# Antimony-121 Mössbauer Spectra of some Six-co-ordinate Mono- and Di-organoantimonate(V) Compounds

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The $^{121}$Sb Mössbauer spectra are reported for a series of mono- and di-organoantimonate(V) salts containing the octahedral species $[SbRX_5]^-$ and $[SbR_2X_4]^-$ (R = Me or Ph, X = $F^-$, $Cl^-$, $Br^-$, $N_3^-$, or $NCS^-$). The data have been analyzed using a transmission-integral analysis and the importance of this approach is emphasized. The results are discussed with reference to the chemical bonding in organoantimony compounds, and to relations with corresponding organotin compounds. The structure of $SbMe_2Cl_3$ is considered to be six-co-ordinate with bridging chlorine atoms and *trans*-organic groups.

THE application of $^{121}$Sb Mössbauer spectroscopy to a study of the structure and bonding of organoantimony(V) derivatives has only recently been developed. Although some measurements have been recorded at liquid-nitrogen temperature, the equivalent data collected at liquid-helium temperature are far superior. Published data [1-7] have been concerned with species containing Sb–Fe bonds, with derivatives of the types $SbR_4X$ and $SbR_3X_2$ (R = alkyl or aryl, X = halide or other electronegative group), $SbPh_2Cl_3$, and $SbPh_2Cl_2L$ [L = pentane-2,4-dionate (pd) or quinolin-8-olate (quin)]. It is noteworthy that the quadrupole splitting parameters for $SbR_4X$ and $SbR_3X_2$ can be rationalized in terms of simple point-charge model calculations based on their known, or presumed, trigonal-bipyramidal structure with X apical.[3-6] There is also some evidence that such a model applies to six-co-ordinate diorganoantimony(V) species.[7] An unambiguous correlation has been observed [6,8,9] between Mössbauer parameters for corresponding tin(IV) and antimony(V) species, and it seems certain that much of the knowledge and experience accumulated from $^{119}$Sn Mössbauer spectroscopy can be fruitfully applied to the nascent field of organoantimony compounds.

The paucity of data for mono- and di-organoantimony(V) derivatives and for six-co-ordinate organoantimony species in general has led to the present work. Unfortunately there are very few compounds of this type which have been characterized by *X*-ray data; consequently we have chosen to investigate a series of mono- and di-organoantimonate(V) salts which might be expected to contain octahedral $[SbRX_5]^-$ and $[SbR_2X_4]^-$ complex species (X = halide or pseudohalide).

## EXPERIMENTAL

The preparation and characterization of phenylantimony derivatives have been described elsewhere.[10-12] The compound $SbMe_2Cl_3$ was obtained [13] by reacting $Sb_2Me_4$ with $SCl_2O_2$ in $CH_2Cl_2$ (Found: C, 9.6; H, 2.35; Cl, 41.4. $C_2H_6Cl_3Sb$ requires C, 9.3; H, 2.35; Cl, 41.2%). The salts $[AsPh_4][SbMe_2Cl_4]$ and $[NMe_4][SbMe_2Cl_4]$ were precipitated by adding $[AsPh_4]Cl$ or $[NMe_4]Cl$ to a solution of $SbMe_2Cl_3$ in methanol containing a few drops of hydrochloric acid, and were recrystallized from MeCN or MeOH respectively (Found: C, 46.4; H, 4.15; Cl, 20.45. $C_{26}H_{26}AsCl_4Sb$ requires C, 46.1; H, 3.85; Cl, 20.95%. Found: C, 20.05; H, 5.15; Cl, 38.35; N, 4.1. $C_6H_{18}Cl_4NSb$ requires C, 19.6; H, 4.95; Cl, 38.6; N, 3.8%). The salt $[NMe_4][SbMe_2F_4]$ was prepared by stirring a suspension of $[NMe_4][SbMe_2Cl_4]$ and an excess of NaF in MeCN for several hours. The residue was filtered off, and the compound precipitated by addition of $OEt_2$. The solid was redissolved in MeCN and reprecipitated with diethyl ether (Found: C, 24.2; H, 5.55; F, 24.65; N, 4.85. $C_6H_{18}NSb$ requires C, 23.9; H, 6.00; F, 25.2; N, 4.6%).

