ion with EDDGA-DA results in the formation of a very stable chelate, $FeH_{-2}L^{3-}$, in which two amide protons have been displaced by the metal ion. This conclusion is further supported by calculation of two successive dissociation constants of the normal chelate, FeL^{-}, from the potentiometric data, showing that the chelate with one negative amide donor group also exists in solution as an intermediate. The structure suggested for the chelate compound $FeH_{-2}L^{3-}$ is indicated by XIII. It is suggested that the negative amide nitrogen donors are arranged in a *trans* position to minimize steric and coulombic repulsions.

The chelate compound represented by XIII is unique in that it is the first stable amide complex in which the Fe(III) ion displaces amide protons. Thus it is seen that suitably designed ligands may be useful in demonstrating previously unknown properties of ligand donor groups. This may be especially true of heavy metal ions and highly charged metal ions that hydrolyze readily at relatively low pH. The presence in the ligand of auxiliary donor groups may serve to stabilize the metal chelate in the low to moderate pH range, until the pH becomes high enough to assist the metal ion in displacing protons from the donor group being studied. Examples of strongly coordinating donor groups that may be studied in this way are peptide, hydrazide, and hydroxamide groups, as well as simple amides, imide linkages, and hydroxyalkyl groups.

Antimony-121 Mössbauer Spectra of Some Organoantimony Compounds[1,2]

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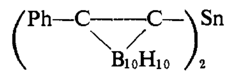
Abstract: The Mössbauer resonance of ^{121}Sb has been studied in a series of 21 organoantimony compounds at ~80°K and 12 of these at 4.2°K. Isomer shift and quadrupole splitting variations within the Ph_4SbX and Ph_3SbX_2 series (where X is a negative group such as F, Cl, ClO_4, etc.) are generally consistent with the electronegativity variation of the X groups. Spectra are much more readily and more precisely determined at the lower temperature owing to the marked increase in the per cent effect. Infrared and electrical conductivity data are presented to support the conclusion from the Mössbauer studies that the Sb–X bonds of most of the Ph_4SbX compounds have considerable covalent character in the solid state. Of the compounds studied, Ph_4SbClO_4 is the only compound found to contain a Ph_4Sb^+ cation in the solid state. Differences in the Mössbauer parameters for the various series studied are discussed in terms of likely bond hybridizations and structures of the compounds.

In recent years a large amount of work has been reported on ^{119}Sn Mössbauer spectra of organotin compounds which has been of value in the study of structure, reactivity, and mechanism of transformation of these compounds.[5] Although a large variety of organotin compounds is known, including compounds in two different oxidation states, the range of isomer shifts (IS) is very narrow and falls between −0.2 and −1.0 mm/sec with respect to gray tin for the vast majority of these compounds; the extremities of the range are −1.22 mm/sec for $[(p\text{-}ClC_6H_4)_2SnO]_n$ and +0.85 mm/sec for the divalent molecule[6]



$$\left(\mathrm{Ph{-}\underset{B_{10}H_{10}}{C{-}C}{-}}\right)_2\mathrm{Sn}$$

^{121}Sb isomer shifts are spread over a much greater range[7] than ^{119}Sn isomer shifts,[8] and thus the opportunity may exist to readily observe differences in the Mössbauer spectra of organoantimony compounds owing to relatively subtle changes in geometric environment, bonding, and substituents. The success of such experiments is not guaranteed, however, because the natural line width[7] of ^{121}Sb is considerably larger than that for ^{119}Sn, the quadrupole splitting of ^{121}Sb is more complex than that for ^{119}Sn, and the per cent effect in organoantimony compounds at liquid nitrogen temperature was found to be rather low (2–6%) in the only ^{121}Sb Mössbauer study of these compounds to date.[9]

We have determined the ^{121}Sb Mössbauer spectra for a number of organoantimony compounds in the initiation of a systematic study of the spectra of these substances. The natural line width and the complexity of the quadrupole splitting pattern cannot be avoided, but a decrease in temperature markedly increases the per cent effect, and thus results are reported for some of the

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[5] V. I. Goldanskii, V. V. Khrapov, O. Yu. Okhlobystin, and V. Ya. Rochev in "Chemical Applications of Mössbauer Spectroscopy," V. I. Goldanskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968, p 338.

