Antimony-121 Mössbauer Spectroscopic Study of Bis(halogenoacetato)-trimethylantimony Derivatives

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Antimony-121 Mössbauer spectra of a number of bis(halogenoacetato)trimethylantimony complexes [$Me_3Sb(OCOR')_2$] have been measured. The compounds are shown to have trigonal bipyramidal structures with essentially planar C_3Sb groups. Comparisons with ^{119}Sn Mössbauer data for the related [$Me_3SnOCOR'$] derivatives reveal a number of linear correlations. The trends in isomer shift δ and quadrupole splitting e^2qQ as R' changes in the [$Me_3Sb(OCOR')_2$] series are very different from those observed upon changing X in the series [Ph_3SbX_2] (X = F, Cl, Br, I, *etc.*). In the former compounds differences in both δ and e^2qQ are dominated by the effects of *p* electron withdrawal, whilst in the latter series there appear to be substantial changes in hybridization of the Sb bonding orbitals.

A LARGE number of organotin compounds have been studied by ^{119}Sn Mössbauer spectroscopy, and a great deal of valuable structural information has been obtained.[1,2] This is particularly true of magnetic perturbation studies which allow one to deduce the sign of the quadrupole coupling constant e^2qQ and magnitude of the asymmetry parameter η of the electric field gradient (e.f.g.).[3,4] Although only a few ^{121}Sb Mössbauer studies of organoantimony derivatives have been reported,[5-9] it appears that the technique will provide a useful source of structural data in this area as well. Since the ^{121}Sb Mössbauer transition is between states with nuclear spins 7/2 and 5/2, with eight allowed transitions in the presence of a non-zero e.f.g., the shape

[1] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971, ch. 14.

[2] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101.

[3] R. V. Parish and C. E. Johnson, *J. Chem. Soc.* (*A*), 1971, 1906.

[4] J. N. R. Ruddick and J. R. Sams, *J.C.S. Dalton*, 1974, 470.

[5] S. E. Gukasyan and V. S. Shpinel, *Phys. Stat. Sol.*, 1968, **29**, 49.

[6] G. G. Long, J. G. Stevens, R. J. Tullbane, and L. H. Bowen, *J. Amer. Chem. Soc.*, 1970, **92**, 4230.

[7] L. H. Bowen, P. E. Garrou, and G. G. Long, *Inorg. Chem.*, 1972, **11**, 182.

[8] T. B. Brill, G. E. Parris, G. G. Long, and L. H. Bowen, *Inorg. Chem.*, 1973, **12**, 1888.

[9] G. K. Shenoy and J. M. Friedt, *Phys. Rev. Letters*, 1973, **31**, 419.

of the resulting absorption envelope is usually sufficient to give the sign as well as the magnitude of e^2qQ without application of an external magnetic field. In favourable cases η values can also be deduced. Fits of the spectra are not very sensitive to small values of η (less than *ca.* 0·3), but for quadrupole splittings of the magnitudes observed here η values greater than this can usually be determined with an uncertainty of *ca.* $\pm 0{\cdot}05$.[10]

A study of complexes of the type $[R_{4-n}Sb\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_n]^+$ using both ^{57}Fe and ^{121}Sb resonances [10] has revealed a number of correlations between the ^{121}Sb Mössbauer parameters and the ^{119}Sn parameters of the nominally isoelectronic tin species $[R_{4-n}Sn\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_n]$. Very recently we have shown [11] that an additive model for the e.f.g., such as used extensively in interpreting quadrupole splitting data for organotin(IV) complexes,[12] is also applicable to trigonal bipyramidal antimony compounds of the types $[Ph_4SbX]$ and $[Ph_3SbX_2]$ (X = various electronegative groups).