Mössbauer absorbers containing 12—16 mg cm$^{-2}$ of antimony were prepared in an atmosphere of dry nitrogen. The appropriate quantity of each compound was ground with an equal volume of polyethylene powder and mounted in a sealed holder. The source was *ca.* 500 µCi of Ca$^{121m}$SnO$_3$ from New England Nuclear Corp., and the spectra were obtained with both source and absorber immersed in liquid helium in an Elscint model MHC-3 cryostat. The spectrometer consisted of a linear-velocity drive unit (Elscint units model MVT-3, MD-3, and MFG-3), a thin NaI(Tl) scintillation counter, and a 400-channel (Laben) or 512-channel (Northern Scientific) analyser. The discriminator was set to count the escape peak of the 37 keV $^{121}$Sb $\gamma$-ray. The velocity range scanned was $\pm 20$ mm s$^{-1}$, and was calibrated using a $^{57}$Co/Pd source and an enriched metallic iron-foil absorber at room temperature. The spectra were folded (200 or 256 channels) before being computed. Chemical-isomer-shift data are quoted with respect to the Ca$^{121m}$SnO$_3$ source. Satisfactory spectra were obtained in a period of 24—36 h with 20 000—30 000 counts per channel.

## DATA TREATMENT AND RESULTS

The 37 keV M1 transition in $^{121}$Sb is from the $I_g = \frac{5}{2}$ ground state to the $I_e = \frac{7}{2}$ excited state. Accordingly, in the absence of a magnetic field the energy levels may be

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calculated for each state from a Hamiltonian of the form (1),

$$\mathscr{H} = \frac{e^2qQ}{4I(2I-1)} \cdot [3\hat{I}_z^2 - I(I+1) + \eta(\hat{I}_x^2 - \hat{I}_y^2)] \quad (1)$$

where $e^2qQ$ is the quadrupole coupling constant and $\eta$ is the asymmetry parameter of the electric-field-gradient (e.f.g.) tensor at the antimony nucleus. The quotient of the nuclear quadrupole moments $Q_e/Q_g$ is known [4] to be 1.34 ± 0.01. The energies and intensities of the 12 possible transitions can be calculated by diagonalizing the Hamiltonian for both spin states. The procedure used here is essentially similar to that already described for the $^{99}$Ru resonance.[14] If the asymmetry parameter $\eta = 0$, then there are only eight transitions with a finite intensity.

The resulting quadrupole pattern is highly asymmetric, but is poorly resolved in the $^{121}$Sb resonance because of the large natural linewidth of $2\Gamma = 2.1$ mm s$^{-1}$. As a result it is not possible to determine the line positions by visual inspection, and a complete spectrum envelope must be fitted by least-squares techniques. Although in the case of a very thin absorber the envelope can be represented as a summation of Lorentzian lines, this is unfortunately not valid in general because of saturation effects on the absorption intensity and it has been convincingly shown that a transmission integral [15] must then be used.[5,16] All the spectra reported here were fitted using two different least-squares programs. The first utilizes a conventional summation of Lorentzian lines, whereas the second uses a transmission integral for the absorption intensity of the form (2), where $I_0$

$$I(v) = I_0\left\{1 - \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{(\Gamma/2)\mathrm{d}E}{[(E + (vE_0/c)]^2 + (\Gamma/2)^2} \times \exp\left[-\sum_k \frac{A_k T_\mathrm{A}(\Gamma/2)^2}{(E - E_k)^2 + (\Gamma/2)^2}\right]\right\} \quad (2)$$

is a scaling parameter to include background effects, $I(v)$ is the absorption intensity at a Doppler shift $v$ from the emitted $\gamma$-ray energy $E_0$, $c$ is the velocity of light, $2\Gamma$ is the full width at half-maximum of the resonance at zero thickness, $E_k$ is the energy and $A_k$ the fractional ideal intensity of the $k$'th hyperfine line, and $T_\mathrm{A}$ is the effective absorber thickness (which is a dimensionless parameter). This integral was incorporated into the fitting procedure and evaluated by standard Gauss–Legendre quadrature techniques following essentially the procedure outlined previously by Shenoy and Friedt.[16]

