to exist as a cubic pyrite structure when prepared and quenched from 800 to 850° and as a partially ordered (orthorhombic $Pca2_1$ space group) structure when synthesized between 700 and 800°; this partially ordered structure contained ordered As–S pairs. The compounds CoSbS and CoPSe crystallize with an orthorhombic structure, apparently similar to that of $\alpha$-$NiAs_2$ (pararammelsbergite). CoAsSe and CoSbSe are orthorhombic with the $c/a$ and $c/b$ axial ratios of the anomalous marcasite.

The temperature-independent magnetic data found for all CoXY materials studied is indicative of low-spin $Co^{3+}$ ($d^6$). The electrical data for these materials may reflect the specific effect of anions and crystallography on both the broadness and degree of separation of the valence and conduction bands.

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**Registry No.** CoPS, 51021-56-8; CoAsS, 12254-82-9; CoSbS, 51021-58-0; CoPSe, 51021-57-9; CoAsSe, 51021-48-8; CoSbSe, 51021-59-1.

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# Additive Model for the Electric Field Gradient at Antimony in Some Pentacoordinate Organoantimony(V) Derivatives

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$^{121}$Sb Mossbauer data are reported for several compounds of the types $Ph_4SbX$ and $Ph_3SbX_2$ (Ph = $C_6H_5$; X = various electronegative groups) and are consistent with trigonal-bipyramidal structures in which the X groups occupy one or both axial positions, respectively. The first explicit application of an additive model for the electric field gradient at Sb in organoantimony(V) compounds has been made to these and other derivatives of like stoichiometries. Calculated and observed quadrupole coupling constants ($e^2qQ$) are in good agreement, indicating the adequacy of such a model for these systems. For compounds of the type $Ph_3SbX_2$ there is an approximately linear relation between isomer shift ($\delta$) and $e^2qQ$, the slope of which is consistent with $\sigma$-bonding effects being the dominant factor in determining the Mossbauer parameters. In derivatives containing Sb–O bonds the $\delta$ values are more positive than would be expected on the basis of electronegativity arguments alone.

## Introduction

Additive models for the electric field gradient (efg) have been extensively employed to interpret Mossbauer quadrupole splitting data on organometallic Sn(IV) derivatives (and to a lesser extent, spin-paired Fe(II) and Fe(−II) complexes).[1] Such models have had considerable success in predicting both signs and magnitudes of quadrupole splittings in compounds with fairly regular geometry, although the converse application of predicting molecular geometry from measured efg parameters has met with more limited success. This is due in part to the fact that similar efg parameters may arise from two or more possible structures, so that an unequivocal choice is not always possible. Moreover, no really satisfactory method has yet been devised to account for distortions from regular geometry.

In view of the usefulness of the additive approximation for $^{119}$Sn quadrupole splittings in organotin(IV) compounds it is obviously of interest to extend the treatment to $^{121}$Sb quadrupole splittings in organoantimony(V) complexes, since the model should be equally applicable here.[1a] Although $^{121}$Sb Mossbauer results for only a few organoantimony(V) derivatives have appeared in the literature, the data of Long, *et al.*,[2] at 4.2°K for compounds of the type $R_{5-n}SbX_n$ (R = $C_6H_5$, $CH_3$; X = F, Cl, Br, I; $n$ = 0–2, but not all combinations) constitute a suitable starting point for such a treatment. In the present paper we report $^{121}$Sb Mossbauer data for several other $Ph_{5-n}SbX_n$ (Ph = $C_6H_5$) complexes which together with the results of Long, *et al.*,[2] allow us to make a limited test of the additive model for $^{121}$Sb quadrupole splittings.

X-Ray crystallographic studies of compounds such as $Ph_3SbCl_2$,[3] $Me_3SbCl_2$[4] (Me = $CH_3$), $Ph_4SbOMe$,[5] $Ph_3Sb(OMe)_2$,[5] and $Ph_4SbOH$[6] have shown that they adopt trigonal-bipyramidal structures with the electronegative groups in the axial positions. Infrared and Raman data are also consistent with this type of structure for compounds of the types $R_3SbX_2$ and $R_4SbX$.[7-9] There are a few exceptions such as $Ph_4SbClO_4$ which is apparently ionic, but both ir[8] and Mossbauer[2] studies show when such exceptions occur. The absence of quadrupole splitting in the Mossbauer spectra (as expected for a tetrahedral $Ph_4Sb^+$ cation) and the high-resonance fractions support ionic structures for both $Ph_4SbClO_4$[2] and $Ph_4SbBF_4$.[10]