Since no systematic Mössbauer study of trimethylantimony compounds has been made, the present work was undertaken to establish the trends to be expected in the Mössbauer parameters of such compounds, and hopefully to extend the range of applicability of the additive e.f.g. model for Sb. It was also of interest to discern if the types of parameter correlations observed for isoelectronic tin and antimony species would also be found for structurally similar but anisoelectronic species. For this reason we chose to investigate a series of bis(halogenoacetato)trimethylantimony derivatives, $[Me_3Sb(OCOR')_2]$. Mössbauer data for the corresponding tin complexes, $[Me_3SnOCOR']$, have been published previously.[13]

RESULTS AND DISCUSSION

Shenoy and Friedt [9] have recently pointed out the need to control the absorber thickness carefully in determining ^{121}Sb Mössbauer spectra. They found that with sample thicknesses of 12 mg cm^{-2} of Sb or greater, significant departures from theoretical intensity ratios of the component spectral lines were observed. Such departures had earlier led Stevens and Ruby [14] to postulate a Gol'danskii–Karyagin (GK) effect in some R_3SbX_2 derivatives, even at 4·2 K. Each of our samples contained 8 mg cm^{-2} of Sb, and in no case was there evidence for any GK effect. These findings reinforce the suggestions [9,11] that Stevens and Ruby [14] were actually observing absorber thickness effects rather than GK effects.

Mössbauer spectra for the $[Me_3Sb(OCOR')_2]$ complexes were fitted first with η constrained to be zero, and then with η as an adjustable parameter. There was no significant improvement in fit (as judged by χ^2 values) when η was allowed to vary, and the η values obtained were always small ($\eta \leqslant 0{\cdot}2$). We therefore conclude that η is essentially zero in these compounds.

From i.r. data in the carbonyl/carboxyl stretching frequency region Goel and Ridley [15a] have deduced that the carboxylate groups are unidentate in solid $[R_3Sb(OCOR')_2]$ compounds. Poder and Sams [13] have shown that the halogenoacetatotrimethyltin compounds $[Me_3SnOCOR']$ are five-co-ordinate linear polymers in the solid state with bridging bidentate OCOR′ groups in axial positions,[16] but are four-co-ordinate monomers with ester-like OCOR′ moieties in CCl_4 solution. In Figure 1 we have plotted $\nu_{as}(C{=}O)$ for the trimethyltin species in solution [13] against the same band for the solid-state trimethylantimony derivatives.[15a] The straight line was constructed with unit slope and zero intercept, and the points lie quite close to this line. Thus the carboxylate group is clearly performing the same function in the solid $[Me_3Sb(OCOR')_2]$ compounds as in the CCl_4 solutions of $[Me_3SnOCOR']$. This 1 : 1 correspondence confirms that the carboxylate groups in the antimony complexes are unidentate, and that antimony is therefore five-co-ordinate in these compounds.

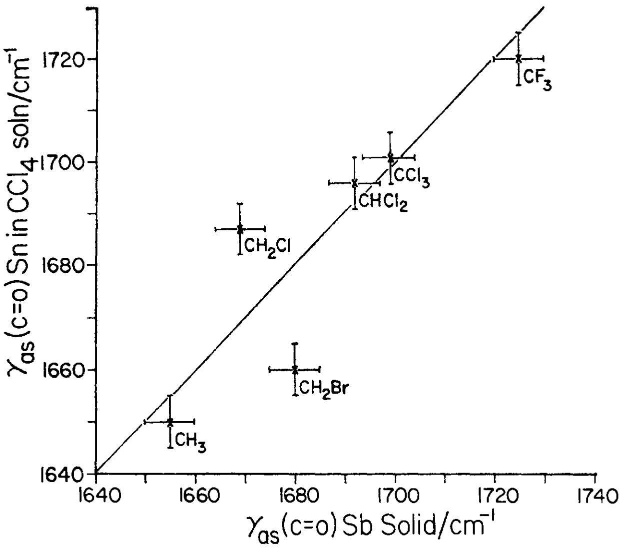

FIGURE 1 Plot of $\nu_{as}(C{=}O)$ for $[Me_3SnOCOR']$ species in CCl_4 solution against $\nu_{as}(C{=}O)$ for $[Me_3Sb(OCOR')_2]$ species in the solid state. Points are identified by the R′ group. The straight line has unit slope and zero intercept

Since Ph_5Sb has a square pyramidal structure [17] while $[(p\text{-}MeC_6H_4)_5Sb]$ is trigonal bipyramidal,[18] it is conceivable that either structural type could form the basis for the $[Me_3Sb(OCOR')_2]$ structures. There are

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[10] W. R. Cullen, D. J. Patmore, J. R. Sams, and J. C. Scott, *Inorg. Chem.*, 1974, **13**, 649.

[11] J. N. R. Ruddick, J. R. Sams, and J. C. Scott, *Inorg. Chem.*, 1974, **13**, 1503.