The value of $Q_e/Q_g$ was kept constant, so that the variables fitted were the ground-state coupling constant $e^2qQ_g$, the asymmetry parameter $\eta$ (where necessary), the chemical isomer shift $\delta$, the linewidth $2\Gamma$, the thickness $T_\mathrm{A}$, and values for the intensity scaling and baseline. The linewidth $2\Gamma$ was left as a variable to take into account any instrumental broadening or inherent broadening in the source matrix. The program was written in Algol 60 for running on an ICL 1906A computer. Despite the complexity of the calculation, it was found that careful optimization of the integration calculation could reduce the computation time to 6—8 min in most instances.

Representative spectra are shown in Figure 1, and the numerical data are given in the Table. In all instances the asymmetry parameter was fixed at zero. (Finite values of $\eta$ have been found in other series of compounds to be reported separately, and we are confident that $\eta \leqslant 0.1$ for all the compounds referred to in the present work.) The transmission integral gave a much superior fit when the quadrupole splitting was partly resolved ($e^2qQ_g$ *ca.* 25 mm s$^{-1}$), but the differences were not so readily apparent when the fine structure was not resolved ($e^2qQ_g$ *ca.* 12 mm s$^{-1}$). However, close inspection of data displayed by a high-precision incremental plotter revealed a significant improvement in fit which is further confirmed by the chi-squared values per degree of freedom, $\chi^2/d$, in the Table. The linewidth calculated by a Lorentzian-type fit varies between 2.65 and 3.61 mm s$^{-1}$, but the mean width given by the transmission integral of 2.23 ± 0.13 mm s$^{-1}$ agrees well with the natural width of 2.1 mm s$^{-1}$. Moreover, the individual values for the width are remarkably self-consistent despite the large range of the calculated values of the effective thickness ($T_\mathrm{A}$ 1.5—6.8). We are therefore confident that the transmission-integral calculation is a worthwhile improvement on the Lorentzian summation. From a comparison of the two sets of computed values it is apparent that the Lorentzian fit systematically overestimates $e^2qQ_g$ by *ca.* 7% for the absorber thicknesses used here, and gives a value for the chemical isomer shift which is too negative (or positive if $e^2qQ_g$ is negative). This should be borne in mind when drawing comparisons with data from earlier papers where the transmission integral has not been used. Although reasonably accurate parameters may be obtained from a multiple-Lorentzian fit, the higher $\chi^2/d$ values obtained make it difficult to detect false minima or defective data.

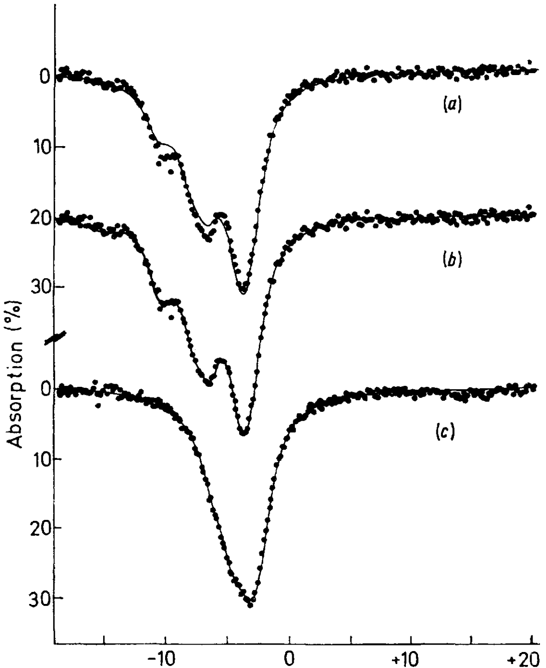

FIGURE 1 Antimony-121 spectra at 4.2 K for: (*a*) [AsPh$_4$][SbPh$_2$Cl$_4$] with a Lorentzian-type fit; (*b*) [AsPh$_4$][SbPh$_2$Cl$_4$] with a transmission-integral fit; and (*c*) [AsPh$_4$][SbPhCl$_5$] with a transmission-integral fit