[6] See ref 5, pp 336–376.

[7] S. L. Ruby in "Mössbauer Effect Methodology," Vol. 3, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, pp 203–215.

[8] M. C. Hayes in ref 5, pp 314–335.

[9] S. E. Gukasyan and V. S. Shpinel, *Phys. Status Solidi*, **29**, 49 (1968).

compounds at both liquid nitrogen and liquid helium temperatures. We have compared the Mössbauer spectra of several different types of organoantimony compounds and have used the Mössbauer data in conjunction with other experimental data to learn something about the structures of the $(C_6H_5)_4SbX$ compounds (where X = F, Cl, Br, I, NO_3, etc.).

Experimental Section

Spectra at Liquid Nitrogen Temperature. These spectra were determined with both source and absorber at liquid nitrogen temperature on a spectrometer which consisted of an Austin Science Associates S-3 constant acceleration drive unit, a xenon–methane proportional counter, a Nuclear Data 512 channel analyzer, a single channel analyzer set on the escape peak of the 37-keV ^{121}Sb γ and a $\sim$150-μCi $^{121}SnO_2$ (^{121}Sb) source. The velocity scale was calibrated by using a Pd (^{57}Co) source and metallic iron foil absorbers. Samples were prepared by mixing the compound with polyethylene powder and then placing a sufficient quantity of this mixture in Lucite holders so as to give the desired sample thickness (9–50 mg of Sb/cm^2). Generally 2–3 $\times$ 10^5 counts/channel were collected over a period of several days.

Spectra at Liquid Helium Temperature. These spectra were determined with the $Ca^{121}SnO_3$ source and spectrometer at Argonne National Laboratory which have been previously described by Ruby.[10] Absorbers containing 8.5–11 mg of Sb/cm^2 were prepared by mixing the organoantimony compound with powdered boron nitride. The spectra were determined with both the source and absorber immersed in liquid helium. About 5 $\times$ 10^4 counts/channel were generally collected. The high precision in the determination of parameters from the spectra at liquid helium temperature is reflected in the small errors reported (Table II). However, it should be pointed out that particularly in the case of the isomer shifts, the absolute errors are an order of magnitude larger. There appear to be variations of 0.1–0.2 mm/sec in isomer shifts determined with different spectrometers and different calibration methods. For the series of compounds studied under identical experimental conditions, the smaller errors as reported appear to be a true reflection of the *relative* precision among the shifts, and thus small differences between compounds are significant at liquid helium temperature.

Data Treatment. Data points were computer fit to either a single Lorentzian or to an eight-line quadrupole split pattern. In the latter case, the relative intensities of the eight-line pattern were taken from Clebsch–Gordon coefficients. The value 1.32 was used[11] for R (the ratio of the quadrupole moment of the excited state to that of the ground state) for spectra taken at liquid nitrogen temperature. Since the intensities are much larger at liquid helium temperature and hence the Mössbauer parameters can be more accurately determined, the spectra of the six trimethyl- and triphenylantimony dihalides were used to determine a new value of R. The average result of these six determinations, $R = 1.34 \pm 0.01$, was used in fitting the other spectra determined at liquid helium temperature.

Synthesis and Characterization of Compounds. The organoantimony compounds were synthesized by methods taken from the literature,[12] recrystallized until the determined per cent antimony agreed satisfactorily with the theoretical per cent antimony; carbon-hydrogen was determined in many instances and found in accord with theoretical carbon–hydrogen values; and infrared spectra, nmr spectra, and melting points were determined[13] and compared, when possible, with literature values. Electrical conductivity measurements in anhydrous acetonitrile were made on compounds of the type Ph_4SbX according to a procedure reported in an earlier paper.[14]

