Complex Formation between Antimony Trifluoride and Alkali-metal Sulphates: The *X*-Ray Crystal Structure of $K_2SO_4 \cdot SbF_3$ and Antimony-121 Mössbauer Studies of Some Related Compounds †

Thomas Birchall *
Department of Chemistry and Institute of Materials Research, McMaster University, 1280 Main Street W., Hamilton, Ontario, Canada L8S 4M1
Bernard Ducourant, Robert Fourcade, and Guy Mascherpa
Laboratoire des Acides Minéraux, Université des Sciences et Techniques du Languedoc, Place Eugéne Bataillon, 34060 Montpellier Cedex, France

The *X*-ray crystal structure of $K_2SO_4 \cdot SbF_3$ is reported. It crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 5.601(2)$, $b = 9.072(4)$, $c = 14.180(6)$ Å, and $Z = 4$ and a final $R = 0.035$. The antimony environment is that of a distorted octahedron, SbF_3O_2E, where E represents the non-bonding electron pair of Sb^{III}. The ^{121}Sb Mössbauer data of this and other $M_2SO_4 \cdot SbF_3$ complexes are interpreted in terms of SbX_5E and SbX_6E environments. In all cases the non-bonding electron pair is stereochemically active.

Antimony trifluoride is a strong fluoride-ion acceptor and a variety of fluoroantimonate(III) complexes have been examined by antimony-121 Mössbauer spectroscopy.[1-3] Oxo-anions also form complexes with SbF_3 and ^{121}Sb Mössbauer [4] and *X*-ray crystallographic studies have been reported for a number of these complexes.[5-8] This paper presents the *X*-ray crystal structure of $K_2SO_4 \cdot SbF_3$ to further extend this series. In all of these compounds the antimony(III) is in a distorted environment indicating that the non-bonding electron pair is stereochemically active. Alkali-metal sulphates form strong complexes with antimony trifluoride and in order better to understand the bonding in these complexes we have measured the ^{121}Sb Mössbauer spectra of a number of complexes formed with SbF_3. These spectra are discussed here with reference to the known structural data.

Experimental

The complex $K_2SO_4 \cdot SbF_3$ was prepared by the simultaneous dissolution of stoicheiometric quantities of K_2SO_4 and SbF_3 in water followed by slow evaporation of the solution at 20 °C. This procedure resulted in fine colourless needles which were used for the subsequent studies.

Antimony-121 Mössbauer spectra were recorded using an Elscint drive system in conjunction with a Promeda multichannel analyzer. The source was nominally 0.5 mCi $Ba^{121m}SnO_3$, purchased from New England Nuclear, and together with the sample was cooled to 80 K in a cryostat designed by B. Ducourant and manufactured by Aire Liquide. The window of the single-channel analyzer was set on the escape peak of the 37-keV (*ca.* 5.9×10^{-15} J) γ-ray. Samples contained *ca.* 15 mg Sb cm^{-2} and all isomer shifts were measured with respect to InSb at 80 K. The velocity range was calibrated periodically using a ^{57}Co source and a standard iron foil. About 10^5 counts per folded channel were accumulated and the data were computer fitted using the program described by Ruebenbauer and Birchall [9] which incorporated the full transmission-integral procedures which are necessary for the successful refinement of ^{121}Sb Mössbauer spectra.

Crystal Data.—$K_2SO_4 \cdot SbF_3$, $M = 352.95$, Orthorhombic, space group $P2_12_12_1$, $a = 5.601(2)$, $b = 9.072(4)$, $c = 14.180(6)$ Å, $U = 720.52$ Å^3, $D_m = 3.22$ g cm^{-3}, $Z = 4$, $D_c = 3.25$ g cm^{-3}, $F(000) = 656$, λ (Mo-K_α) = 0.7107 Å, and μ(Mo-K_α) = 52.95 cm^{-1}.

