The Antimony-121 Mössbauer Effect. Part II.[1] The Spectra of Some Halide Complexes of Antimony(III)

By **J. D. Donaldson,*** **J. T. Southern,** and **M. J. Tricker,** Department of Chemistry, Chelsea College, University of London, Manresa Road, London SW3 6LX

The antimony-121 Mössbauer parameters of a number of fluoride, chloride, bromide, and iodide complexes of antimony(III) are reported. The chemical isomer shift data are discussed in terms of the formation of complexes from the parent antimony(III) halide. The magnitudes and signs of eQV_{zz} are interpreted on the basis of the known structures and of the likely distribution of electron density around the antimony nuclei.

THE ^{121}Sb Mössbauer parameters of a number of halide complexes of antimony(III) have recently been reported.[1-5] The data for a number of hexahalogenoantimonates(III) [1-3] and intervalence compounds [1-3] containing chloride and bromide have been discussed. We have shown [1] that the increase in the number of Sb–X bonds in materials of the type $M_3Sb_2X_9$ ($M = Cs$ and Rb; $X = Cl$, Br, and I) and $Co(NH_3)_6SbX_6$ ($X = Cl$ and Br) compared with their parent trihalides leads to a decrease in the Mössbauer chemical shift. Birchall *et al.*[4] have presented data on a number of complex antimony(III) fluorides and have discussed these in terms of known crystal structures. We now report the ^{121}Sb Mössbauer parameters for complexes of the type SbX_4^- ($X = Cl$, Br, and I), $SbCl_3Br^-$, and $SbBr_3X^-$ ($X = Cl$ and I) and for a number of additional antimony(III) fluoride complexes. Most of the data for the chloride, bromide, and iodide complexes (Table 1) and for the fluoride complexes (Table 2) are presented for the first time.

Chloride, Bromide, and Iodide Complexes.—The chemical shifts (δ) for the SbX_4^- derivatives increase in the order $Cl < Br < I$, *i.e.*, the order expected for increasing covalent character in the order $Cl < Br < I$. Two factors could influence the chemical shift parameters: (*a*) the *s*-electron character of the non-bonding orbital and (*b*) the *s*-electron density associated with the Sb contribution to the bonding orbitals. Electronegativity arguments predict that the electron density withdrawn from Sb orbitals by halide ions should increase in the order $I < Br < Cl$. If the electrons being withdrawn were *s*-electrons [6] then the chemical shifts would be ordered $SbCl_4^- > SbBr_4^- > SbI_4^-$; this would also be the order if Sb *s*-electrons were shielded by π-bonding effects, if these effects were important. The fact that the opposite ordering is observed suggests that *p*-electrons are being withdrawn from Sb and that the contribution from the *s*-electron character of the lone-pair is dominant in determining the shift. $SbCl_4^-$ would then have the highest *s*-character for the non-bonding orbital. The shifts for the chloride and bromide complexes fall between

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the values[1] for the corresponding SbX_3 and $M_3Sb_2X_9$ materials (Table 1) and also show positive quadrupole coupling constants. The chemical shift for $Bu^n{}_4NSbI_4$ is however greater than that for SbI_3 and has a small negative quadrupole coupling constant. These parameters can be rationalised in terms of the known and probable structures of the SbX_4^- species. The crystal structure of $(pyH)SbCl_4$ is known;[7] It contains two Sb–Cl distances of 2·38 Å, two of 2·64 Å, and two of 3·12 Å and Cl–Sb–Cl bond angles close to 90°. The two 3·12 Å distances are *cis* to each other and, if these are considered to be non-bonding, the antimony is four-co-ordinated and the $SbCl_4^-$ species has approximately C_{2v} symmetry. If we regard the $SbCl_4^-$ ion as being based on a trigonal bipyramidal distribution of electron-pairs around Sn, the 2·38 and 2·64 Å distances are in equatorial and axial positions respectively. $SbCl_3$ has Sb in a pyramidal three-co-ordinated environment with Sb–Cl distances[8] of 2·36 Å. The increases in co-ordination and in Sb–X bond lengths in going from $SbCl_3$ to $SbCl_4^-$ are thus compatible with an increased electrostatic character for the Sb–Cl bonds in $SbCl_4^-$ and with the chemical-shift data which suggest a greater *s*-electron density at the Sb nucleus for $SbCl_4^-$.