The structural parameters of $Ph_4SbOMe$ and $Ph_3Sb(OMe)_2$

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are of particular interest since they show there are no large deviations in O-Sb bond lengths or in equatorial Ph-Sb bond lengths between the two compounds.[5] These data lend some confidence in the application of an additive model for the quadrupole splitting to related compounds, since the model depends critically on the assumption that the contribution to the efg from a given ligand does not change appreciably from one compound to another.

## Experimental Section

The $^{121}$Sb Mossbauer spectra were recorded with a 1-mCi Ba$^{121}$SnO$_3$ source (New England Nuclear) at liquid nitrogen temperature and the absorbers at 8.5-9.0°K in a Janis Model 6DT cryostat. The powdered absorbers were contained in a copper cell with Mylar windows and had a thickness of 8-10 mg/cm$^2$ of Sb. The single-channel analyzer was set on the escape peak (Xe-CO$_2$ proportional counter) of the 37-keV $^{121}$Sb $\gamma$ ray, and other details of the spectrometer have been described elsewhere.[11] The velocity scale was calibrated with an iron foil absorber and a 10-mCi $^{57}$Co(Cu) source, and isomer shifts are reported relative to the Ba$^{121}$SnO$_3$ source. The spectra were computer fitted to eight-line quadrupole-split patterns using the appropriate Clebsch-Gordan coefficients and a ratio of the quadrupole moments $R = Q_{ex}/Q_{gr} = 1.34$.[2] In cases where the asymmetry parameter $\eta$ was apparently nonzero, the spectra were fitted with $\eta$ as a variable. A program was written[12] for calculating $^{121}$Sb spectra with $\eta \neq 0$, in which the energy eigenvalues were found by machine diagonalization of the Hamiltonian matrices for the ground and excited states. The intensities of the 12 possible transitions connecting the two states were calculated from appropriate combinations of the Clebsch-Gordan coefficients. The integrals for the angular-dependent part of the above were carried out assuming randomly oriented polycrystalline samples.

All the compounds used in this work were prepared by published procedures: $Ph_4SbCl$,[13] $Ph_4SbNCS$,[13] $Ph_4SbOH$,[6] $Ph_3Sb(NCS)_2$,[14] $Ph_3Sb(NO_3)_2$,[15] $(Ph_3Sb)_2OCrO_4$,[16] $Ph_2SbCl_3$.[17] The identities of the compounds were confirmed by melting points and infrared spectra, and in the case of $Ph_2SbCl_3$ by microanalysis. *Anal.* Calcd for $Ph_2SbCl_3$: C, 37.67; H, 2.49; Cl, 27.85. Found: C, 37.52; H, 2.42; Cl, 27.78.

## Results and Discussion

**General Comments.** The results of the present $^{121}$Sb Mossbauer measurements are summarized in Table I together with the earlier data of Long, *et al.*[2] A typical spectrum for an $R_3SbX_2$ type compound is illustrated in Figure 1. In general, our data for the $Ph_4SbX$ and $Ph_3SbX_2$ derivatives are in good agreement with previously reported values for similar compounds.[2,18] In particular, the magnitudes of the quadrupole splittings $|e^2qQ|$ and the zero asymmetry parameters $\eta$ show that these compounds adopt trigonal-bipyramidal structures with effective $C_{3v}$ or $D_{3h}$ symmetry about antimony. Previous ir studies on these compounds[7,13,19] and the X-ray study of $Ph_4SbOH$[6] have come to similar conclusions.

From Raman and ir spectral data Goel and coworkers[7,20] have assigned a trigonal-bipyramidal structure with essentially planar $C_3Sb$ groups and axial ester-like acetate groups to $Ph_3Sb(OCOMe)_2$. Since a somewhat larger than usual $\chi^2$ value was found upon fitting the Mossbauer spectrum of this derivative with $\eta$ constrained to zero, the fit was repeated with $\eta$ as an adjustable parameter. The best-fit value of $\eta$ so obtained was $\eta = 0.29$, but there was no significant reduction in $\chi^2$ compared to the fit for $\eta = 0$ (see Table I). Thus, one cannot attach much meaning to the nonzero asymmetry parameter, and there seems little reason to doubt the essential correctness of Goel's[7,20] structural assignment for this compound.