A preliminary examination of a single crystal using a Weissenberg camera allowed us to determine the cell parameters and establish the space group as $P2_12_12_1$. The cell parameters were refined from powder diffraction data using the method of least squares according to Norbert.[10] The observed bands and their relative intensities are given in Table 1 up to a value of $\theta = 20°$ for Cu-K_α radiation. The equivalent positions for $P2_12_12_1$ are: x, y, z; $\frac{1}{2}-x, -y, \frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}-y, -z$; $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

X-Ray Intensity Measurement.—A fine needle-like crystal of dimensions 0.20 × 0.05 × 0.02 mm was mounted on a fibre and *h,k,l* intensity measurements obtained by means of an automatic Nonius CAD4 diffractometer, until the value of $(\sin\theta)/\lambda = 0.70$. In view of the small size of the crystal, absorption corrections were not made.

Structure Determination and Refinement.—The location of the antimony atom in the unit cell was obtained from a three-dimensional Patterson synthesis using 1 016 reflections previously corrected for Lorentz and polarization factors. Successive refinements by a difference-Fourier synthesis allowed the other atoms to be located. Using isotropic thermal parameters R was 0.055 ($R = \Sigma|kF_o - |F_o||/\Sigma kF_o$ and $k = \Sigma|F_c|/\Sigma|F_o|$). A final refinement with varying anisotropic thermal parameters gave R 0.035. The final difference synthesis showed peak maxima corresponding to 2 e Å^{-3} in the neighbourhood of the antimony atoms. Programs used in the refinement of the structure were DATAP2, DRF, LINUS, DISTAN, and ORTEP.[11] Scattering factors used in the calculation of F_o were those of Doyle and Turner.[12] Table 2 summarizes the final positional co-ordinates of the atoms.

Discussion

The Structure.—A representation of the structure in the 1 0 0 plane is shown in Figure 1 where the SbF_3 and $[SO_4]^{2-}$ units are clearly distinguishable. Each antimony of the SbF_3 is bonded to two sulphates by Sb–O bonds of intermediate length. Each of the two sulphate groups have the same relationship to two antimony atoms. The groups form a helix which stretches out along the *z* axis and this is represented in Figure 2. The helices, of formula $(SbF_3 \cdot SO_4)_x^{2x-}$, are

† *Supplementary data available* (No. SUP 23402, 10 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Powder pattern data for $K_2SO_4 \cdot SbF_3$

h k l	$d_{calc.}$/Å	$d_{obs.}$/Å	Intensity	h k l	$d_{calc.}$/Å	$d_{obs.}$/Å	Intensity
0 1 1	7.642	7.622	39	1 2 2	3.156	3.155	17
0 0 2	7.090	7.086	43	1 0 4	2.995	2.995	10
0 1 2	5.586	5.562	20	0 3 1	2.957	2.957	13
1 0 1	5.209	5.205	1	1 1 4	2.844	2.841	7
1 1 0	4.766	4.766	2	1 2 3	2.825	2.825	7
1 1 1	4.517	4.525	43	2 0 0	2.800	2.791	77
0 2 1	4.320	4.350	2	0 2 4	2.793		
0 1 3	4.192	4.179	10	0 1 5	2.707	2.710	22
1 1 2	3.955	3.958	4	1 3 1	2.615	2.615	10
0 2 2	3.821	3.827	100	0 3 3	2.547	2.544	33
0 0 4	3.545	3.550	5	1 2 4	2.500	2.497	10
1 2 0	3.525	3.525	5	0 2 5	2.404	2.402	24
1 2 1	3.421	3.421	31	0 0 6	2.363	2.363	8
1 1 3	3.356	3.353	42	0 3 4	2.301	2.301	14
0 1 4	3.302	3.302	20				

Table 2. Atomic co-ordinates

Atom	X/a	Y/b	Z/c
Sb	0.473(1)	0.057 76(6)	0.022 44(4)
K(1)	0.020 0(4)	0.313 6(2)	0.388 9(1)
K(2)	0.495 7(4)	0.490 7(2)	0.191 2(1)
S	0.022 3(4)	0.206 4(2)	0.161 5(1)
F(1)	0.246(1)	0.077 3(6)	0.461 2(4)
F(2)	0.215(1)	0.573 6(7)	0.035 4(5)
F(3)	0.461(1)	0.906 2(6)	0.124 3(4)
O(1)	0.069(1)	0.120 3(8)	0.075 7(5)
O(2)	0.241(1)	0.224 5(9)	0.214 2(5)
O(3)	0.070(2)	0.852 0(8)	0.368 4(5)
O(4)	0.844(2)	0.134(2)	0.218 1(8)