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Mössbauer data (in mm $s^{-1}$) for six-co-ordinate organoantimony(v) compounds at 4.2 K

| | Lorentzian summation | | | | Transmission integral | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $e^2qQ_g$ | $\delta$ | $2\Gamma$ | $\chi^2/d$ | $e^2qQ_g$ | $\delta$ | $2\Gamma$ | $T_A$ | $\chi^2/d$ |
| $[AsPh_4][SbPhF_5]$ | 12.64(24) | −0.29(2) | 2.69(6) | 1.29 | 11.94(27) | −0.20(3) | 2.28(12) | 2.0(6) | 1.21 |
| $[NMe_4][SbPhF_5]$ | 13.70(21) | −0.49(2) | 2.78(5) | 1.47 | 12.69(20) | −0.35(2) | 2.18(8) | 3.0(5) | 1.23 |
| $[AsPh_4][SbPhCl_5]$ | 12.53(22) | −4.12(2) | 2.85(5) | 1.23 | 11.82(25) | −4.03(3) | 2.42(11) | 2.0(5) | 1.15 |
| $[NMe_4][SbPhCl_5]$ | 12.20(22) | −4.41(2) | 2.89(5) | 1.23 | 11.28(22) | −4.28(2) | 2.26(9) | 3.0(5) | 1.04 |
| $[NH_4][SbPhCl_5]$ | 12.09(23) | −4.53(2) | 2.91(5) | 1.28 | 11.50(30) | −4.46(3) | 2.57(13) | 1.5(6) | 1.25 |
| $[AsPh_4][SbBr_5Ph]$ | 11.25(30) | −5.45(2) | 2.85(7) | 1.39 | 9.88(33) | −5.29(3) | 2.08(12) | 4.2(9) | 1.25 |
| $[NMe_4][SbPhBr_5]$ | 11.62(32) | −5.16(2) | 2.72(8) | 1.22 | 10.78(39) | −5.05(4) | 2.23(16) | 2.5(9) | 1.18 |
| $[AsPh_4][SbPh_2F_4]$ | 25.80(26) | −3.09(3) | 2.79(5) | 2.24 | 25.34(13) | −2.99(1) | 2.14(5) | 3.4(3) | 1.06 |
| $[AsPh_4][SbPh_2Cl_4]$ | 24.76(32) | −6.02(3) | 2.87(7) | 3.72 | 24.17(13) | −5.88(2) | 2.03(5) | 4.5(3) | 1.55 |
| $[NMe_4][SbPh_2Cl_4]$ | 24.55(24) | −6.03(2) | 2.70(5) | 2.08 | 24.07(13) | −5.93(1) | 2.12(5) | 3.0(3) | 1.10 |
| $[AsPh_4][SbBr_4Ph_2]$ | 23.27(27) | −6.44(3) | 2.95(6) | 2.30 | 22.59(14) | −6.31(2) | 2.23(5) | 3.4(3) | 1.20 |
| $[AsPh_4][SbPh_2(N_3)_4]$ | 21.49(22) | −4.32(2) | 2.74(5) | 1.71 | 20.99(16) | −4.23(2) | 2.29(6) | 2.1(3) | 1.27 |
| $[AsPh_4][SbPh_2(NCS)_4]$ | 26.74(25) | −4.47(2) | 2.68(5) | 1.94 | 26.37(16) | −4.40(2) | 2.23(5) | 2.4(3) | 1.29 |
| $[AsPh_4][SbBrPh_2Cl_3]$ | 24.25(23) | −6.09(2) | 2.81(5) | 1.89 | 23.73(13) | −5.98(1) | 2.23(5) | 2.8(3) | 1.03 |
| $[AsPh_4][SbPh_2Cl_3(N_3)]$ | 24.39(23) | −5.83(2) | 2.79(5) | 1.97 | 23.91(14) | −5.73(2) | 2.26(5) | 2.6(2) | 1.17 |
| $[AsPh_4][SbPh_2Cl_3(NCS)]$ | 24.80(27) | −5.84(3) | 2.89(6) | 2.44 | 24.27(13) | −5.71(1) | 2.17(5) | 3.6(3) | 1.07 |
| $[NMe_4][SbMe_2F_4]$ | 27.66(24) | −3.46(2) | 2.89(5) | 1.83 | 27.21(17) | −3.37(2) | 2.40(6) | 2.3(3) | 1.32 |
| $[AsPh_4][SbMe_2Cl_4]$ | 26.64(25) | −6.20(3) | 2.65(5) | 2.18 | 26.26(13) | −6.11(1) | 2.07(4) | 3.3(3) | 1.05 |
| $[NMe_4][SbMe_2Cl_4]$ | 27.80(25) | −6.45(2) | 2.71(5) | 2.04 | 27.48(15) | −6.37(2) | 2.22(5) | 2.6(3) | 1.21 |
| $SbMe_2Cl_3$ | 27.54(44) | −7.25(4) | 3.61(10) | 7.90 | 26.58(10) | −7.00(1) | 2.17(4) | 6.8(3) | 1.36 |