Results and Discussion

Comparison of ^{121}Sb Mössbauer Results at 4.2°K and 80°K. Presented in Tables I and II are the ^{121}Sb Mössbauer data for a number of organoantimony compounds at liquid nitrogen temperature ($\sim$80°K) and some of the same compounds at liquid helium temperature (4.2°K). The most striking result obtained by comparing the data in the two tables is that the per cent effect at $\sim$80°K ranges from 0.9 to 5.6% (with most of the compounds in the 1–3% range) while the per cent effect at the lower temperature is markedly increased and ranges from 26 to 45%. In addition the line widths are somewhat narrower at the lower temperature and need not be constrained during the computer fitting. The increased intensity and narrower line widths obtained at 4.2°K allow more precise determination of the various Mössbauer parameters than at liquid nitrogen temperature, and in some instances parameters are determinable at the lower temperature which could not be determined at liquid nitrogen temperature. Quadrupole splitting of less than $\sim$8 mm/sec is not discernible at liquid nitrogen temperature, but can readily be determined at 4.2°K. The ability to determine reasonable values for quadrupole splitting may be more important than the increased precision with which isomer shifts may be determined, since these former values frequently are not otherwise available. Although quadrupole splitting can be precisely determined on a nuclear quadrupole spectrometer, the signals often are not readily located.

The isomer shift values may be directly compared between the two tables, since there is no significant difference between values for the isomer shift of standard InSb as determined with the two sources (see Tables I and II). Indeed, in most instances the values of the isomer shift for a compound determined with these two sources at the different temperatures fall within the limits of the experimental errors.

Reported Isomer Shifts. Spectra of three compounds are reported both in Table I and by Gukasyan and Shpinel[9] (see footnote *b* of Table I). These are Ph_4SbBr, for which there is good agreement for the value of the isomer shift, and the triphenylantimony dihalides (Ph_3SbF_2 and Ph_3SbCl_2), where our values are 0.8 and 0.6 mm/sec more positive than those of Gukasyan and Shpinel. The dihalides show considerable quadrupole splitting which is readily discernible even at $\sim$80°K, and this must be taken into consideration to obtain accurate isomer shift values. Gukasyan and Shpinel certainly were aware of this fact, as they discussed the subject in their paper and noted that the shape of the peaks indicated quadrupole splitting. They reported a value only for Ph_3SbCl_2, $e^2qQ/4 = 1.15$ mm/sec, a value considerably smaller and of opposite sign compared to our result. Indeed, when our spectra were fitted to a single Lorentzian at the expense of a poor χ^2 value, the isomer shift values became -5.3 ± 0.2 mm/sec for

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[13] Infrared spectra were determined on samples mulled in Nujol between CsBr plates on a Perkin-Elmer 521 infrared spectrometer. Spectra of moisture-sensitive materials were determined as mulls sealed between thin polyethylene sheets.

[14] G. E. Parris and G. G. Long, *J. Inorg. Nucl. Chem.*, in press.

Table I. ^{121}Sb Mössbauer Data Taken at Liquid Nitrogen Temperature

Compound	IS,[a] mm/sec	e^2/qQ, mm/sec	Width, mm/sec	% effect	Absorber thickness, mg of Sb/cm^2
Ph_5Sb	−4.6 ± 0.1		3.0 ± 0.15	2.7	16
$Ph_5Sb \cdot {}^1/_2C_6H_{12}$	−4.2 ± 0.1		2.7 ± 0.15	2.1	21
Ph_4SbF	−4.5 ± 0.1		3.1 ± 0.2	2.2	9.2
Ph_4SbCl	−5.2 ± 0.1		2.9 ± 0.3	1.3	10
Ph_4SbBr[b]	−5.5 ± 0.1		3.2 ± 0.2	1.3	9.0
Ph_4SbI	−5.6 ± 0.1		2.9 ± 0.2	0.9	9.8
Ph_4SbNO_3	−5.4 ± 0.1		2.8 ± 0.2	1.4	9.7
Ph_4SbClO_4	−5.9 ± 0.1		2.6 ± 0.1	5.6	11
$Ph_4SbOCHO$	−4.9 ± 0.1		2.9 ± 0.15	2.5	19
$(Ph_4Sb)_2O$	−4.0 ± 0.1		2.7 ± 0.1	3.5	15
$Ph_3(CH_3)SbBF_4$	−5.8 ± 0.1		2.4 ± 0.2	1.6	23
Ph_3SbF_2[b]	−4.9 ± 0.25	−17 ± 2	3.0 ± 0.5	0.9	16
Ph_3SbCl_2[b]	−6.1 ± 0.2	−20 ± 1	2.6 ± 0.2	1.6	25
	−6.0 ± 0.2	−19 ± 1	2.8[c]	2.3	
Ph_3SbBr_2	−6.1 ± 0.1	−18 ± 1	2.1 ± 0.1	3.4	25
	−6.2 ± 0.1	−18 ± 1	2.8[c]	2.8	
Ph_3SbI_2	−6.3 ± 0.2	−16 ± 3	2.4 ± 0.5	0.9	15
$(PhCH_2)_3SbCl_2$	−6.2 ± 0.2	−30 ± 2	4.5 ± 0.5	1.9	25
	−6.2 ± 0.1	−29 ± 1	2.8[c]	2.5	
$(CH_3)_3SbCl_2$	−5.7 ± 0.2	−24 ± 1	3.0 ± 0.2	2.0	25
$(CH_3)_3SbBr_2$	−6.0 ± 0.1	−21 ± 1	3.1 ± 0.2	3.8	25
	−6.0 ± 0.1	−22 ± 1	2.8[c]	4.1	
$(Ph_3SbCl)_2O$	−5.2 ± 0.1	−18 ± 1	2.8 ± 0.25	2.5	20
$(Ph_3SbBr)_2O$	−5.3 ± 0.1	−16 ± 1	2.1 ± 0.25	2.4	20
	−5.3 ± 0.1	−15 ± 1	2.8[c]	2.0	
Ph_3Sb	−9.4 ± 0.2	+17 + 2	3.25 ± 0.4	1.6	50
	−9.4 ± 0.2	+18 ± 1	2.8[c]	1.7	