Table 3. Environments of the potassium atoms and of the sulphate group (distances in Å, angles in degrees)

K(1)–F(1)	2.693(6)	S–O(4)	1.44(1)
K(1)–F(2)	2.750(7)	S–O(2)	1.444(9)
K(1)–F(2)	2.762(7)	S–O(1)	1.469(9)
K(1)–F(1)	2.802(6)	S–O(3)	1.480(7)
K(1)–F(3)	2.828(6)		
K(1)–O(1)	2.871(9)	O(1)–S–O(2)	109.7(6)
K(1)–O(2)	2.884(9)	O(1)–S–O(3)	107.5(4)
K(1)–F(3)	3.032(6)	O(1)–S–O(4)	110.0(6)
K(1)–O(4)	3.081(11)	O(2)–S–O(3)	110.0(4)
		O(2)–S–O(4)	110.0(6)
K(2)–O(4)	2.639(11)	O(3)–S–O(4)	109.0(5)
K(2)–F(1)	2.717(6)		
K(2)–F(3)	2.737(6)		
K(2)–F(2)	2.813(7)		
K(2)–O(2)	2.849(9)		
K(2)–O(3)	2.866(6)		
K(2)–O(2)	2.912(9)		

held together in the crystal by co-ordination of fluorine and oxygen atoms to the two potassium cations K(1) and K(2). One of the potassium cations is nine-co-ordinate while the other is seven-co-ordinate. The main interactions to the potassium are listed in Table 3 along with the bond lengths and angles in the sulphate anions. The sulphate groups are not distorted by their co-ordination to the antimony. This is in contrast to the situation in $MSbF_2 \cdot SO_4$ (M = Rb or Cs) whose significant distortion of the sulphate tetrahedron is observed.[13]

Of most interest is the environment about the antimony (Figure 3) where, based on the criteria defined by Alcock,[14] there are three short Sb–F bonds and two longer Sb–O bonds. Based upon an analytical model developed by Fourcade and Mascherpa [15] for co-ordination polyhedra about atoms having an oxidation state two less than the group maximum, the geometry about the Sb^{III} must be considered as being of the AX_3Y_2E type.[16] From an examination of Figure

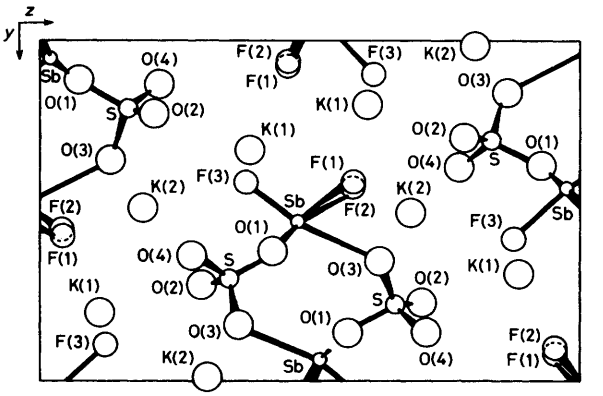

Figure 1. Projection of the structure of $K_2SO_4 \cdot SbF_3$ on the 1 0 0 plane