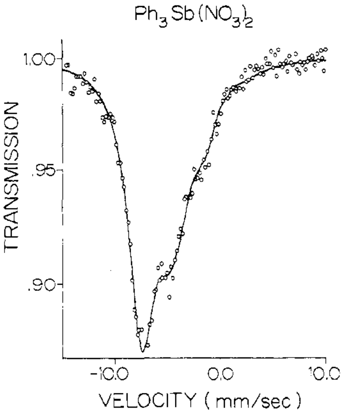

**Figure 1.** $^{121}$Sb Mossbauer spectrum of $Ph_3Sb(NO_3)_2$ at 9°K. The solid line represents the best least-squares fit to the data and yields the parameters $\delta = -5.7$ mm sec$^{-1}$ (relative to Ba$^{121}$SnO$_3$), $e^2qQ = -21.3$ mm sec$^{-1}$, $\Gamma = 3.0$ mm sec$^{-1}$. The asymmetry parameter $\eta$ was constrained to zero.

For the $Ph_3SbX_2$ compounds listed in Table I, there is an approximately linear correlation between $|e^2qQ|$ and the isomer shift $\delta$ (see Figure 2), with the exception of $(Ph_3Sb)_2OCrO_4$. If we exclude this last compound, the best least-squares fit to the points in Figure 2 gives $\delta = -0.51 \cdot (e^2qQ) - 16.20$ mm sec$^{-1}$. Since $e^2qQ$ becomes more negative with increasing electronegativity of ligand X, it is clear that $\sigma$-bonding effects must play the dominant role in determining $e^2qQ$. This fact and the negative gradient of the linear correlation in Figure 2 imply that trends in $\delta$ are governed by changes in s-orbital occupancy due primarily to $\sigma$-bonding interactions. Thus *F* with the highest electronegativity produces the most positive $\delta$ (most like Sb$^{5+}$) and the largest $|e^2qQ|$ since its $\sigma$-donor ability is least (of the X groups studied here) relative to the phenyl group. Similarly, I has the lowest electronegativity of the X groups studied and leads to the most negative $\delta$ and smallest $|e^2qQ|$.

The large deviation of $(Ph_3Sb)_2OCrO_4$ from this linear correlation is probably due to the fact that this compound is more properly formulated as $Ph_3SbXY$, suggesting a different hybridization at Sb compared to the $Ph_3SbX_2$ derivatives. If one of the axial groups X or Y is more effective in competing for electron density than the other, departures from the regular behavior of the $Ph_3SbX_2$ complexes due to changes in hybridization would not be unexpected. That this is probably the situation is shown by the structure of $(Ph_3SbN_3)_2O$, where the Sb-O distance of 1.985 Å[21] is significantly shorter than the Sb-O distances in $Ph_3Sb(OMe)_2$ (2.033 Å, average),[5] $Ph_4SbOMe$ (2.061 Å),[5] and $Ph_4SbOH$ (2.048 Å).[6]

The $\delta$ and $e^2qQ$ values for $(Ph_3SbCl)_2O$ and $(Ph_3SbBr)_2O$ measured at 78°K[2] (although inherently less accurate at this temperature) also depart considerably from the linear correlation of Figure 2. Indeed, departures from predicted isomer shift behavior may well be characteristic of Sb-O bonding

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**Table I.** $^{121}$Sb Mossbauer Data[a]