[a] With respect to $^{121}SnO_2$ (^{121}Sb) source. The isomer shift of InSb with this SnO_2 (^{121}Sb) source is −8.52 ± 0.06 mm/sec. [b] ^{121}Sb Mössbauer spectra have been reported in ref 9 for the following organoantimony compounds [compound, isomer shift from SnO_2 source in mm/sec (width in mm/sec)]: Ph_3SbCl_2, −6.9 ± 0.2 (3.7); Ph_3SbF_2, −5.5 ± 0.3 (−); $(o\text{-}CH_3OC_6H_4)_3SbCl_2$, −6.2 ± 0.2 (5.1); Ph_4SbBr, −5.6 ± 0.2 (3.3); Ph_4SbBF_4, −6.0 ± 0.1 (2.85); $(p\text{-}ClC_6H_4)_3Sb$, −9.3 ± 0.2 (3.7); $(p\text{-}CH_3OC_6H_4)_3Sb$, −9.0 ± 0.2 (5.2). [c] Width constrained by computer program to value indicated.

Table II. ^{121}Sb Mössbauer Data Taken at Liquid Helium Temperature

Compound	IS,[a] mm/sec	e^2qQ, mm/sec	Width, mm/sec	% effect	Absorber thickness, mg of Sb/cm^2
Ph_4SbF	−4.56 ± 0.01	−7.2 ± 0.3	2.62 ± 0.06	33	8.3
Ph_4SbCl	−5.26 ± 0.01	−6.0 ± 0.5	2.73 ± 0.08	26	8.3
Ph_4SbBr	−5.52 ± 0.01	−6.8 ± 0.3	2.75 ± 0.05	36	11.4
Ph_4SbNO_3	−5.49 ± 0.01	−6.4 ± 0.3	2.57 ± 0.06	38	7.8
Ph_3SbF_2	−4.69 ± 0.03	−22.0 ± 0.4	2.66 ± 0.06	30	8.0
Ph_3SbCl_2	−6.02 ± 0.02	−20.6 ± 0.3	2.55 ± 0.04	29	7.4
Ph_3SbBr_2	−6.32 ± 0.02	−19.8 ± 0.3	2.75 ± 0.04	33	8.0
Ph_3SbI_2	−6.72 ± 0.05	−18.1 ± 0.4	2.58 ± 0.14	29	8.1
$(PhCH_2)_3SbCl_2$	−5.86 ± 0.01	−23.0 ± 0.1	2.89 ± 0.03	47	9.9
$(CH_3)_3SbCl_2$	−6.11 ± 0.01	−24.0 ± 0.2[b]	2.74 ± 0.02	27	7.0
$(CH_3)_3SbBr_2$	−6.40 ± 0.02	−22.1 ± 0.3[b]	2.58 ± 0.04	27	7.8
Ph_3Sb	−9.69 ± 0.01	+17.5 ± 0.1	2.82 ± 0.02	45	15.2