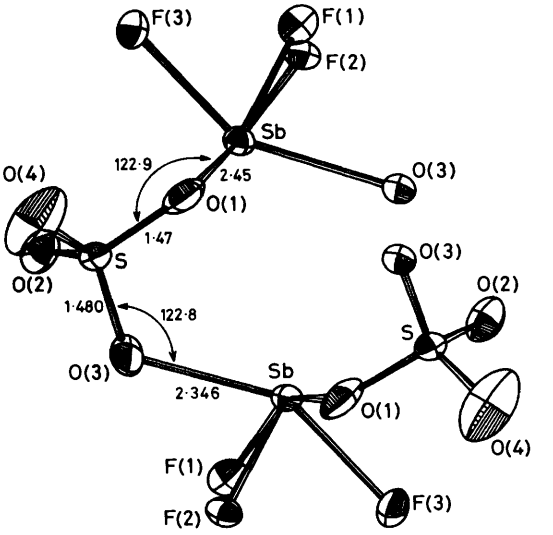

Figure 2. A representation of a fraction of the $(SbF_3 \cdot SO_4)_x^{2x-}$ helix

Table 4. Mössbauer data for some alkali-metal sulphate complexes with antimony trifluoride

Compound	δ	eQV_{zz}	Γ	T_A	χ^2/d	M [a]
	mm s^{-1}					
$Na_2SO_4 \cdot SbF_3$	−5.68 ± 0.01	15.62 ± 0.12	1.16 ± 0.03	3.79 ± 0.10	2.20	0.22
$K_2SO_4 \cdot SbF_3$	−5.53 ± 0.02	14.84 ± 0.18	1.41 ± 0.04	1.90 ± 0.05	2.17	0.42
$K_2SO_4 \cdot 2SbF_3$	−5.20 ± 0.01	16.89 ± 0.15	1.26 ± 0.04	1.84 ± 0.05	2.35	0.38
$RbSbF_2 \cdot SO_4$	−6.41 ± 0.01	16.38 ± 0.17	1.64 ± 0.04	2.14 ± 0.05	2.46	0.38
$CsSbF_2 \cdot SO_4$	−6.18 ± 0.02	17.71 ± 0.16	1.55 ± 0.04	1.92 ± 0.05	2.33	0.38
InSb	0.0 ± 0.01	0.0	1.05 ± 0.04	2.68 ± 0.02	1.27	0.34
SbF_3 [b]	−6.29	19.1	—	0.75	1.25	0.23

[a] Ref. 3. [b] Misfit defined as in S. L. Ruby, 'Mössbauer Effect Methodology,' eds. I. J. Gruverman and C. W. Seidel, Plenum, New York, 1973, vol. 8, p. 263.

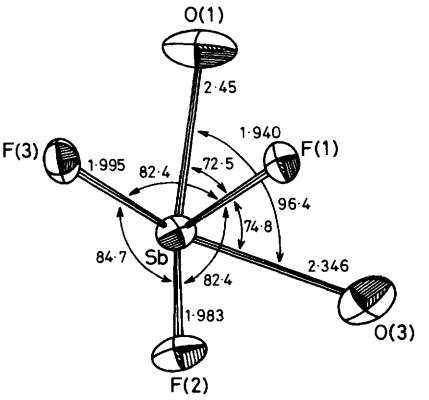

Figure 3. A representation of the SbF_3O_2E octahedron. Additional angles are O(1)SbF(3) 84.5 and O(3)SbF(2) 84.0°; in the basal plane the Sb lies 0.371 Å below while O(1), F(3), F(2), and O(3) lie 0.105, 0.072, 0.123, and 0.071 Å above the plane

3 it is apparent that the non-bonding electron pair of Sb^{III} must occupy the vacant position of the octahedron approximately opposite to Sb–F(1), the shortest antimony–fluorine bond. The longest antimony–fluoride bond, Sb–F(3) is opposite to the shortest antimony–oxygen bond, Sb–O(3), with the bonds of intermediate length also being opposed. The differences observed in the bond angles about the antimony are just what one would expect from an SbF_3O_2E arrangement based on the ideas of Gillespie.[16]