[12] See, *e.g.*, M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

[13] C. Poder and J. R. Sams, *J. Organometallic Chem.*, 1969, **19**, 67.

[14] J. G. Stevens and S. L. Ruby, *Phys. Letters*, 1970, **32A**, 91.

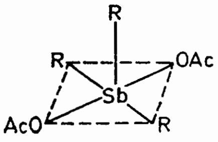
[15] (*a*) R. G. Goel and D. R. Ridley, *J. Organometallic Chem.*, 1972, **38**, 83; (*b*) R. G. Goel, E. Maslowsky, and C. V. Senoff, *Inorg. Chem.*, 1971, **10**, 2572.

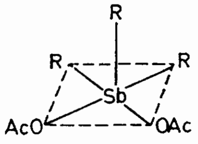
[16] This conclusion has now been confirmed for the two end members of series (R′ = CH_3, CF_3) by *X*-ray crystallography. Hwa Chih and B. R. Penfold, *J. Cryst. Mol. Struct.*, 1973, **3**, 285.

[17] A. L. Beauchamp, M. J. Bennett, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1968, **90**, 6675.

[18] C. Brabant, J. Hubert, and A. L. Beauchamp, *Canad. J. Chem.*, 1973, **51**, 2952.

thus six possibilities, (I)—(VI). Simple symmetry considerations suffice to eliminate (I), (III), (V), and (VI) since in each of these cases η is expected to be close to unity, rather than the values $\eta \simeq 0$ observed. The remaining square pyramidal structure (II) can also be ruled out. A point-charge calculation indicates that this structure should produce only a very small quadrupole splitting, whereas we find $|e^2qQ| > 20$ mm s^{-1} in every case (*vide infra*). Thus, the only structure compatible with the Mössbauer data is (IV), in which the three methyl groups lie in the equatorial plane of a trigonal bipyramid. The D_{3h} point-group symmetry of the local Sb environment in (IV) should produce a large axially symmetric e.f.g., and is also in agreement with the i.r. and Raman spectroscopic data for trimethylantimony diacetate.[15b]


(I)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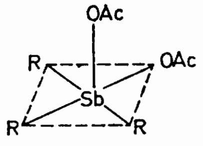
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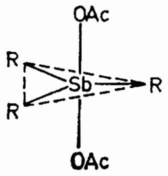
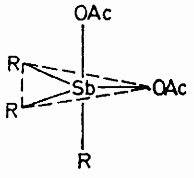
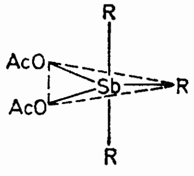

(IV)


(V)


(VI)

^{121}Sb Mössbauer parameters are given in Table 1. The e^2qQ values are large and negative, increasing in magnitude with increasing electron-withdrawing ability of the R′ group. Since $eQ^{121}{}_{\text{Sb}}$ is negative, the principal component of the e.f.g. tensor (V_{zz}) is positive, showing the oblate charge distribution at Sb expected for structure (IV). The increase in $|e^2qQ|$ as R′ varies from CH_3 to CF_3 reflects a greater imbalance in charge densities in the antimony 5*p* orbitals as the effective electronegativity of the R′ group increases. Very similar trends were noted in the trimethyltin halogenoacetates. Here too e^2qQ is negative[4] (V_{zz} positive) and is a linear function of both the Taft constant of the R′ group and the pK_a of the parent carboxylic acid.[13]

As shown in Figure 2 there is a good linear correlation between $(e^2qQ)_{\text{Sb}}$ and $(e^2qQ)_{\text{Sn}}$ for the two series of carboxylates. Hence, $(e^2qQ)_{\text{Sb}}$ must also have an essentially linear dependence on the Taft constant of the R′ group and the pK_a of the parent acid. If Sn and Sb were isoelectronic in these compounds the straight line of Figure 2 should pass through the origin.[19] However, a least-squares treatment of the data gives equation (1). Not only is the intercept far from zero, but the

$$(e^2qQ)_{\text{Sb}} = 4{\cdot}48(e^2qQ)_{\text{Sn}} + 10{\cdot}21 \text{ mm s}^{-1} \qquad (1)$$

slope is substantially greater than that obtained by Bancroft *et al.*[19] for isoelectronic derivatives (3·40). We have found a slope very similar to that of Bancroft *et al.*[19] on comparing e^2qQ for isoelectronic Sn and Sb complexes of the type $[R_{4-n}M\{Fe(CO)_2(\pi\text{-}C_5H_5)\}_n]$ (M = Sn, Sb$^+$).[10]