| Compd | $\delta$,[b] mm sec$^{-1}$ | $e^2qQ$,[c] mm sec$^{-1}$ | $\Gamma$, mm sec$^{-1}$ | $\chi^2$ [d] | Ref[e] |
|---|---|---|---|---|---|
| $Ph_4SbF$ | −4.56 | −7.2 | 2.62 | | 2 |
| $Ph_4SbCl$ | −5.26 | −6.0 | 2.73 | | 2 |
| | −5.2 ± 0.1 | −6.4 ± 0.7 | 2.8 | 151 | |
| $Ph_4SbBr$ | −5.52 | −6.8 | 2.75 | | 2 |
| $Ph_4SbNO_3$ | −5.49 | −6.4 | 2.57 | | 2 |
| $Ph_4SbOH$ | −4.1 ± 0.1 | −5.3 ± 0.5 | 2.9 | 172 | |
| $Ph_4SbNCS$ | −5.2 ± 0.1 | −6.4 ± 0.6 | 2.9 | 188 | |
| $Ph_3SbF_2$ | −4.69 | −22.0 | 2.66 | | 2 |
| $Ph_3SbCl_2$ | −6.02 | −20.6 | 2.55 | | 2 |
| $Ph_3SbBr_2$ | −6.32 | −19.8 | 2.75 | | 2 |
| $Ph_3SbI_2$ | −6.72 | −18.1 | 2.58 | | 2 |
| $Ph_3Sb(NO_3)_2$ | −5.7 ± 0.1 | −21.3 ± 1.0 | 3.0 | 147 | |
| $Ph_3Sb(NCS)_2$ | −5.6 ± 0.1 | −20.4 ± 0.7 | 2.6 | 147 | |
| $Ph_3Sb(OCOMe)_2$ | −4.8 ± 0.1 | −21.8 ± 0.5 | 2.8 | 147 | |
| | −4.9 ± 0.1 | −20.9 ± 0.5[f] | 2.9 | 140[g] | |
| $(Ph_3Sb)_2OCrO_4$ | −4.3 ± 0.1 | −16.6 ± 0.8 | 2.8 | 143 | |
| $Me_3SbCl_2$ | −6.11 | −24.0 | 2.74 | | 2 |
| $Me_3SbBr_2$ | −6.40 | −22.1 | 2.58 | | 2 |
| $Ph_2SbCl_3$ | −7.0 ± 0.1 | +25.9 ± 0.7 | 3.0 | 194 | |
| | −7.0 ± 0.1 | +25.2 ± 0.7[h] | 3.0 | 189[g,h] | |

[a] Present data recorded with source at 77°K and absorber at 9°K; data from ref 2 recorded with both source and absorber at 4.2°K. [b] Present data relative to $Ba^{121}SnO_3$; data from ref 2 relative to $Ca^{121}SnO_3$. [c] $\eta = 0.0$ unless otherwise noted. [d] Approximately 180 degrees of freedom. [e] This work unless otherwise noted. [f] Alternative fit of data with $\eta$ as adjustable parameter; best-fit value is $\eta = 0.29 \pm 0.07$. [g] No significant improvement in fit for $\eta \neq 0$. [h] Alternative fit of the data with $\eta$ as adjustable parameter; best-fit value is $\eta = 0.22 \pm 0.05$.

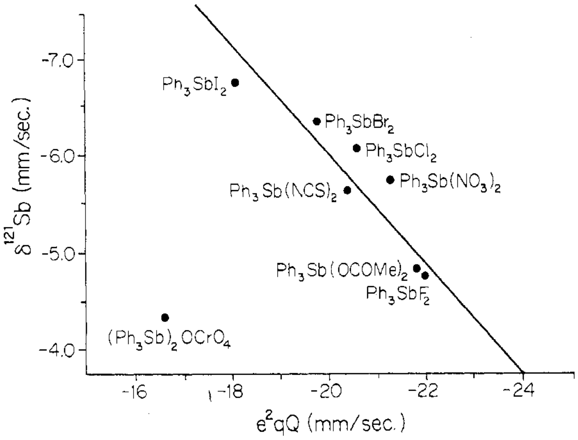

**Figure 2.** Correlation of $^{121}$Sb isomer shifts $\delta$ and quadrupole coupling constants $e^2qQ$ for derivatives of the type $Ph_3SbX_2$. The straight line follows the equation $\delta = -0.51(e^2qQ) - 16.20$ mm sec$^{-1}$ and was constructed by least squares, omitting the point due to $(Ph_3Sb)_2OCrO_4$.

since compounds containing this linkage appear to have $\delta$ values somewhat more positive than might be anticipated strictly on the basis of electronegativity arguments. For example, the isomer shift of $Ph_4SbOH$ is more positive than that of $Ph_4SbF$, while the $\delta$ value of $(Ph_3Sb)_2OCrO_4$ is more positive than that of $Ph_3SbF_2$. In this connection it should be noted that the $^{119}$Sn isomer shift of $(Bu_2SnCl)_2O$[22] (Bu $= n\text{-}C_4H_9$) is lower than that of any of the dibutyltin dihalides,[22,23] and $\delta$($^{119}$Sn) of BuSn(O)OH[24] is much lower than those of organotin trihalides.[25] Since the change in nuclear charge radius between ground and excited states ($\delta r/r$) is opposite in sign for $^{119}$Sn and $^{121}$Sb, there is an evident parallel between the effects of Sn–O and Sb–O linkages on isomer shift values.