## DISCUSSION

All the compounds listed in the Table show a positive sign for the quadrupole coupling constant $e^2qQ_g$. The sign of $Q_g$ is known to be negative, so that the sign of $q$ is also negative, indicating an excess of electron density along the principal axis of the e.f.g. tensor. Furthermore, the values of $e^2qQ_g$ for corresponding mono- and diorgano-species $[SbR_nX_{6-n}]^-$ (X = F, Cl, or Br) are essentially in the ratio of 1 : 2 as predicted by a simple point-charge model for the octahedral species $[SbRX_5]^-$ and $[trans\text{-}SbR_2X_4]^-$. The principal axis of the e.f.g. tensor would lie along the Sb–R bond axis in both cases, and this is consistent with a higher electron density in the Sb–C bonds, a positive sign for $e^2qQ_g$, and a negligible asymmetry parameter.

Further evidence for a *trans* disposition of the organo-groups in $[SbPh_2F_4]^-$ and $[SbPh_2Cl_4]^-$ has been obtained from their vibrational spectra.[12] In addition, the magnitude and sign of $e^2qQ_g$ for all diorgano-derivatives compares favourably with values reported for $SbPh_2Cl_3$[3] and $SbPh_2Cl_2$(pd)[7] which are known from *X*-ray studies[17,18] to possess *trans*-$SbPh_2$ units. The similarity of Mössbauer parameters in those cases where both the $[AsPh_4]^+$ and $[NMe_4]^+$ derivatives were measured lends confidence to the assumption that the solids contain discrete $[SbRX_5]^-$ and $[trans\text{-}SbR_2X_4]^-$ anions whose structure and bonding are only slightly influenced by the nature of the cation.

A more detailed interpretation of the Mössbauer parameters can be achieved by comparison with published $^{121}Sb$ data for other organoantimony(v) compounds, and by correlation with $^{119}Sn$ data from corresponding organotin(IV) compounds (notionally isoelectronic and isostructural). In Figure 2 the chemical isomer shifts $\delta(^{121}Sb)$ of the halogenophenyl compounds are plotted as a function of the number of organic groups bonded to antimony (refs. 2 and 19 and this work). In the series $[SbPh_nX_{6-n}]^-$ ($n$ = 0—2) there is a general decrease in $\delta(^{121}Sb)$ as $n$ increases. The one exception is the anomalous value for $[SbBr_6]^-$, although it may be significant that this value derives from mixed-valence compounds of the type $M_2SbBr_6$ which also contain $Sb^{III}$.[19]