TABLE 1

	δ/mm s^{-1} ±0·1	eQV_{zz}/mm s^{-1} ±1·0	Full width at half peak height/mm s^{-1}	Resonance dip (%)
Et_4NSbCl_4	−7·47	+10·6	3·3	9
$(pyH)SbCl_4$	−7·98	+ 9·1	2·2	10
$(pyH)SbBr_4$	−7·25	+11·5	3·2	15
$Bu^n{}_4NSbI_4$	−6·88	−3·3 †	3·4	4
$Bu^n{}_4NSbCl_3Br$	−6·78	−6·7	3·7	8
Et_4NSbBr_3Cl	−7·93	−4·9	3·2	9
$Bu^n{}_4NSbBr_3I$	−8·10	+5·3	2·9	4
$SbCl_3$ *	−5·24	12·2	—	—
$SbBr_3$ *	−5·34	9·4	—	—
SbF_3 *	−6·0	19·6	—	—
SbI_3*	−7·34	—	—	—
InSb	+8·5	—	—	—

* Ref. 6.

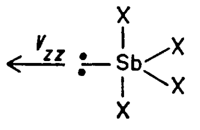
† eQV_{zz} For this material is too small to be certain of the sign.

TABLE 2

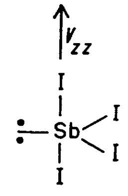
	δ/mm s^{-1} ±0·1	eQV_{zz}/mm s^{-1} ±1·0	Full width at half peak height/mm s^{-1}	Resonance dip (%)
Na_2SbF_5	−4·75	−8·3	3·3	13·7
K_2SbF_5	−4·09	+14·3	3·6	17·5
Cs_2SbF_5	−4·42	+14·8	3·2	7·2
$(NH_4)_2SbF_5$	−4·52	+13·5	3·9	12·2
$NaSbF_4$	−5·48	+18·6	3·9	14·5
$KSbF_4$	−5·48	+18·8	3·8	15·5
$CsSbF_4$	−5·61	+18·6	3·4	12·8
$(NH_4)SbF_4$	−5·6	+14·2	3·9	10·1
KSb_2F_7	−4·82	+16·7	3·0	7·3
$CsSb_2F_7$	−5·50	+18·6	4·0	14·7
$NH_4Sb_2F_7$	−5·33	+17·7	3·8	8·1
InSb	+8·5	—	—	—

The similarity between the Mössbauer parameters for the two complexes Et_4NSbCl_4 and $(pyH)SbBr_4$ and those of $(pyH)SbCl_4$ suggest that the structures of the anions in all three materials are similar. It therefore seems likely that both Et_4NSbCl_4 and $(pyH)SbBr_4$ contain SbX_4^- anions similar to that of $SbCl_4^-$ in $(pyH)SbCl_4$ and that there is an increase in the average Sb–X bond length in these materials compared with their parent trihalide. This interpretation is consistent with an i.r. and Raman study[9] of the derivatives of the $SbCl_4^-$ and $SbBr_4^-$ ions, in which it was suggested that all of them contained SbX_4^- species with C_{2v} symmetry arising from sp^3d hybridisation of the Sb orbitals with a lone-pair orbitial in an equatorial position.

The quadrupole coupling constants (eQV_{zz}) for the $SbCl_4^-$ and $SbBr_4^-$ derivatives are positive. Since eQ for ^{121}Sb is negative, V_{zz} must be negative in these materials. In the interpretation of tin(II) Mössbauer data, it has been suggested[10] that the lone-pair orbital provides a dominant negative contribution to the principal component (V_{zz}) of the electric field gradient. Consequently the observed positive values for eQV_{zz} for the $SbCl_4^-$ and $SbBr_4^-$ species are compatible with a dominant negative contribution from a *p*-electron excess in the antimony lone-pair. The direction of the principal component of the field gradient would thus be through the lone-pair as shown in (I).



(I)



(II)

The chemical shift of $Bu^n{}_4NSbI_4$ is greater than that of SbI_3 but this is consistent with an increase in the co-ordination number from four in SbI_4^- to six in SbI_3. The value of eQV_{zz} found for $Bu^n{}_4NSbI_4$ is small. In $SbCl_4^-$ there should be a transfer of electron density from Sb to the ligand and therefore the lone-pair *p*-(or *d*-)electron density should provide the dominant contribution to V_{zz}. The observed positive value for eQV_{zz} is consistent with this view. The chemical-shift data suggest that the lone-pair in SbI_4^- has more *p*-character than in $SbCl_4^-$; why then is a large negative V_{zz} not observed? We suggest that this is because the equatorial Sb–I bonds are more covalent than the axial bonds. The electron density in the direction of the equatorial Sb–I bonds will have more Sb *p*-character and, in view of the small value observed for eQV_{zz}, it seems likely that the Sb *p*-character in the lone pair and in the equatorial bonds is nearly equal. It is then possible for the direction of V_{zz} to be coincident with the

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axial direction as shown in (II) and this could result in a change of sign for eQV_{zz}.