We also note that the $Ph_4SbX$ derivatives do not show a linear correlation between $\delta$ and $e^2qQ$. Of course, these are also compounds of the $Ph_3SbXY$ type since the two axial ligands differ, and the remarks above concerning hybridization effects should apply here as well. However, there *is* a general trend to more positive $\delta$ with increasing electronegativity of X in the $Ph_4SbX$ derivatives, with the exception of X = OH (*vide supra*).

There are two other isomer shift trends in these compounds which deserve comment. The first is that the $\delta$ values of $Ph_3SbX_2$ derivatives are more positive than those of the corresponding $Me_3SbX_2$ compounds, consistent with the better $\sigma$-donor ability of alkyl groups relative to aryl groups. This trend has also been observed for $[Ph_3SbFe(CO)_2Cp](PF_6)$ and $[Bu_3SbFe(CO)_2Cp](PF_6)$[11] (Cp = $\pi\text{-}C_5H_5$), and parallel behavior has been found in $^{119}$Sn Mossbauer studies.

The second trend is that for a given X the isomer shift of $R_4SbX$ is more positive than that of $R_3SbX_2$. In tin chemistry the $^{119}$Sn isomer shifts of compounds of the type $R_{4-n}SnX_n$ increase initially as $n$ increases, reach a maximum at $n = 2$, and then decrease again.[26] The explanation advanced for this nonmonotonic behavior is that when an organic R group is replaced by a more electronegative ligand, some rehybridization occurs leading to more s character in the Sn–C bonds and more p character in the Sn–X bonds. Thus, although the X groups are more electron withdrawing, they withdraw electrons which are primarily p in character so that the net result is a deshielding of the s electrons and an increase in isomer shift.[26] Of course this process must reach a maximum at some value of $n$, after which a decrease in $\delta$($^{119}$Sn) should occur. A similar explanation can account for the decrease in isomer shift (increase in s-electron density at the nucleus) in compounds of the type $R_{5-n}SbX_n$ as $n$ increases from 1 to 2. For antimony, however, the value of $n$ which minimizes $\delta$($^{121}$Sb) has not yet been established, but it is clear that this may well depend both on the electronegativity of the X group and on the hybridization at antimony.

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**Additive Model for the efg at Sb.** To a first approximation the efg at the $^{121}$Sb nucleus can be separated into two terms, a lattice contribution due to charges on the ligands and other ions in the crystal and a valence contribution due to an asymmetric distribution of electrons in bonding and nonbonding valence shell orbitals.[27] For highly covalent molecular systems the contribution from external ions is expected to be small and to a good approximation the lattice term arises solely from charges on the ligands. Moreover, if there are no nonbonding electron pairs on the central atom (as is the case here), the valence term will consist of contributions from each ligand L. In this situation the so-called point-charge model may be applied, in which the efg can be written as[25]

$$eq = \sum_{\mathrm{L}} [\mathrm{L}](3 \cos^2 \theta_{\mathrm{L}} - 1) \qquad (1)$$

where

$$[\mathrm{L}] = \frac{eq_{\mathrm{L}}(1 - \gamma_\infty)}{r_{\mathrm{L}}^3} - \frac{ep_{\mathrm{L}}(1 - R)}{\langle r_{\mathrm{L}}'^3 \rangle} \qquad (2)$$

$q_{\mathrm{L}}$ is the charge on ligand L with coordinates $\theta_{\mathrm{L}}$ and $r_{\mathrm{L}}$, and $p_{\mathrm{L}}$ is the effective population in the hybrid orbital directed toward L with effective electron coordinates $\theta_{\mathrm{L}}$ and $r_{\mathrm{L}}'$. The Sternheimer factors $\gamma_\infty$ and $R$ account for induced polarization of core electrons.