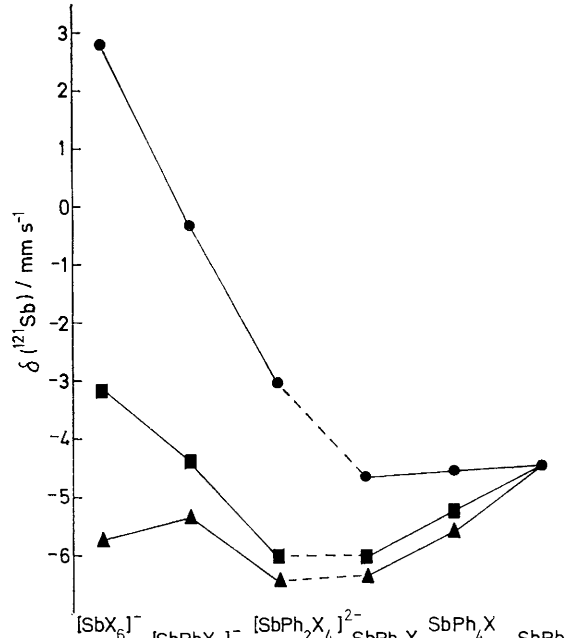

FIGURE 2 Variation in the chemical isomer shift, $\delta(^{121}Sb)$, in the series $[SbPh_nX_{6-n}]^-$ ($n$ = 0—2) and $SbPh_nX_{5-n}$ ($n$ = 3—5) for X = F (●), Cl (■), or Br (▲)

Since the change in nuclear radius, $\delta R/R$, is negative for $^{121}Sb$, this trend reflects a steady augmentation of *s*-electron density at the Sb nucleus when a polar Sb–X bond is replaced by a more covalent Sb–C bond. However, the opposite trend is observed for the series $SbR_nX_{5-n}$ ($n$ = 3—5) where $\delta(^{121}Sb)$ increases slightly as $n$ increases.[2,3] This behaviour is mirrored by the $^{119}Sn$

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chemical isomer shifts ($\delta R/R$ positive) of organotin compounds in the series $[SnR_nX_{6-n}]^{2-}$ ($n = 0$—3), $[SnR_nX_{5-n}]^-$ ($n = 0$—3), and $SnR_nX_{4-n}$ ($n = 0$—4) where $\delta(^{119}Sn)$ reaches a maximum value for $n = 2$ (fairly complete data are available only for X = Cl [20-22]).

The question [3] as to which value of $n$ would minimize $\delta(^{121}Sb)$ cannot be clearly answered from Figure 1 because of the structural change occurring as $n$ changes from 2 to 3. However, other data from this laboratory [23] on various complexes of the type $[SbR_2Cl(trid)]$ and $[SbR_3(trid)]$ (trid = tridentate dianionic ligand with ONO or ONS donor atoms) indicate that, at least for six-co-ordinate species, a minimum value of $\delta(^{121}Sb)$ occurs at $n = 2$.

The close parallel with organotin data [20,24] suggests that a similar redistribution of $s$ and $p$ electrons is probably occurring in the Sb–X and Sb–C bonds, and plays an important rôle in determining the value of $\delta(^{121}Sb)$. In each of the series $[SbRX_5]^-$, $[SbR_2X_4]^-$, $SbR_3X_2$, and $SbR_4X$ the $\delta(^{121}Sb)$ value becomes more positive ($s$-electron density at Sb decreases) as the electronegativity of X increases. This is consistent with the interpretation that although Sb–X bonds are generally considered to possess a higher $p$ character than Sb–C bonds, the withdrawal of $s$ electrons along Sb–X more than compensates for the deshielding effects of $p$-electron withdrawal.

The $\delta(^{121}Sb)$ values for the tetra-azido- and tetrathiocyanato- (N-bonded [12]) diphenyl species lie between those of the fluoro- and chloro-salts as expected, and show that the electronegativities of $[N_3]^-$ and $[NCS]^-$ ligands are nearly the same in these complexes. Although only very small differences in $\delta(^{121}Sb)$ are observed in the mixed species $[SbPh_2Cl_3X]^-$ (X = Cl, Br, $N_3$, or NCS), essentially the same trend may be recognized as the sixth ligand is varied. The more negative chemical-isomer-shift values for $[SbMe_2X_4]^-$ (X = F or Cl) compared with the corresponding phenyl compounds are accounted for by the better $\sigma$-donor ability of the methyl group.