[a] With respect to $Ca^{121}SnO_3$ (^{12}Sb) source. The isomer shift of InSb with this $Ca^{121}SnO_3$ (^{121}Sb) source is −8.4 ± 0.2 mm/sec (ref 7). [b] Quadrupole splittings, e^2qQ/h, are reported from radiofrequency quadrupole resonance spectra (NQR) by D. L. Macalady, Ph.D. Dissertation, University of Wisconsin, Madison, Wis, 1969; $(CH_3)_3SbCl_2$, −660,393 ± 105 KHz and $(CH_3)_3SbBr_2$ −631,127 ± 175 KHz at room temperature. These correspond in terms of units of mm/sec, respectively, to 22.13 ± 0.04 and 21.06 ± 0.06.

Ph_3SbF_2 and −6.7 ± 0.2 mm/sec for Ph_3SbCl_2, which are in good agreement with the data of Gukasyan and Shpinel.

Triarylstibines. The only organoantimony(III) compound for which we have determined the Mössbauer spectrum is triphenylstibine, which has an isomer shift of −9.69 mm/sec and quadrupole splitting of +17.5 ± 0.1 mm/sec. Gukasyan and Shpinel[9] determined values for two additional substituted aromatic stibines and found similar isomer shift values (see footnote *b* of Table I). Thus, it would seem that aromatic organoantimony(III) compounds have isomer shifts which fall at the positive end of the range found for inorganic antimony(III) compounds (more negative than −11 mm/sec);[11,15] this corresponds to less s electron density at the antimony nucleus for the organoantimony compounds as compared to the inorganic antimony(III) compounds. The positive sign of the quadrupole splitting implies excess p electron density along the *z* axis, the threefold rotational axis of triphenylstibine, as compared to that in the *x*–*y* plane. These data can be understood in terms of the observation that the C–Sb–C bond angles are ~113° in triphenylstibine,[16] a

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fact which implies that this trigonal-pyramidal molecule has σ bonds which are essentially sp^3 hybrids, and that the lone pair occupies one of these hybrids. There can be resonance between the phenyl rings and the lone pair[17,18] which permits some of the electron density of the lone pair to be dissipated into the aromatic rings, thereby giving rise to smaller s electron density on the antimony than usually found on inorganic antimony(III). Sufficient electron density, however, is still found in the sp^3 orbital utilized by the lone pair to produce the imbalance of p electron density along the z axis, and hence, the observed positive quadrupole splitting. Since delocalization of the lone electron pair would not be possible in the trialkylstibines, it would be anticipated that the isomer shifts of these compounds would be more in line with those for inorganic antimony(III) compounds.

Organoantimony(V) Compounds. Examination of Tables I and II shows that for the three general types of organoantimony(V) compounds studied, substances in which there are respectively three, four, and five organic groups bound to the antimony, the isomer shifts fall between -4.0 and -6.72 mm/sec. These values are at the negative end of the range of values found for inorganic antimony(V) compounds[15] and indicate greater s electron density on the antimony nucleus of the organoantimony(V) derivatives than for inorganic antimony(V) compounds.

The triorganoantimony(V) compounds all have large negative quadrupole splittings, a fact which means that the p electron density is greater along the x and y directions than that along the z axis. This is just as one would expect for a trigonal-bipyramidal molecule where the more electronegative groups occupy the apical positions (along the z axis). In cases where the structures have been determined for the R_3SbX_2 type compound, this is the geometry that was found.[19] As the electronegativity of the halide increases, the isomer shift of the antimony becomes less negative, in accord with increased withdrawal of electron density as the electronegativity difference between the halogen and antimony increases. As expected for molecules with similar geometry,[11] the variation of isomer shift with electronegativity difference is linear. As electron density is withdrawn along the z axis, the quadrupole splitting increases. It can be concluded that the Sb–X bond has some s character (from the isomer shift variation) and considerable p character (from the quadrupole splittings); hence, the Mössbauer data are in accord with the expected dsp^3 bonding. The results at liquid helium temperature indicate a possible trend, since the isomer shifts for $(CH_3)_3SbCl_2$ (-6.11 mm/sec) and $(CH_3)_3SbBr_2$ (-6.40 mm/sec) are both slightly more negative than the corresponding phenyl compounds (-6.02 and -6.32 mm/sec, respectively). Taken into consideration with the somewhat larger quadrupole splittings for the methyl compounds, these results could indicate that the phenyl groups are slightly more electron withdrawing than methyl, removing both $p_{x,y}$ and s electrons, thus lowering both the s electron density and the p electron imbalance. However, the isomer shift for tribenzylantimony dichloride is less negative than for the phenyl compound. More data of this type are necessary to form any significant generalization. In any event it appears that the difference between aromatic and aliphatic substituents is small. It would thus seem that both types of substituents form essentially σ bonds with antimony, in which the electron pair is more closely associated with antimony than in covalent inorganic antimony(V) compounds. This is in accord with the observations of the ultraviolet spectra of triphenylantimony dihalides by Jaffé,[17] in which it was concluded that there is little or no conjugation of the phenyl rings through the antimony.

