the antimony environments are very similar. Preliminary *X*-ray measurements on $Cs[SbClF_3]$ would appear to support this.[11]

Similar trends in the Mössbauer parameters of the $M[SbBrF_3]$ series are also noted. The Rb^+ and Cs^+ salts have similar parameters, and indeed are isostructural,[6] but different from the Na^+ and $[NH_4]^+$ salts. The sodium salt has the most negative isomer shift of the series and like the chloro-analogue crystallizes as the monohydrate. A dodecahedral ($SbBr_4F_3E$) environment is again observed[12] with the lone pair (E) presumably located between the heavier halogens on the opposite side to the fluorines. As with the chloro-analogue, the water molecule forms hydrogen bonds to the halogens making them less effective at withdrawing electron density from the antimony and partially accounting for the isomer shift observed. Since there is a stereochemically active lone pair in all these $M[SbXF_3]$ complexes there must be appreciable *s* character in the antimony–halogen bonds. One would then expect that the less electronegative halogen, *i.e.* bromine, would be less effective at withdrawing electron density from the antimony than chlorine and as a result the $[SbBrF_3]^-$ salts should have more negative isomer shifts than their $[SbClF_3]^-$ analogues. This is what is found, although subtle structural changes discussed earlier have a modifying influence in some instances.

In all these halide complexes the quadrupole coupling constants are positive and since eQ_g for ^{121}Sb is negative the sign of V_{ZZ} must also be negative. The principle component of the electric-field gradient must then lie in the direction of the non-bonding electron pair. Since there is some variation in Sb–X bond distances in these molecules the axial symmetry through the lone pair and the three Sb–F bonds will be destroyed. This should result in η being greater than zero. Attempts were made to fit these spectra using a variable η value. The maximum value found was 0.26 for the $Cs[SbClF_3]$ salt but in no case was there a significant improvement in the χ^2 value. We conclude that η is small or zero and that V_{ZZ} lies along the axis formed by the non-bonded electron pair and bisects the F–Sb–F angles.

Antimony trifluoride is found to form complex salts with the oxalate ion, crystallizing in the ratio of two molecules of SbF_3 to one of $[C_2O_4]^{2-}$. The Mössbauer data are summarized in the Table. The oxalate ion could link the two SbF_3 molecules either in a uni- or bidentate fashion. Since the structure of SbF_3 is known[13] and has been described as having an AX_6E monocapped octahedral arrangement, co-ordination of oxalate would result in the breaking of at least some of the fluorine bridges in the original SbF_3 structure. If all the long Sb–F contacts are broken and the oxalate ion co-ordinates in a unidentate fashion to each of two SbF_3 molecules, then the geometry about the Sb could be described as AX_4E; bidentate co-ordination would lead to an AX_5E arrangement. We have discussed in an earlier paper[3] the prevalence of the AX_6E arrangement in these antimony–fluorine systems and in this paper even higher co-ordination numbers are discussed. It therefore seems highly unlikely that the antimony environments in these complexes would be of the AX_4E type. This is borne out by the quite negative isomer shifts obtained for these materials. An AX_4E arrangement would result in a high *s* character for the Sb–X bonds and hence a lowering of the *s*-electron density. Such an arrangement is found in $K[Sb_2F_7]$ and its isomer shift is -4.82 mm s^{-1}.[2] Localization of both oxalate charges on one antimony is also unlikely, since species such as $[SbF_5]^{2-}$ are found to have isomer shifts close to, or more positive than, -5 mm s^{-1},[2,3] whereas the measured shifts for our oxalato-complexes are more negative (Table).

The parameters for the potassium salt are comparable to those for $K[SbF_4]$ (i.s. $= -5.48$ mm s^{-1}, $eQ_gV_{ZZ} = 18.6$ mm s^{-1})[2] suggesting, perhaps, that the environments are similar, *i.e.* AX_6E. No significant value for η could be found in the data analysis for this complex and as eQ_gV_{ZZ} is positive we conclude that the principle component of the electric-field gradient is again collinear with the direction of the non-bonded electron pair as discussed earlier. The more negative isomer shifts for the Rb^+ and Cs^+ salts could possibly be the result of hydrogen bonding between the water molecules and the electronegative fluorines. Such an interaction would make the fluorines less effective at withdrawing electron density from the antimony, the net result being a higher *s*-electron density at antimony and a very negative shift. However, the same arguments cannot be used to explain the large negative shift found for the sodium salt since it is not hydrated. Preliminary *X*-ray data[14] have shown that there are in fact two different antimony environments in this structure. Attempts to analyze the Mössbauer spectrum for two sites were not successful and it is clear that the two environments are not sufficiently different to allow them to be distinguished by this technique. This was found to be the case for $K[Sb_2F_7]$ and $K[SbF_4]$, both complexes having two antimony environments which could not be resolved.[1,2] This being the case it seems unwarranted to speculate further about the detailed structure of the oxalato-complexes of K^+, Rb^+, and Cs^+, where more than one antimony environment might also be present. Crystallographic analyses must be carried out on these complexes before the Mössbauer results can be analyzed in any more detail.

We thank the National Research Council of Canada for support.

[8/334 *Received*, *24th February*, 1978]

REFERENCES

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

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

[3] J. G. Ballard, T. Birchall, R. Fourcade, and G. Mascherpa, *J.C.S. Dalton*, 1976, 2409.

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

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

[6] B. Ducourant, B. Bonnet, R. Fourcade, and G. Mascherpa, *Compt. rend.*, 1976, **C283**, 203.

[7] B. Ducourant, B. Bonnet, R, Fourcade, and G. Mascherpa, *Bull. Soc. chim. France*, 1976, 1089.

[8] P. Escande, D. Tichit, B. Ducourant, and R. Fourcade, *Compt. rend.*, 1977, **C284**, 925.

[9] B. Ducourant, R. Fourcade, E. Philippot, and G. Mascherpa, *Rev. Chim. minérale*, 1976, **13**, 433.

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

[11] B. Ducourant, R. Fourcade, and G. Mascherpa, *J. Fluorine Chem.*, 1978, **11**, 149.

[12] B. Ducourant, B. Bonnet, R. Fourcade, and G. Mascherpa, *Acta Cryst.*, 1977, **B33**, 3693.

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

[14] P. Escande, D. Tichit, B. Ducourant, R. Fourcade, and G. Mascherpa, unpublished work.