It is interesting to draw comparisons with available data [25-28] for $[SnR_2X_4]^{2-}$ species [R = Me, X = F, Cl, Br, or $N_3$; R = Et, X = F or Cl; R = Bu, X = NCS; R = Ph, X = Cl, NCS, and $X_4 = (N_3)_2(NCS)_2$]. In this instance $\delta(^{119}Sn)$ usually decreases as the electronegativity of X increases and methyl derivatives show a more positive value than phenyl species, which is fully consistent with the $\delta(^{121}Sb)$ data. If we use the notation $\delta(X\text{–}X')_M$ to indicate the difference in $\delta$ between $MR_2X_4$ and $MR_2X'_4$ and the notation $\delta(R\text{–}R')_M$ for $MR_2X_4$ and $MR'_2X_4$, and with the assumption that all alkyl groups are similar in effect to methyl, it is possible to derive the following values (in mm s$^{-1}$): $\delta(Br\text{–}F)_{Sn}$ *ca.* 0.35, $\delta(Br\text{–}F)_{Sb}$ *ca.* $-3.3$; $\delta(Cl\text{–}F)_{Sn}$ *ca.* 0.23, $\delta(Cl\text{–}F)_{Sb}$ *ca.* $-2.9$; $\delta(Me\text{–}Ph)_{Sn}$ *ca.* 0.18, $\delta(Me\text{–}Ph)_{Sb}$ *ca.* $-0.4$. It can be seen that the antimony species show a much larger sensitivity to a change in the X groups than to a change in the R groups, but in the corresponding tin species the tendency is far less marked. Apparently an analogous situation is found in the trigonal-bipyramidal series $[MR_3X_2]$, where, for example, $\delta(Br\text{–}Cl)_{Sn}$ *ca.* 0, $\delta(Br\text{–}Cl)_{Sb}$ *ca.* $-0.3$, $\delta(Me\text{–}Ph)_{Sn}$ *ca.* 0.18, and $\delta(Me\text{–}Ph)_{Sb}$ *ca.* $-0.1$, and the tin species are insensitive to a change in the X group.[2,5,26,29-31] This evidence presumably indicates some fundamental difference in bonding between derivatives of Sn and Sb. A possible explanation is that Sb–C bonds have less $s$ character than Sn–C bonds in corresponding isoelectronic and isostructural $MR_2X_4$ and $MR_3X_2$ species.

The quadrupole coupling constant in the series $[SbPhX_5]^-$ and $[SbR_2X_4]^-$ depends on the nature of both X and R. For the halogens $e^2qQ_g$ becomes more positive in the order Br < Cl < F, and with the $[SbR_2X_4]^-$ species it can be seen that $e^2qQ_g$ becomes smaller when phenyl replaces methyl. The accepted electron-donation properties of these substituents are in the order Br > Cl > F and Me > Ph. The observed trends in $e^2qQ_g$ can therefore be interpreted in terms of a $\sigma$-bonded octahedral framework in which the $p$-electron imbalance between the $z$ axis and the $xy$ plane increases either when the donor ability of ligands in the $xy$ plane decreases or that of ligands along the $z$ axis increases. The lowest and highest values of $e^2qQ_g$ in the diphenylantimony(V) species are shown by $[SbPh_2(N_3)_4]^-$ and $[SbPh_2(NCS)_4]^-$, which would indicate that the donor strength of $[N_3]^-$ is significantly higher than that of $[NCS]^-$. In view of the negligible difference in chemical isomer shift in these two compounds, the observation is not easily explained, and we merely note that an analogous situation arises in the $^{119}Sn$ data for azido- and thiocyanato-organotin species.[25,28]

The present data provide a striking confirmation of the existence of a relation between the $e^2qQ$ parameters of corresponding organotin and organoantimony derivatives. In Figure 3 are shown the correlations published previously [8] for trigonal-bipyramidal species with negative $e^2qQ$ values, together with correlations of the present data with the octahedral species $[SnPhCl_5]^{2-}$, $[SnMe_2X_4]^{2-}$ (X = F or Cl), and $[SnPh_2X_4]^{2-}$ (X = Cl or NCS).[25-28,30] The graph also shows the correlation for the pairs $[MPh_2X_4]^-$ (X = Br or $N_3$), where the $e^2qQ$ values for the diphenyltin species have been inferred from those of $[SnBr_4Me_2]^{2-}$ and $[SnMe_2(N_3)_4]^{2-}$ by taking

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into account the difference in partial-quadrupole-splitting values for Me and Ph.[21] Values from published antimony spectra which were not computed using a transmission integral[2] have been decreased by 3% to correct approximately for the effect of absorber thickness.