TABLE 1

^{121}Sb Mössbauer parameters for the complexes

	δ/mm s^{-1} [a,b]	e^2qQ/mm s^{-1} [b]	Γ/mm s^{-1}	ε [c]	χ^2
$[Me_3Sb(OCOCH_3)_2]$	$-5{\cdot}17 \pm 0{\cdot}08$	$-23{\cdot}3 \pm 0{\cdot}1$	2·51	0·14	181
$[Me_3Sb(OCOCH_2Cl)_2]$	$-5{\cdot}27 \pm 0{\cdot}10$	$-25{\cdot}1 \pm 0{\cdot}3$	3·01	0·10	175
$[Me_3Sb(OCOCHCl_2)_2]$	$-5{\cdot}3 \pm 0{\cdot}2$	$-25{\cdot}2 \pm 0{\cdot}5$	2·97	0·15	189
$[Me_3Sb(OCOCCl_3)_2]$	$-5{\cdot}50 \pm 0{\cdot}05$	$-27{\cdot}5 \pm 0{\cdot}3$	2·53	0·10	180
$[Me_3Sb(OCOCH_2F)_2]$	$-5{\cdot}3 \pm 0{\cdot}2$	$-24{\cdot}4 \pm 0{\cdot}4$	2·72	0·17	164
$[Me_3Sb(OCOCHF_2)_2]$	$-5{\cdot}4 \pm 0{\cdot}1$	$-26{\cdot}4 \pm 0{\cdot}7$	2·67	0·19	161
$[Me_3Sb(OCOCF_3)_2]$	$-5{\cdot}5 \pm 0{\cdot}1$	$-28{\cdot}0 \pm 0{\cdot}4$	2·71	0·19	186
$[Me_3Sb(OCOCH_2NC)_2]$	$-5{\cdot}37 \pm 0{\cdot}06$	$-25{\cdot}8 \pm 0{\cdot}9$	2·90	0·12	168
$[Me_3Sb(OCOCH_2Br)_2]$	$-5{\cdot}24 \pm 0{\cdot}05$	$-23{\cdot}8 \pm 0{\cdot}5$	2·60	0·12	182
$[Me_3Sb(OCOCHBr_2)_2]$	$-5{\cdot}4 \pm 0{\cdot}1$	$-26{\cdot}2 \pm 0{\cdot}1$	2·60	0·21	188

[a] Isomer shift relative to Ba^{121}SnO$_3$. [b] All data recorded with sample at 8 K, and Ba^{121}SnO$_3$ source at 80 K. [c] Resonance effect.

One important consequence of the non-zero intercept in Figure 2 is that in general it will not be possible to make a direct conversion of partial quadrupole splitting (p.q.s.) values from Sn to Sb compounds of similar

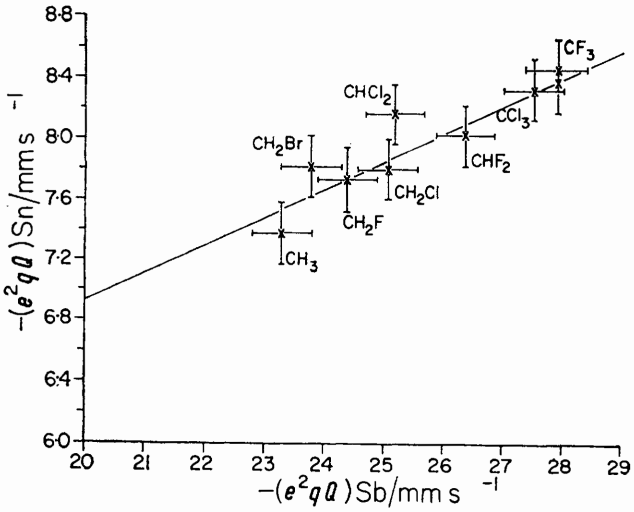


FIGURE 2 Correlation of tin and antimony quadrupole coupling constants in $[Me_3M(OCOR')_n]$ (M = Sn, n = 1; M = Sb, n = 2). The straight line was constructed by least squares