It has been reported[9] that the vibrational spectra of $Bu^n_4NSbI_4$ are not consistent with a structure of C_{2v} symmetry but that the spectra suggest a monomeric rather than a polymeric structure. As the chemical shift for this material is in the region expected for 4-co-ordinated Sb, the Mössbauer data are also consistent with a 4-co-ordinated antimony environment.

The chemical shifts for the mixed halide complexes are also in the region expected for 4-co-ordinated antimony and this is in agreement with the interpretation[11] of their i.r. and Raman spectra. From the signs of the quadrupole coupling constants we suggest that the direction of V_{zz} is through the lone-pair in $Bu^n_4SbBr_3I$ but in the axial direction along a more polar bond in the $SbCl_3Br^-$ and $SbBr_3Cl^-$ derivatives.

The nature of the cation present in a complex is known to influence the Mössbauer chemical shifts[12] for tin(II) materials and similar effects must be operating in the Sb derivatives [*e.g.*, (pyH)$SbCl_4$ and Et_4NSbCl_4]. More data will, however, have to be accumulated on a wider range of complexes before detailed conclusions on this effect can be drawn.

The data for the complex antimony(III) fluorides (Table 2) can be described in terms of known structural information.[4,13-16] Birchall *et al.* have previously discussed[4] the data for $MSbF_4$ (M = Na and K), KSb_2F_7, and K_2SbF_5.

The M_2SbF_5 complexes (M = K, Cs, and NH_4) are isostructural[13] and contain discrete SbF_5^{2-} ions in which the antimony is surrounded by five fluoride ions but in which an octahedron of electron-pairs is completed by a lone-pair orbital. The Mössbauer parameters for these complexes are similar, in agreement with the series being isostructural. The positive values for the quadrupole coupling constants for these materials are consistent with a dominant contribution to the principal component of the electric-field gradient by the lone pair. The powder data for Na_2SbF_5 show that it is not isostructural with the other M_2SbF_5 materials. Although the chemical shift for this complex is not unusual the small value for its quadrupole coupling constant shows that the Sb environment in Na_2SbF_5 must be different from that in the isostructural M_2SbF_5 series.

The Mössbauer parameters for complexes of the type $MSbF_4$ (M = Na, K, Cs, and NH_4) are similar suggesting that the Sb environments are similar in all these materials. $NaSbF_4$ and $KSbF_4$ are reported[4] to have polymeric structures containing Sb in a five-co-ordinated environment with a lone-pair taking up the sixth octahedral position. There is every reason to suppose that the Cs and NH_4 derivatives contain similar Sb environments although the powder data for the SbF_4^- complexes do not indicate an isostructural series. The positive values of the quadrupole coupling constants for these complexes are again consistent with a dominant contribution from *p*-electron density in the lone-pair orbital.

Although the Mössbauer data for the MSb_2F_7 complexes (M = K, Cs, and NH_4) have been fitted to one site, the fit is not satisfactory and this could be due to the presence of two Sb sites as suggested[4] by Birchall *et al.*

In contrast to the data for the other complex halides, the chemical shifts of the complex fluorides are all greater than that for the parent trihalide. This means that there cannot simply be a transfer of Sb *p*-electron density to fluorine, but that there must also be a considerable usage of Sb 5*s* electrons in the bonding. This can arise either from the Sb wavefunctions involved in the Sb–F bonds being largely *s* in character or from electrostatic *s*–*p* mixing.[12] The increase in chemical shift with the number of F atoms bonded to Sb (*e.g.*, SbF_5^{2-} and SbF_4^-) is also consistent with these arguments. Such effects would also mean a low *s*- and therefore a high *p*-character for the non-bonding orbital. Since it seems that the non-bonding electron pair provides the dominant contribution to the field gradient, its high *p*-character would give rise to the large values of the quadrupole coupling constants observed. In this respect the data for the complex antimony fluorides are similar to those for the complex tin(II) fluorides.[11]

EXPERIMENTAL

Details of the Mössbauer spectrometer have been reported.[1] Measurements were made with both source and absorber at 4·2 K. Absorbers were prepared by mixing a finely ground sample (containing 10 mg of Sb) with grease and spreading the mull over 1 cm^2 of aluminium foil. The spectra were computer-fitted by a least-squares procedure to the sum of eight Lorentzian peaks as previously reported.[1]

All isomer shifts are quoted with respect to InSb at 4·2 K as zero isomer shift. The errors quoted in Tables 1 and 2 are experimental errors not simply the small errors arising from computer fitting.

Preparation of the chloride, bromide, and iodide complexes is outlined in refs. 9 and 11. The fluorides were prepared by the methods described by Byström.[13-16] Antimony analyses were in good agreement with the formulae given.

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