The lattice and valence contributions are opposite in sign, and in most covalent compounds one expects the valence term to be of much greater importance. Such is obviously the case for the types of organoantimony complexes considered here. For example, in the compound $\mathrm{Ph_4Sb^+ClO_4^-}$, one expects the valence contribution to be effectively zero so that only the lattice term should contribute to the efg. Since $e^2qQ = 0$ with a line width of only 2.6 mm sec$^{-1}$[2] (natural width 2.1 mm sec$^{-1}$), it is clear that the valence term makes the dominant contribution to the efg at the antimony nucleus. A similar conclusion has been drawn from data on $\mathrm{Sb[Co(CO)_3PPh_3]_4{}^+PF_6{}^-}$.[11]

Although the treatment outlined here is based on the point-charge formalism, one could equally well use a molecular orbital approach analogous to that of Clark, *et al.*,[28] for Sn(IV) compounds. For our present purposes, however, there is no advantage to be gained by using a molecular orbital model. The central feature of both treatments is the assumption that the efg can be taken as the sum of contributions [L], one for each ligand, and it is the validity of this additivity approximation for organoantimony(V) compounds which we wish to assess here at a purely empirical level.

For numerical computations the value assigned to the contribution to $e^2qQ$ from a ligand L will be expressed in terms of the value of [L] as defined in eq 2 times $e|Q|$, so that [L] has units of mm sec$^{-1}$. Our [L] values will thus have the same significance as the $(\mathrm{pqs})_{\mathrm{L}}$ values (pqs = partial quadrupole splitting) of Bancroft and Platt.[1a] This also means that values of $V_{zz}$, the principal component of the efg tensor, derived from our calculations will be scaled up by $e|Q|$ times the nuclear $V_{zz}$. We adopt this procedure since it is the *sign* of $V_{zz}$ which is of physical significance: if $V_{zz} < 0$, the equivalent ellipsoid of charge is prolate, while if $V_{zz} > 0$, the charge distribution is oblate. On the other hand, $e^2qQ$ is the experimentally determined quantity and the two are simply related by $e^2qQ = \mathrm{sign}(Q)V_{zz}$. Since $Q$ is negative for $^{121}$Sb, $e^2qQ = -V_{zz}$ in this case.

As the [L] values cannot be derived from first principles it is necessary to deduce them from compounds of known structure. Since the components of $e^2qQ$ consist of sums and differences of [L] values in such a manner that the addition of an arbitrary constant to each [L] value makes no difference to the final result, the usual practice is to assign an [L] value of 0.0 to one particular ligand and to derive [L] values for other ligands from this arbitrary starting point.[28] For molecules with regular geometries the principal components of the efg tensor for various combinations of ligands have been tabulated in terms of [L] values,[1] and we shall not list them here. Although it is not readily apparent from the foregoing, the values of [L] are also dependent on the coordination number of the complex and for a trigonal-bipyramidal system on whether a given ligand occupies an axial or equatorial position. We therefore use the fairly obvious notation[1a] $[\mathrm{L}]^{\mathrm{TET}}$, $[\mathrm{L}]^{\mathrm{OCT}}$, $[\mathrm{L}]^{\mathrm{TBA}}$, and $[\mathrm{L}]^{\mathrm{TBE}}$ for the pqs value of a ligand in tetrahedral, octahedral, trigonal-bipyramidal axial, and trigonal-bipyramidal equatorial coordination, respectively.

From the data in Table I it is possible to derive pqs values for various ligands and from these to predict $e^2qQ$ values for other derivatives as a test of the additive model. As a starting point we have chosen the compound $\mathrm{Ph_3SbCl_2}$ since its X-ray crystal structure is known.[3] All the bond angles about Sb are within 3° of those for a regular trigonal bipyramid, so we can safely treat this molecule as being undistorted. To set the zero point of our pqs scale, we arbitrarily assign the value $[\mathrm{Cl}]^{\mathrm{TBA}} = 0.0$ mm sec$^{-1}$. Then from the $e^2qQ$ value for $\mathrm{Ph_3SbCl_2}$ in Table I, we have[1a]

$$V_{zz} = 4[\mathrm{Cl}]^{\mathrm{TBA}} - 3[\mathrm{Ph}]^{\mathrm{TBE}} = +20.6 \text{ mm sec}^{-1}$$

from which $[\mathrm{Ph}]^{\mathrm{TBE}} = -6.9$ mm sec$^{-1}$. Note that $V_{zz}$ is positive, indicating that the electronegative Cl ligands withdraw charge along the $z$ axis so that the charge distribution about the Sb nucleus is oblate (excess electron density in the $xy$ plane).