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[19] G. M. Bancroft, K. D. Butler, and E. T. Libbey, *J.C.S. Dalton*, 1972, 2643.

structure unless the compounds are also isoelectronic. {Note that the unknown compounds $[Me_3Sn(OCOR')_2]^-$ are isoelectronic with the $[Me_3Sb(OCOR')_2]$ derivatives.}

In our previous study of $[Ph_4SbX]$ and $[Ph_3SbX_2]$ complexes[11] we derived a number of ligand p.q.s. values (denoted $[L]^{TBA}$ or $[L]^{TBE}$ to indicate trigonal bipyramidal apical or trigonal bipyramidal equatorial coordination of the ligand). The results in Table 1 enable us to compute some additional p.q.s. values which are listed in Table 2 together with the source compounds from which they were derived. The $[Me]^{TBE}$ value given here was obtained from the recent and very precise data for $[Me_3SbBr_2]$,[9] and is somewhat more positive than the value given in ref. 11 derived from earlier data for $[Me_3SbCl_2]$.[6] We consider the present value to be preferable. From the $[Me]^{TBE}$ and $[OAc]^{TBA}$ values in Table 2 {the latter derived from $[Ph_3Sb(OAc)_2]$} the predicted e^2qQ for $[Me_3Sb(OAc)_2]$ is $-23\cdot27$ mm s^{-1}, essentially in perfect agreement with the measured value ($-23\cdot32$ mm s^{-1}).

TABLE 2

Partial quadrupole splittings for the ligands of trigonal bipyramidal molecules

[L]	p.q.s/ mm s^{-1}	Source compound	e^2qQ/ mm s^{-1}
$[Cl]^{TBA}$	0	—	—
$[Ph]^{TBE}$	$-6\cdot9$ [a]	$[Ph_3SbCl_2]$	$-20\cdot6$
$[Br]^{TBA}$	$-0\cdot2$ [a]	$[Ph_3SbBr_2]$	$-19\cdot8$
$[OAc]^{TBA}$	$+0\cdot26$	$[Ph_3Sb(OAc)_2]$	$-21\cdot8$
$[Me]^{TBE}$	$-7\cdot41$	$[Me_3SbBr_2]$	$-21\cdot4$
$[OCOCF_3]^{TBA}$	$+1\cdot45$	$[Me_3Sb(OCOCF_3)_2]$	$-28\cdot0$
$[OCOCHF_2]^{TBA}$	$+1\cdot05$	$[Me_3Sb(OCOCHF_2)_2]$	$-26\cdot4$
$[OCOCH_2F]^{TBA}$	$+0\cdot53$	$[Me_3Sb(OCOCH_2F)_2]$	$-24\cdot4$
$[F]^{TBA}$	$+0\cdot3$ [a]	$[Ph_3SbF_2]$	$-22\cdot0$
$[NO_3]^{TBA}$	$+0\cdot2$ [a]	$[Ph_3Sb(NO_3)_2]$	$-21\cdot3$
$[NCS]^{TBA}$	$-0\cdot1$ [a]	$[Ph_3Sb(NCS)_2]$	$-20\cdot4$

[a] Data from ref. 11.

In discussing the isomer shifts δ, it must be remembered that $\delta R/R$, the fractional change in nuclear charge radius between excited and ground states, is negative for ^{121}Sb. It will be seen from Table 1 that as the effective electronegativity of the R′ group increases δ becomes more negative, indicating an increase in the *s*-electron density at the Sb nucleus. This trend is opposite to that found[11] in the dihalogenotriphenylantimony compounds $[Ph_3SbX_2]$, where δ becomes more positive in the order $X = I < Br < Cl < F$. These differences will be discussed in more detail below. For the moment we merely note that for the halogenoacetates the observed trend is consistent with increasing withdrawal of Sb $5p_z$ electron density as the R′ group electronegativity increases, resulting in deshielding of the *s* electrons. Very similar trends of increasing *s* electron density at Sn with increasing electronegativity have also been observed in the series $[Me_3SnOCOR']$[20] and $[Ph_3SnOCOR']$.[21] In fact, a plot of antimony isomer shift in $[Me_3Sb(OCOR')_2]$ against tin isomer shift in $[Me_3SnOCOR']$ is essentially linear with negative slope (since $\delta R/R > 0$ for ^{119}Sn).