Comparison of this structure with $K_2SO_4 \cdot 2SbF_3$ [7] and $Na_2SO_4 \cdot SbF_3$ [8] shows some interesting differences. The average Sb–F primary contact distance is 1.973 Å in the title compound compared to an average value of 1.95 Å in the related compounds.[7,8] More significant differences are found in the Sb–O distances which are 2.346 and 2.45 Å in $K_2SO_4 \cdot SbF_3$ while the average Sb–O distance in the other two compounds is longer at 2.50 Å.[7,8] This lengthening of the Sb–O distances is undoubtedly caused by the additional fluorine contact to antimony in the last two compounds. This occurs on the side of the polyhedron away from the three short Sb–F bonds and is 2.972 Å in $Na_2SO_4 \cdot SbF_3$ and 2.799 Å in $K_2SO_4 \cdot 2SbF_3$. This lengthening of the Sb–O bonds and the greater distortion of the antimony polyhedron is necessary in order to accommodate this additional fluorine contact. There are no long Sb–F interactions of this kind in the title compound.

^{121}Sb *Mössbauer Spectra.*—Antimony-121 spectra were recorded for the compounds discussed above together with two related compounds $MSbF_2 \cdot SO_4$ (M = Rb or Cs). These compounds all have a high recoil-free fraction and good spectra could be obtained at liquid-nitrogen temperature. The χ^2/d values are somewhat on the high side for the computer fits but the misfit values indicate that these spectra are of good quality. These spectra showed a broad absorption envelope to high negative velocity of the source with the envelope tail at negative velocity relative to the peak minimum. This indicates that the quadrupole coupling constant is positive and since eQ for ^{121}Sb is negative the sign of V_{zz} must also be negative. The negative isomer shift indicates a high s-electron density at the antimony, since $\delta R/R$ for ^{121}Sb is negative. This is typical for antimony(III) fluorine complexes [1–4] where the non-bonded electron pair is stereochemically active. We have summarized the Mössbauer data in Table 4 and included data for SbF_3 for comparison.

Table 4 shows that the sodium and potassium compounds have isomer shifts which are less negative than those for the rubidium and caesium compounds and antimony trifluoride. This indicates a significantly lower s-electron density in the sodium and potassium compounds compared to the others. This is either the result of an increased participation of the antimony(III) 5s electrons in the bonding or increased shielding of the s electrons from the nuclear charge by an increase in the strength of the secondary interactions compared to the situation in SbF_3. The latter factor is probably the more important one since the average primary Sb–F distance is shorter in SbF_3 than in the compounds discussed here, while the secondary contacts to oxygen are quite strong in the sulphate–antimony trifluoride cases. The increased s participation may be significant only for $K_2SO_4 \cdot SbF_3$ since this is the only compound in which there are only five bonding contacts to antimony. Here the geometry can be described as being AX_5E rather than AX_6E.

The quadrupole coupling constants are not as negative as in SbF_3 indicating a more regular environment. This again is a consequence of the longer primary interactions and shorter secondary ones. The sign of the coupling constant indicates that V_{zz} is dominated by the stereochemical activity of the non-bonding electron pair of Sb which must have some 5p character and that the principal component of the electric field gradient tensor must be through the lone-pair orbital and the cone made by the three primary Sb–F bonds. The $K_2SO_4 \cdot SbF_3$ compound has the smallest quadrupole coupling constant and X-ray crystallography shows that the antimony indeed does have the most regular structure, *i.e.* closest to octahedral. The most distorted antimony environment of these three compounds occurs in $K_2SO_4 \cdot 2SbF_3$ which shows the largest variation in Sb–F bond lengths, from 1.917 to 1.963 Å, and has the shortest secondary fluorine contact at 2.799 Å. It should also be pointed out that in this compound there are also two crystallographically different antimony environments and that the Mössbauer spectra were fitted to only one absorption envelope.

The rubidium and caesium salts have a different composition from that of the sodium and potassium compounds even though the method of preparation was the same.[13] They have significantly more negative isomer shifts than the sodium and potassium salts indicating a much larger *s*-electron density at the antimony. In $RbSbF_2{\cdot}SO_4$ there are only two fluorine contacts to the antimony, 1.91 and 1.93 Å, and this is very similar to the situation in other fluoroantimony complexes containing an $[SbF_2]^+$ unit.[17] In these latter compounds the $[SbF_2]^+$ is co-ordinated by two additional fluorines from each of two $[SbF_6]^-$ anions to give a $[Sb_3F_{14}]^-$ anion and the co-ordination number is completed by four much longer Sb^{III}–F interactions. These interactions are however rather weak and result in rather large negative isomer shifts ranging from -6.5 to -7.6 mm s^{-1}.[17] The implication for the $MSbF_2{\cdot}SO_4$ compounds is that the SbF_2 unit here has much less positive charge residing on the antimony thus accounting for the somewhat less negative isomer shifts.