Some comparisons of the isomer shifts of the R_3SbX_2 compounds with other series of compounds can be made. Replacement of one of the chlorines or bromines of Ph_3SbX_2 by an oxygen to give a $(Ph_3SbX)_2O$ compound results in a less negative isomer shift in accord with the increased electronegativity of the oxygen. Comparison of the quadrupole splitting data is probably meaningless since the only values available at the present for the oxobis[triphenylantimony(V)] halides were obtained at ~80°K and are not particularly accurate. The isomer shifts for the Ph_3SbX_2 compounds are consistently more negative than those for the corresponding Ph_4SbX compounds (comparison between compounds where X is the same), and the differences in isomer shifts between pairs of compounds become less as the electronegativity of the X group increases. It is not surprising to find that the quadrupole splitting of a Ph_3SbX_2 compound is relatively large, but it is surprising to find that compounds which were thought to contain symmetrical Ph_4Sb^+ cations have quadrupole splitting at all. This can be better understood after discussion of the structures of the latter group of compounds in the next section.

Compounds of the Type Ph_4SbX. The ^{121}Sb Mössbauer spectra show that the Ph_4SbX compounds have isomer shifts which vary between -5.9 and -4.0 mm/sec. The spectra of these compounds at 4.2°K (X = F, Cl, Br, and NO_3) all show negative quadrupole splittings of approximately 7 mm/sec. One would expect that a tetrahedral Ph_4Sb^+ cation would neither have variation in isomer shift as the negative counterion is varied nor give a spectrum showing quadrupole splitting. Thus, with the possible exception of the perchlorate, the Sb–X bond in the Ph_4SbX compounds must have considerable covalent character in the solid state.

Although the assumption is generally made in Mössbauer work that structures of solids do not change over the 4–300°K range, it would be desirable to verify these conclusions based on the Mössbauer studies by other experimental techniques. Some of the Ph_4SbX compounds, *e.g.*, Ph_4SbF[12d] and the corresponding carboxylates,[12f] have been known to have relatively high solubilities in nonpolar solvents, but nevertheless these were still designated as salts. Although recently Ph_4SbOH[20] and Ph_4SbOCH_3[21] have been shown to be covalent with trigonal-bipyramidal structures in which the oxygen occupies one of the apical positions, com-