Following Ruby *et al.*[22] we can construct an isoelectronic line for δ_{Sb} *vs.* δ_{Sn}, using the points Sb(β-Sn)—β-Sn and $KSbF_6$—K_2SnF_6 as shown in Figure 3. Interestingly, we find that the points for the corresponding $[Me_3Sb(OCOR')_2]$ and $[Me_3SnOCOR']$ derivatives fall on this line despite the fact that the compounds are not isoelectronic. One possible explanation is that the slope and/or position of the isoelectronic line are incorrect, but it should be noted that a very sizeable change in the location of one or both end points would be required to alter the qualitative significance of the plot. It seems more likely that δ is simply very insensitive to changes arising solely from *p* electron withdrawal effects, so that quite a large difference in, say, p_z densities has very little effect on δ. That is, two compounds can have virtually equivalent *s* electron densities at the respective nuclei as shown by δ values, without in fact being isoelectronic. This means, of course, that one must be extremely cautious in concluding from a plot such as Figure 3 that any two series of compounds are isoelectronic. However, if the data do fall on the isoelectronic line on a δ_{Sb} *vs.* δ_{Sn} graph and also give a linear plot of $(e^2qQ)_{Sb}$ *vs.* $(e^2qQ)_{Sn}$ which passes through the origin, then not only is the *s* orbital charge density equivalent for a given pair of Sn and Sb compounds but so is the *p* orbital imbalance. In this case it would seem entirely safe to conclude that the two were isoelectronic.

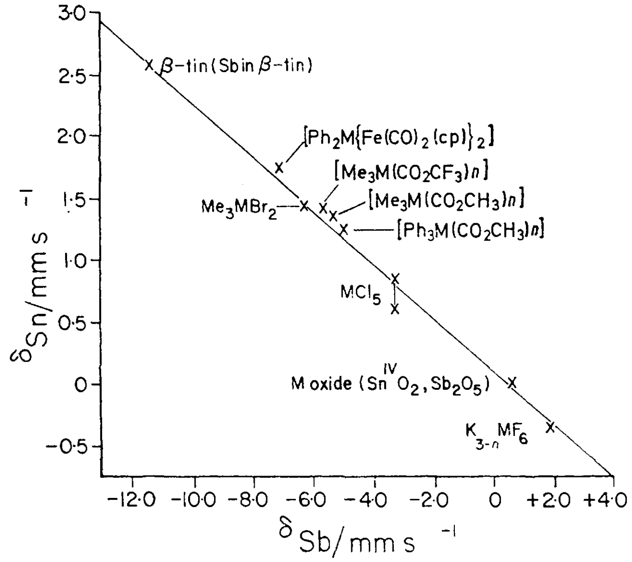

FIGURE 3 Plot of δ_{Sb} *vs.* δ_{Sn}, the straight line connecting corresponding values expected for isoelectronic species. Note that for M = Sb, *n* = 1 and for M = Sn, *n* = 2. Data are from this work, refs. 2, 9, 10, 11, 22, and the following papers: L. H. Bowen, J. G. Stevens, and G. G. Long, *J. Chem. Phys.*, 1969, **51**, 2010; R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65; T. Birchall and B. Della Valle, *Canad. J. Chem.*, 1971, **49**, 2808; H. Micklitz and P. H. Barrett, *Phys. Rev. B*, 1972, **5**, 1704; D. J. Stewart, O. Knop, C. Ayasse, and F. W. D. Woodhams, *Canad. J. Chem.*, 1972, **50**, 690

Since for the present series of compounds plots of

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[20] N. W. G. Debye, D. E. Fenton, S. E. Ulrich, and J. J. Zuckerman, *J. Organometallic Chem.*, 1971, **28**, 339.

[21] B. F. E. Ford and J. R. Sams, *J. Organometallic Chem.*, 1971, **31**, 47.

[22] S. L. Ruby, G. M. Kalvius, R. E. Snyder, and G. B. Beard, *Phys. Rev.*, 1967, **159**, 239.

$(e^2qQ)_{\mathrm{Sb}}$ *vs.* $(e^2qQ)_{\mathrm{Sn}}$ and of δ_{Sb} *vs.* δ_{Sn} are both linear, it follows that a plot of δ_{Sb} *vs.* $(e^2qQ)_{\mathrm{Sb}}$ should also be linear. A least-squares treatment of the data yields equation (2), with a standard deviation of $4{\cdot}9 \times 10^{-2}$.

