An Antimony-121 Mössbauer Spectroscopic Study of Some Dihalogeno(halogen-substituted benzene-1,2-diolato)antimonate(III) Complexes and of Some Tetrabromoantimonates(III)

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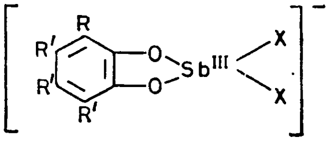
The ^{121}Sb Mössbauer parameters are reported for a series of heterocyclic base salts of tetrabromoantimonate(III) and dihalogeno(halogen-substituted benzene-1,2-diolato)antimonate(III) anions. A close relationship is found between chemical isomer shifts (δ) and the number of short bonds fomed by Sb. It is shown that the shift is determined by the length of the shortest bonds and their number rather than by the total number of bonding interactions formed by the Sb^{III} in the highly distorted environments of the complexes. The larger negative shifts for the $SbBr_4^-$ complexes compared with $SbBr_3$ is consistent with a decrease in the number of short Sb–Br bonds and hence in the covalent character of the Sb–Br interactions. The shift for the benzenediolatoantimonates(III) is shown to be dominated by the presence of two short Sb–O bonds. It is suggested that the size of the ^{121}Sb quadrupole-coupling constant (eQV_{zz}) in these antimony(III) materials depends not only on the p-electron excess in the lone-pair orbital but also on the details of the use of Sb p electrons in bond formation.

A WIDE range of solid complexes can be obtained by treating antimony(III) halides with halogen-substituted catechols in the presence of heterocyclic bases. The



(I)

X = Cl or Br
R = H, Cl, or Br
R′ = Cl or Br

complexes are all formally derivatives of the dihalogeno(substituted benzene-1,2-diolato)antimonate(III) anion (I) together with the cation of a heterocyclic base, *e.g.* pyridinium.

The ^{121}Sb Mössbauer parameters of a number of these complexes together with some of the heterocyclic base derivatives of the tetrabromoantimonate(III) anion have been obtained and are discussed in terms of known and likely structures of the complex antimony(III) species.

TABLE 1

Antimony-121 Mössbauer data (mm s^{-1}) for antimony(III) compounds studied in this work [a]

	Compound	δ [b] ±0.1	eQV_{zz} ±0.5
(1)	$[C_5H_5NH][SbCl_2(O_2C_6Cl_4)]$	−15.6	+16.48
(2)	$[2\text{-}CH_3C_5H_4NH][SbCl_2(O_2C_6Cl_4)]$	−16.0	+16.27
(3)	$[3\text{-}CH_3C_5H_4NH][SbCl_2(O_2C_6Cl_4)]$	−15.8	+17.62
(4)	$[4\text{-}CH_3C_5H_4NH][SbCl_2(O_2C_6Cl_4)]$	−14.3	+15.95
(5)	$[C_5H_5NH][SbBr_2(O_2C_6Br_4])$	−15.4	+16.43
(6)	$[2\text{-}CH_3C_5H_4NH][SbBr_2(O_2C_6Br_4)]$	−17.0	0
(7)	$[2\text{-}CH_3C_5H_4NH][SbCl_2(O_2C_6HCl_3)]$	−15.5	+16.30
(8)	$[C_5H_5NH][SbBr_2(O_2C_6HBr_3)]$	−16.8	0
(9)	$[2\text{-}CH_3C_5H_4NH][SbBr_4]$	−18.1	0
(10)	$[3\text{-}CH_3C_5H_4NH][SbBr_4]$	−18.61	0
(11)	$[C_9H_7NH][SbBr_4]$	−18.82	0
(12)	$[iso\text{-}C_9H_7NH][SbBr_4]$	−17.78	0

[a] All measured at 4.2 K; the $\Delta R/R$ value is negative for ^{121}Sb. [b] Relative to $Ba^{121}SnO_3$ source.

EXPERIMENTAL

The solid complexes (I) were precipitated by addition of the appropriate heterocyclic base to a 1 : 1 solution of antimony(III) halide and substituted catechol in methanol. The precipitates were recrystallised from acetonitrile and the final crystalline products gave analysis results consistent with the formulae in Table 1.

The tetrabromoantimonates(III) were precipitated by addition of the appropriate heteroaromatic base to a solution of antimony(III) bromide in hydrobromic acid and were crystallised from the hot mother-liquor. They were finally recrystallised from acetonitrile and analysed to give results consistent with the formulae in Table 1.