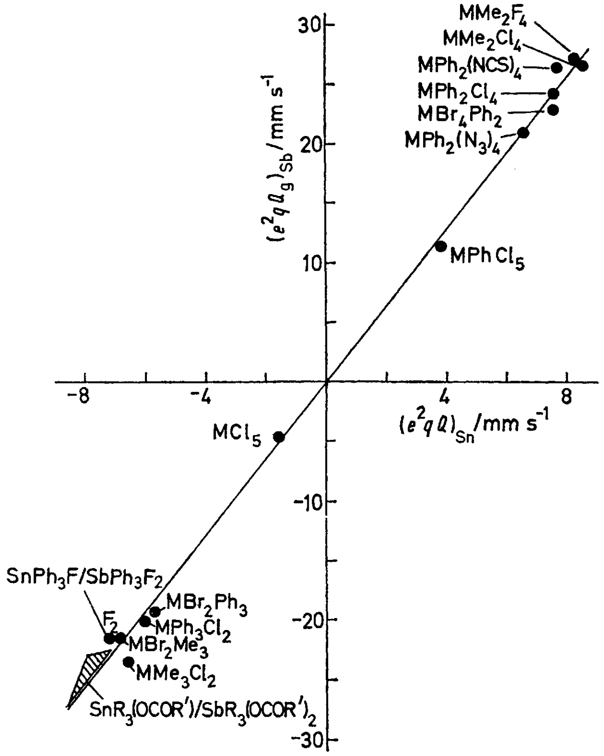

FIGURE 3 Correlation of $e^2qQ$ for corresponding organotin and organoantimony derivatives. The new data from the present work all have positive values of $e^2qQ$ and the previously published data (corrected for thickness effects where necessary) are those with negative values. The overall charge on each species is not indicated

The plot of $(e^2q_gQ)_{Sb}$ against $(e^2qQ)_{Sn}$ for octahedral and bipyramidal complexes appears to be reasonably placed along a straight line passing through the origin and with a gradient of +3.19. This can be compared to the value of +3.40 obtained previously.[8] The inherent assumptions of isoelectronic and isostructural behaviour in corresponding tin and antimony species have already been discussed.[8] In this respect we note that points for the non-isoelectronic pairs from the series $[SnR_3(OCOR')]$ and $[SbR_3(OCOR')_2]$[6,32] do not appear seriously out of place in the plot of Figure 3, although by themselves they produce a line with a different gradient which does not pass through the origin.[6] Similarly, the straight line of Figure 3 can provide a satisfactory correlation for the $e^2qQ$ values[2,33] in $SnPh_3F$ and $SbPh_3F_2$, and in $[SnPh_2Cl_4]^-$ and $SbPh_2Cl_3$.[3,27] In each pair of compounds the groups of donor atoms about the central atom result in a nearly equivalent effect on the magnitude and sign of the e.f.g. tensor.

As a final point, it should be noted that the Mössbauer parameters for $SbMe_2Cl_3$ are very similar to those obtained for $[SbR_2Cl_4]^-$ and $SbPh_2Cl_3$.[3] It therefore appears reasonable to propose for this compound a six-co-ordinate structure with bridging chlorines and *trans*-organic groups analogous to that already established[17] in $SbPh_2Cl_3$. The chemical isomer shift of $SbMe_2Cl_3$ is more negative than that of $[SbMe_2Cl_4]^-$. A similar situation apparently occurs for the corresponding phenyl species (comparing our value for $[SbPh_2Cl_4]^-$ without thickness corrections with the value given[3] for $SbPh_2Cl_3$) which implies a lower electron-withdrawing ability of bridging chloride ligands with respect to terminal ones.

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