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pounds containing the Ph_4Sb group usually have been assumed to be ionic and accordingly have been named as tetraphenylstibonium salts. Indeed, the infrared spectra of Nujol mulls and KBr pellets of the chloride, bromide, iodide, and triiodide have been interpreted to be in accord with each of these substances containing the Ph_4Sb^+ cation.[22] Antimony–halogen stretching vibrations were not observed above 250 cm^{-1}, and the variations in the phenyl modes, even the X-sensitive modes, were suggested as largely due to solid-state effects and differences between the symmetry of the Ph_4Sb^+ site and tetrahedral symmetry. We examined[23] the infrared spectra of a number of similar compounds which included the fluoride, nitrate, and perchlorate. The spectrum of a Nujol mull of Ph_4SbF showed a strong band at 404 cm^{-1}, which was assigned by Doak and Long to the Sb–F stretching frequency[23] (the asymmetric Sb–F stretching mode is found at 505 cm^{-1} in Ph_3SbF_2[12d]). In the spectrum of the nitrate there are very strong bands at 1460, 1295, and 728 cm^{-1}, and medium intensity bands at 1275, 1020, and 818 cm^{-1} which definitely are not phenyl frequencies. These can be readily assigned in terms of C_{2v} symmetry for the nitrate with the band at 1460 cm^{-1} corresponding to ν_4, those at 1295 and 1275 cm^{-1} to ν_1, 1020 cm^{-1} to ν_2, and 818 cm^{-1} to ν_6.[24] The 750–700-cm^{-1} region of the spectrum shows a number of bands which are undoubtedly associated with the f phenyl mode (notation of Whiffen[25]), but two of these could very easily be ν_3 and ν_5 for the nitrate. The splitting between ν_1 and ν_4 is 165 cm^{-1}, which certainly indicates that the NO_3 group deviates from D_{3h} symmetry, and suggests[26] at least partial covalent bonding between the nitrate and antimony.[27] The infrared spectrum of the perchlorate shows a strong band at 1090 cm^{-1}, a medium band at 622 cm^{-1}, and a weak band at 920 cm^{-1} which are characteristic of a perchlorate ion.[28] It is interesting to note that the phenyl frequencies show very little splitting compared to what is usually found in the spectra of Ph_4SbX compounds and are similar to the relatively simple phenyl spectrum reported for Ph_4SbI_3,[20] which suggests that undistorted Ph_4Sb^+ cations do exist. Other indications that something is different about the perchlorate come from the Mössbauer data; the per cent effect is markedly higher for the perchlorate as compared to the other Ph_4SbX compounds (5.6% *vs.* a range of 0.9–3.5%) at liquid nitrogen temperature. A higher per cent effect is to be expected in an ionic compound than in one made up of discrete molecules. Also, although quadrupole splitting parameters cannot be evaluated for the Ph_4SbX compounds at ~80°K, it is interesting to note the variation in line width (Table I) for absorbers of similar thickness (3.2 mm/sec for Ph_4SbBr to 2.6 mm/sec for Ph_4SbClO_4). The larger width of the former is perhaps indicative of a small quadrupole splitting. When a few of these spectra were fitted with splittings, the result gave $e^2qQ \simeq -5$ mm/sec with errors larger than the values. As seen in Table II, the splitting is readily obtained at 4.2°K for the four compounds measured. However, the spectrum of Ph_4SbClO_4 at ~80°K is the narrowest as well as having by far the largest per cent effect, and thus complete absence of quadrupole splitting is likely. Additional evidence from the study of vibrational spectra as to the nature of the Sb–X bond in Ph_4SbX compounds was recently presented by Orenberg, *et al.*,[29] in a Raman study of Ph_4SbCl and $(Ph_4Sb)_2SO_4$ in both the solid state and in solutions. The conclusion reached, in contrast to that of MacKay and Sowerby,[22] was that "the antimony derivatives generally appear to be pentacoordinate trigonal bipyramids with the fifth coordination position occupied by an anion or by a solvent molecule."

In order to better understand the nature of the R_4SbX compounds, a study of the electrical conductivities of these compounds in anhydrous acetonitrile was undertaken. The fact that a given substance is a strong electrolyte indicates nothing about the nature of the solid, but where weak electrolytes are found, the solid almost certainly is made up of molecules. The data for the electrical conductivity of the R_4SbX compounds are presented in Table III; for comparison, silver nitrate, a strong 1:1 electrolyte in acetonitrile, has a molar conductance, $\Lambda_{M,25°}$, of 155.2 ohm^{-1} cm^2 mol^{-1} at a concentration of 0.00228 mol/l.[30] Certainly the data in Table III indicate that Ph_4SbF, $Ph_4Sb(O\cdot CO\cdot CH_3)$, and $Ph_4Sb(O\cdot CO\cdot H)$ are essentially undissociated, that Ph_4SbCl is dissociated only to a small extent, and that the other compounds could well be 1:1 electrolytes.[27]