TABLE 2

Antimony-121 Mössbauer data from the literature

Compound	δ [a]/mm s^{-1}	eQV_{zz}/mm s^{-1}	T/K	Ref.
$SbCl_3$	−13.7	+12.2	4.2	*b*
$SbBr_3$	−13.8	+9.4	4.2	*b*
$[C_5H_5NH][SbCl_4]$	−16.5	+9.1	4.2	*c*
$[C_5H_5NH][SbBr_4]$	−15.8	+11.5	4.2	*c*
$[NBu^n_4][SbBr_4]$	−16.65	+4.5		*d*
Sb_2O_3	−11.3	+18.8	4.2	*b*
Antimony(III) oxide glass	−11.4 to −11.6	16.5—18.8	4.2	*e*
$KSbC_4H_4O_7\cdot0.5\ H_2O$	−11.7		80	*f*

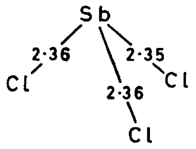
[a] Relative to $Ba^{121}SnO_3$ source. [b] L. H. Bowen, J. G. Stevens, and G. G. Long, *J. Chem. Phys.*, 1969, **57**, 2016. [c] J. D. Donaldson, J. T. Southern, and M. J. Tricker, *J.C.S. Dalton*, 1972, 2637. [d] J. G. Ballard, T. Birchall, J. B. Milne, and W. D. Moffett, *Canad. J. Chem.*, 1974, **52**, 2375. [e] A. Paul, J. D. Donaldson, and M. J. K. Thomas, *J. Mater. Sci.*, 1977, **12**, 219. [f] S. L. Ruby, G. M. Kalvius, R. E. Snyder, and G. B. Beard, *Phys. Rev.*, 1966, **148**, 176.

The ^{121}Sb Mössbauer spectra were obtained and curve fitted by methods described previously.[1]

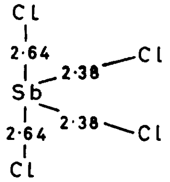
RESULTS AND DISCUSSION

The ^{121}Sb Mössbauer parameters for eight of the benzene-1,2-diolato-complexes and for four tetrabromoantimonates(III) described in this work are listed in Table 1. They may be compared with the data for some other antimony(III) compounds in Table 2.

Because $\Delta R/R$ for ^{121}Sb is negative, the chemical isomer shifts (δ) for the tetrabromoantimonates(III), which have large negative values, are indicative of the presence of antimony(III). These shifts are, moreover, more negative than that for $SbBr_3$ (—13.8 mm s^{-1}) and are similar to those observed in the formation of $SbCl_4^-$ from $SbCl_3$. The reasons for the increase in negative shift on complex formation are well illustrated by comparison of the data for $SbCl_3$ and $[C_5H_5NH][SbCl_4]$ both of which are of known crystal structure. The more negative shift obtained for $[C_5H_5NH][SbCl_4]$ is consistent with the increase in average Sb–Cl bond length in going from $SbCl_3$ (II) to the tetrachloro-anion (III). The increase in negative shift, which is associated with complex formation, leads to an increase in the average antimony–ligand bond lengths, an increase in the electrostatic character of the bonding, and hence more negative chemical isomer shifts as the Sb *s*-electron density moves towards the $Sb^{3+}(5s^2)$ configuration.



(II)



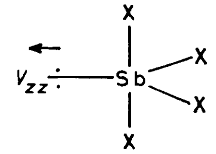
(III)

It appears to be a general feature in antimony(III) chemistry that the number of short bonds and their bond lengths, rather than the total number of bonds, largely determines the use of the Sb *s*-electrons and hence the chemical isomer shift. Thus the three short Sb–Cl bonds in $SbCl_3$ (2.36 Å) give rise on complex formation to only two short bonds (2.38 Å) in $[C_5H_5NH][SbCl_4]$. For antimony(III)-chloride systems this increase in the average bond length is the main consequence of the increase in electrostatic bond character on complex formation. The large negative values for the shifts for the tetrabromoantimonates(III) [compounds (9)—(12), Table 1] are therefore also consistent with complex formation of $SbBr_4^-$ from $SbBr_3$. The shifts for compounds (9)—(12) are, however, more negative than those for the tetrabromoantimonates(III) studied previously (see Table 2). This means that (9)—(12) must have longer average Sb–Br bond lengths and more electrostatic Sb–Br bond character than the corresponding $C_5H_5NH^+$ and $NBu^n{}_4{}^+$ derivatives. This may be associated with the requirements of packing $SbBr_4^-$ ions in a crystal lattice with the bulky 2- or 3-methylpyridinium, quinolinium, and isoquinolinium cations or with the formation of polymeric Sb–Br anions.

It is of interest to note the relative values of the quadrupole coupling constant, eQV_{zz}, listed in Tables 1 and 2. When the anion is $SbBr_4^-$ we observe that for the cation $C_5H_5NH^+$ eQV_{zz} is +11.5 mm s^{-1}; however, introduction of a methyl group in the cation [compounds (9) and (10)] reduces eQV_{zz} to zero. We find that this pattern of behaviour is repeated when the anion is the dibromo(tetrabromobenzene-1,2-diolato)antimonate(III) ion [compounds (5) and (6)]. One may speculate that the introduction of a $+I$ inductive effect, through the substituent CH_3, on the pyridine ring has produced a similar change in the asymmetric electric field caused by the extranuclear charges in both these examples. However, the fact that the immediate environments of the Sb atoms in the two cations considered are very different leads to the conclusion that this simple explanation is far from complete. Further investigations on this particular point are being pursued.