The pqs value for an axial phenyl group can be obtained from $\mathrm{Ph_4SbCl}$ if we assume the $e^2qQ$ value for this compound to be the mean of the two values given in Table I. Then[1a]

$$V_{zz} = 2[\mathrm{Cl}]^{\mathrm{TBA}} - 3[\mathrm{Ph}]^{\mathrm{TBE}} + 2[\mathrm{Ph}]^{\mathrm{TBA}} = +6.2 \text{ mm sec}^{-1}$$

and from the above values of $[\mathrm{Cl}]^{\mathrm{TBA}}$ and $[\mathrm{Ph}]^{\mathrm{TBE}}$ we find $[\mathrm{Ph}]^{\mathrm{TBA}} = -7.2$ mm sec$^{-1}$. In a similar way pqs values for other ligands have been derived from data in Table I on compounds of the type $\mathrm{R_3SbX_2}$, and these are given in Table II. From these [L] values we have calculated values of $e^2qQ$ for several other trigonal-bipyramidal organoantimony derivatives and a comparison with the measured values is presented in Table III.

Although the number of compounds available for comparison is limited, agreement between calculated and observed $e^2qQ$ values must be considered very satisfactory in view of the experimental uncertainties of about ±0.3 to ±0.7 mm sec$^{-1}$ for compounds of the type $\mathrm{Ph_4SbX}$. The agreement is somewhat less good for the two bromide derivatives, and in view of the fact that $|e^2qQ|$ values for $\mathrm{R_3SbBr_2}$ (R = Me, Ph) are less than those for the corresponding $\mathrm{R_3SbCl_2}$ species it is surprising that $|e^2qQ|$ for $\mathrm{Ph_4SbBr}$ is greater than $|e^2qQ|$ for $\mathrm{Ph_4SbCl}$. It has been suggested[28] that in comparing

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[27] N. N. Greenwood and T. C. Gibb, "Mossbauer Spectroscopy," Chapman and Hall, London, 1971, p 58.

[28] M. G. Clark, A. G. Maddock, and R. H. Platt, *J. Chem. Soc., Dalton Trans.*, 281 (1972).

**Table II.** $^{121}$Sb Partial Quadrupole Splitting Parameters for Various Ligands

| Parameter[a,b] | Value,[a] mm sec$^{-1}$ | Source compd | Parameter[a,b] | Value,[a] mm sec$^{-1}$ | Source compd |
|---|---|---|---|---|---|
| $[\mathrm{Ph}]^{\mathrm{TBE}}$ | −6.9 | $Ph_3SbCl_2$ | $[\mathrm{Br}]^{\mathrm{TBA}}$ | −0.2 | $Ph_3SbBr_2$ |
| $[\mathrm{Me}]^{\mathrm{TBE}}$ | −8.0 | $Me_3SbCl_2$ | $[\mathrm{I}]^{\mathrm{TBA}}$ | −0.7 | $Ph_3SbI_2$ |
| $[\mathrm{Cl}]^{\mathrm{TBE}}$ | ±0.9[c] | $SbCl_5$ | $[\mathrm{NCS}]^{\mathrm{TBA}}$ | −0.1 | $Ph_3Sb(NCS)_2$ |
| $[\mathrm{Ph}]^{\mathrm{TBA}}$ | −7.2 | $Ph_4SbCl$ | $[\mathrm{NO_3}]^{\mathrm{TBA}}$ | +0.2 | $Ph_3Sb(NO_3)_2$ |
| $[\mathrm{F}]^{\mathrm{TBA}}$ | +0.3 | $Ph_3SbF_2$ | $[\mathrm{OH}]^{\mathrm{TBA}}$ | −0.3 | $Ph_4SbOH$ |

[a] Quantity tabulated is $e|Q|([\mathrm{L}] - [\mathrm{Cl}]^{\mathrm{TBA}})$, assuming $[\mathrm{Cl}]^{\mathrm{TBA}} = 0.0$ mm sec$^{-1}$. [b] TBA = trigonal-bipyramidal apical; TBE = trigonal-bipyramidal equatorial. [c] Estimated from nqr data.[37]