It is instructive to compare the gradient of this line

$$\delta_{\mathrm{Sb}} = 0{\cdot}075(e^2qQ)_{\mathrm{Sb}} - 3{\cdot}38 \text{ mm s}^{-1} \qquad (2)$$

with that of a similar plot for a series of seven compounds of the type $[\mathrm{Ph_3SbX_2}]$ (X = I, Br, Cl, F, NCS, $\mathrm{NO_3}$, OAc).[11] In this case a least-squares fit of the data yielded equation (3), from which it is seen that the gradient is much larger in magnitude and opposite in sign to that for the halogenoacetate derivatives.

$$\delta_{\mathrm{Sb}} = -0{\cdot}51(e^2qQ)_{\mathrm{Sb}} - 16{\cdot}20 \text{ mm s}^{-1} \qquad (3)$$

We have seen above that the trends observed in both e^2qQ and δ for the $[\mathrm{Me_3Sb(OCOR')_2}]$ complexes are explicable if one assumes that the major effect of changing R′ is to alter the extent of *p* electron withdrawal in the axial (O–Sb–O) direction. Since a relatively small amount of *s* character is expected in the Sb–O bonds, these differences in *p* electron-shielding effects should lead to a small positive gradient for the δ *vs.* e^2qQ line as observed. This argument cannot explain the much larger negative slope for the $[\mathrm{Ph_3SbX_2}]$ derivatives, and here we must conclude that the predominant effect is one of rehybridization of the antimony bonding orbitals as X is varied. Thus, going from $\mathrm{Ph_3SbI_2}$ to $\mathrm{Ph_3SbF_2}$ involves a substantial change in the *s* character of orbitals directed towards the axial ligands. Indeed, the negative gradient requires removal of *s* electron density from Sb as the electronegativity of X increases, which must be more than sufficient to overcome the deshielding effect of any concomitant *p* electron withdrawal.

It is interesting to note that the differences between the $[\mathrm{Ph_3SbX_2}]$ and $[\mathrm{Me_3Sb(OCOR')_2}]$ series are precisely parallel to those between the related trimethyltin halides and halogenoacetates.[23] For the tin compounds, however, the situation is complicated by the fact that although the halogenoacetates[16] and $[\mathrm{Me_3SnF}]$[24] are bridged five-co-ordinate polymers there is some doubt as to the structures of the remaining trimethyltin halides. The essentially identical trends in Mössbauer parameters for the tin compounds and the present antimony derivatives seems to provide good evidence that all the trimethyltin halides are five-co-ordinate.

Finally we note that Spinner[25] has shown the $\nu_{\mathrm{as}}(\mathrm{C{=}O})$ band in the i.r. spectra of α-substituted carboxylates to be sensitive to the electron-withdrawing ability of the substituent group, while Goel and Ridley[15a] have related the position of this band to the Taft constant of the R′ group. Since the effect of increasing the electron withdrawal by the carboxylate moiety is to increase both (δ) and $|e^2qQ|$, we might expect a correlation between the Mössbauer parameters and $\nu_{\mathrm{as}}(\mathrm{C{=}O})$, and in fact a plot of δ against $\nu_{\mathrm{as}}(\mathrm{C{=}O})$ for the $[\mathrm{Me_3Sb(OCOR')_2}]$ derivatives is found to be effectively linear.

EXPERIMENTAL

All the compounds employed in this study were prepared by published methods and their physical data were in agreement with those reported.[15a] Absorbers were prepared by carefully powdering the organoantimony compounds prior to mounting in a copper cell with Mylar windows, and a sample thickness of 8 mg cm^{-2} of Sb was used.

The ^{121}Sb Mössbauser spectra were recorded with the absorbers at 8 K and a 1 mCi $\mathrm{Ba^{121}SnO_3}$ source (New England Nuclear) at 80 K. The spectrometer has been described.[10] Velocity calibration was effected with an iron foil absorber and ^{57}Co(Cu) source, and isomer shifts are reported relative to the $\mathrm{Ba^{121}SnO_3}$ source. The spectra were computer fitted using programmes which have been described in detail elsewhere.[11,26] The asymmetry parameter could either be constrained to zero or treated as a variable fitting parameter.

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