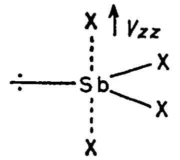
The simple interpretation of quadrupole-splitting data for compounds of ns^2 ions always presents difficulties.[2] We are presented with the striking feature for the tetrabromoantimonates(III) that the quadrupole coupling constant varies from +11.5 mm s^{-1} in the $C_5H_5NH^+$ derivative to +4.5 mm s^{-1} in the $NBu^n{}_4{}^+$ derivative to zero for the compounds (9)—(12) presented in this work. At first sight it might be expected that the presence of a non-bonding electron pair on antimony in species like $SbCl_3$ and $SbCl_4^-$ would give rise to an imbalance in the electron density around the Sb atom and a resolvable splitting. An excess of *p*-electron density in a stereochemically active lone pair would, because of the negative value of eQ for ^{121}Sb, give rise to a positive value for the quadrupole coupling eQV_{zz}. For these reasons the positive values for eQV_{zz} for many antimony(III) compounds have therefore been interpreted in terms of an excess of *p*-electron density in the direction of the lone-pair orbitals on the Sb atoms.

It is a well known feature of the stereochemistry based on a trigonal-bipyramidal distribution of electron pairs that the axial bonds are always considerably longer than those in equatorial positions. This fact in itself leads to two possible directions of imbalance in the antimony(III) electron density: (*a*) where there is an excess of electron density in the direction of the lone-pair orbital; and (*b*) where there is a deficiency of electron density along the axial bond directions. If it is assumed that these imbalances are in the *p*-electron density, this would give rise to the situation for cases (IV) and (V).



eQV_{zz} positive

(IV)



eQV_{zz} negative

(V)

The sign of the quadrupole coupling in any compound would then depend upon whether the *p*-electron density in the equatorial bond directions was more in balance with the lone-pair *p*-electron density or with the axial-bond *p*-electron density. The zero quadrupole splitting obtained for the four tetrabromoantimonates(III) studied in this work (Table 1) can be rationalised in terms of an approach towards a balance both between the *p*-electron density in the lone-pair orbital and in the equatorial Sb–Br bonds and between the total *p*- and *d*-electron densities in the equatorial plane and along the axial Sb–Br bond directions.

The chemical isomer shifts of the substituted benzene-1,2-diolatoantimony derivatives [compounds (1)—(8) Table 1] also have large negative values indicative of the presence of antimony(III). Again these shifts are more negative than for both the parent antimony(III) halides and the Sb–O compounds listed in Table 2. These observations suggest an increase in the co-ordination around Sb and an increase in the average antimony-ligand bond lengths on complex formation. The crystal structures of the complexes $[C_5H_5NH][SbCl_2(O_2C_6Cl_4)]$ and $[C_5H_5NH][SbBr_2(O_2C_6Br_4)]$ are known.[3] Both complexes have antimony in a distorted site with two short (*ca.* 2.06 Å) Sb–O bonds, one short antimony–halogen bond (Sb–Cl 2.45, Sb–Br 2.63 Å), and two longer antimony-halogen distances (Sb–Cl 2.87 and 3.00, Sb–Br 2.89 and 3.05 Å) to bridging halogen atoms. The crystal structure of the 3,4,5-tribromo-substituted complex [(8), Table 1], $[C_5H_5NH][SbBr_2(O_2C_6HBr_3)]$,[3] is similar to those of the complexes just described with short Sb–O bonds (2.04 Å), short Sb–Br (2.72 Å), and longer Sb–Br bonds (2.91 and 3.07 Å). The fact that the compounds have similar chemical isomer shifts, within experimental error, shows that the use of antimony(III) electrons in these materials is dominated by the short Sb–O bonds. The Sb–O bonds in the substituted catechol complexes are similar to those found in other compounds with strong Sb^{III}–O bonding, *e.g.* Sb_2O_3 (2.00 Å) and $SbNbO_4$ (2.01—2.06 Å). The antimony–halogen contacts, on the other hand, are longer than those in the parent trihalides and it is these changes that cause the increase in electrostatic character and in the negative value of the shift. The dominance of the number of short bonds, in this case Sb–O bonds, rather than the total number of bonds is again illustrated by the data for these complexes. The shift data for the pair of compounds (2) and (6) (Table 1) are consistent with domination of the use of Sb electrons by short covalent Sb–O bonds in which the shifts for the bromides are slightly more negative than those of the corresponding chlorides. If covalent antimony–halogen interactions were playing a dominating part in the bonding, the shift for the bromide complexes would have been more positive than those of the chlorides. It should be pointed out that the quadrupole-splitting constant for the tribromo-substituted complex [(8), Table 1] is zero in spite of the fact that it is structurally similar to compounds (1) and (5). This result appears to be anomalous because the other pyridinium compounds considered all have large positive values of eQV_{zz}.

The similarities in the Mössbauer parameters for compounds (1)—(4) and (7) together with *X*-ray structural data for $[C_5H_5NH][SbCl_2(O_2C_6Cl_4)]$ suggest that these compounds probably have similar Sb environments.

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