**Table III.** Comparison of Observed $e^2qQ$ Values with Those Predicted from the Additive Field Gradient Model

| | $e^2qQ$, mm sec$^{-1}$ | | | $e^2qQ$, mm sec$^{-1}$ | |
|---|---|---|---|---|---|
| Compd | Pred | Obsd | Compd | Pred | Obsd |
| $Ph_4SbF$ | −6.9 | −7.2 | $Ph_4SbNCS$ | −6.5 | −6.4 |
| $Ph_4SbBr$ | −5.9 | −6.8 | $Me_3SbBr_2$ | −23.2 | −22.1 |
| $Ph_4SbNO_3$ | −6.7 | −6.4 | | | |

calculated and observed $^{119}$Sn quadrupole splittings agreement can be considered satisfactory if the two values differ by less than about ±0.4 mm sec$^{-1}$. From the correlation[29] of $^{119}$Sn and $^{121}$Sb quadrupole splittings the equivalent criterion for judging $^{121}$Sb $e^2qQ$ values would be a difference of about ±2.7 mm sec$^{-1}$ between calculated and observed values.[30] This seems to us to be an overly generous estimate, but even if we halve this and assume that a difference of less than about ±1.4 mm sec$^{-1}$ constitutes satisfactory agreement between observed and computed $e^2qQ$ values,[31] it will be seen from Table III that this criterion is satisfied in every case. Thus, for the pentacoordinate derivatives considered here we conclude that contributions to the efg at the antimony nucleus are essentially additive.

The $^{121}$Sb Mossbauer parameters of $Ph_2SbCl_3$, whose structure is unknown,[32,33] were also determined (Table I). This compound may adopt a trigonal-bipyramidal structure similar to that of $Me_2SnCl_3^-$,[34] or it may be six-coordinate with bridging chlorines as recently suggested for $Me_2SbCl_3$.[35] At present it is not possible to employ an additive efg model to distinguish between these possibilities, since no Mossbauer data have been reported for hexacoordinate organoantimony compounds nor is a satisfactory value available for $[\mathrm{Cl}]^{\mathrm{TBE}}$. $SbCl_5$, which is pentacoordinate at −30°,[36] might be considered as a model compound for deriving a $[\mathrm{Cl}]^{\mathrm{TBE}}$ value. However, the chlorine nqr data of Schneider and DiLorenzo[37] indicate a structural change below 195°K. Since the $^{121}$Sb Mossbauer data for $SbCl_5$ were determined at 77°K,[38,39] the use of this compound to obtain a $[\mathrm{Cl}]^{\mathrm{TBE}}$ value is precluded. We should also note that the recent assignment[29] of a negative sign for $e^2qQ$ in $SnCl_5^-$ based on its equivalence to the sign of $e^2qQ$ in $SbCl_5$ must be considered as doubtful at best.

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**Registry No.** $Ph_4SbCl$, 51153-49-2; $Ph_4SbOH$, 51195-94-9; $Ph_4SbNCS$, 51065-43-1; $Ph_3Sb(NO_3)_2$, 18514-00-6; $Ph_3Sb(NCS)_2$, 34716-93-3; $Ph_3Sb(OCOMe)_2$, 34716-94-4; $(Ph_3Sb)_2OCrO_4$, 22613-19-0; $Me_3SbBr_2$, 24606-08-4; $Ph_2SbCl_3$, 21907-22-2; $^{121}$Sb, 14265-72-6.

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(29) G. M. Bancroft, K. D. Butler, and E. T. Libbey, *J. Chem. Soc., Dalton Trans.*, 2643 (1972).

(30) The value +3.40 is obtained for the slope of the linear plot of $e^2qQ$(Sb) against $e^2qQ$(Sn) for isoelectronic Sb(V) and Sn(IV) compounds in ref 29. We have found a similar value on comparing $e^2qQ$ data for isoelectronic tin and antimony derivatives of the type $X_{4-n}M[Fe(CO)_2Cp]_n$ (M = Sn, Sb$^+$).[11]

(31) This is only a preliminary estimate which will be subject to revision as more data become available.

(32) T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem. (USSR)*, 2, 445 (1961).

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(39) J. G. Stevens and L. H. Bowen in "Mossbauer Effect Methodology," Vol. 5, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1970.