A further difference between the $[SbF_2]^+$-containing compounds is that the Sb^{III} in the $[Sb_3F_{14}]^-$ anions all have very large asymmetry parameters whereas in the $MSbF_2{\cdot}SO_4$ compounds the spectra were fitted with η values which were not significantly different from zero. It is clear then that we cannot consider the $[SbF_2]^+$ unit in the sulphate complexes to exist as a cation and that other strong interactions must occur to give the antimony a pseudo-three-fold symmetry. This is indeed the situation and a Sb–O contact at 2.11 Å comprises the third strong bond to the Sb^{III} in $RbSbF_2{\cdot}SO_4$. Three other longer oxygen contacts complete the SbX_6E geometry and a quite distorted antimony environment. The observed quadrupole coupling constant is large and negative indicating that the lone-pair axis is coincident with the pseudo-three-fold axis through the SbF_2O cone. The caesium salt has a less negative isomer shift but a more negative quadrupole coupling constant. This suggests that the primary SbF_2–O contact is stronger in this compound than in the rubidium case while the secondary oxygen contacts are correspondingly weaker.

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada are thanked for funds which enabled T. B. to participate in the Canada–France Cultural Exchange Scheme. This work was carried out at U.S.T.L. Montpellier.

References

1 T. Birchall and B. Della Valle, *Can. J. Chem.*, 1971, **49**, 2808.
2 J. D. Donaldson, J. T. Southern, and M. J. Tricker, *J. Chem. Soc., Dalton Trans.*, 1972, 2637.
3 J. G. Ballard, T. Birchall, R. Fourcade, and G. Mascherpa, *J. Chem. Soc., Dalton Trans.*, 1976, 2409.
4 T. Birchall and B. Ducourant, *J. Chem. Soc., Dalton Trans.*, 1979, 131.
5 P. Escande, D. Tichit, B. Ducourant, R. Fourcade, and G. Mascherpa, *Ann. Chim. (Paris)*, 1978, **3**, 117.
6 M. Bourgault, R. Fourcade, B. Ducourant, and G. Mascherpa, *Rev. Chim. Miner.*, 1979, **16**, 151.
7 B. Bonnet, B. Ducourant, R. Fourcade, and G. Mascherpa, *Rev. Chim. Miner.*, 1980, **17**, 88.
8 M. Bourgault, B. Ducourant, B. Bonnet, and R. Fourcade, *J. Solid State Chem.*, 1981, **36**, 183.
9 K. Ruebenbauer and T. Birchall, *Hyperfine Interact.*, 1979, **7**, 125.
10 A. Norbert, *Rev. Chim. Miner.*, 1969, **6**, 687.
11 DATAP2, P. Coppens, L. Lizerowitz, and P. Robinovich; DRF, A. Zalkin; LINUS, P. Coppens and W. C. Hamilton; DISTAN, A. Zalkin; all adapted by E. Philippot.
12 P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, 1968, **24**, 390.
13 M. Bourgault, Thesis, Maitre ès Sciences, Université des Sciences et Techniques du Landguedoc, 1980.
14 N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.
15 R. Fourcade and G. Mascherpa, *Rev. Chim. Miner.*, 1978, **15**, 295.
16 R. J. Gillespie, ' Molecular Geometry,' Van Nostrand Reinhold, Princeton, New Jersey, 1972.
17 J. F. Ballard, T. Birchall, R. J. Gillespie, E. Maharajh, D. Tyrer, and J. E. Vekris, *Can. J. Chem.*, 1978, **18**, 2417.

Received 26*th February* 1982; *Paper* 2/350