Table III. Electrical Conductivity Measurements in Acetonitrile Solutions

Compound	$10^4\kappa$, ohm^{-1} cm^{-1}	C_M, mol/l.	Λ_M, ohm^{-1} cm^2 mol^{-1}	Temp, °C
Ph_4SbF	0.014	0.01073	0.13	25
$Ph_4Sb\cdot O\cdot CO\cdot CH_3$	0.064	0.00971	0.66	26
$Ph_4Sb\cdot O\cdot CO\cdot H$	0.213	0.01001	2.13	27
Ph_4SbCl	1.23	0.00958	12.8	26
Ph_4SbBr	7.10	0.01005	70.6	27
$(CH_3)_4SbBr$	17.6	0.02001	88.0	25
Ph_4SbNO_3	10.8	0.00984	110	26
$(CH_3)_4SbI$	22.3	0.01975	113	25

Conclusions

Although useful information can be obtained from ^{121}Sb Mössbauer spectra taken at liquid nitrogen temperature, the various Mössbauer parameters can be determined more precisely and more readily at 4.2°K. In molecular compounds where the per cent effect is small at ~80°K, *e.g.*, the organoantimony compounds, operation at a lower temperature is almost required in order to obtain meaningful data. The fact that quad-

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ruple splitting can be readily determined and reasonably precise values obtained should be of great importance, since NQR results frequently are not obtainable.

The Mössbauer data lead one to the conclusion that a great majority of Ph_4SbX compounds do not contain a simple tetrahedral Ph_4Sb^+ cation in the solid state. In some cases there is considerable covalent character to the Sb–X bond, in others the effect of the X group might be best described as causing distortion of the Ph_4Sb^+ group, and finally in a few cases the Ph_4Sb^+ cation does exist. Of the compounds studied only tetraphenylstibonium perchlorate belongs to this last category. The experimental observation that the isomer shift for the ionic Ph_4SbClO_4 corresponds to the largest s electron density in the Ph_4SbX series requires some comment. The tetrahedral bonding in the Ph_4Sb^+ cation would be described as sp^3. Pentacoordinate bonding, such as required in a covalent Ph_4SbX molecule, would be described as some sort of dsp^3 hybridization. Significantly, the basic s electron density and p shielding should be identical for these two types of hybridization. In the case of pentacoordinate bonding, as in covalent Ph_4SbX, the Sb–X bond should have some s character. If X is an electronegative group, it should withdraw electrons along the bond, thus reducing the s density at Sb. This electron withdrawal would not occur for a $Ph_4Sb^+ X^-$ ionic compound, and thus the Ph_4Sb^+ cation would have the largest s electron density at Sb and the lowest value for the isomer shift in a series Ph_4SbX.

The general observation that the isomer shifts for the Ph_3SbX_2 series are lower than for the corresponding members of the Ph_4SbX series indicates either more s density at the antimony in the Ph_3SbX_2 series or less p density. It is difficult to imagine how the substitution of an electronegative X group for a phenyl could increase electron density at antimony. The situation is complicated by the possibility of variations in geometry and hybridization in the Ph_4SbX series. However, both isomer shift and quadrupole splitting data are in agreement that the Ph_3SbX_2 compounds have less p electron density. The p density would be removed along the apical Sb–X bonds, giving rise to the characteristically large negative quadrupole splitting observed in these compounds.

It is apparent from the results presented above that ^{121}Sb Mössbauer studies of organoantimony compounds, especially at liquid helium temperature, can be valuable in structural analysis of these compounds. Indeed, the variations observed appear considerably more sensitive than those reported for ^{119}Sn in organotin compounds.

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An Electron Spin Resonance Study of Coordination to the Fifth and Sixth Positions of α,β,γ,δ-Tetra(*p*-methoxyphenyl)porphinatocobalt(II)

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Abstract: Esr studies of α,β,γ,δ-tetra(*p*-methoxyphenyl)porphinatocobalt(II) in toluene glasses in the presence of various concentrations of a number of different amines show the formation of both five- and six-coordinate complexes. The esr parameters are quite insensitive to the basicity of the amine, and the resolution of the spectrum is determined by the composition of the glass. In the presence of air, the esr spectrum undergoes a dramatic change, attributed to the formation of a six-coordinate complex containing one amine and one oxygen molecule as the fifth and sixth ligands.

Several esr studies of planar, square-pyramidal, and octahedral low-spin cobalt(II) complexes have indicated the sensitivity of their esr parameters to solvation or crystalline environment.[2–6] This has been attributed to the fact that the single unpaired electron is in the d_{z^2} orbital of cobalt.[2,3,5] Assour[3] has correlated bonding parameters of cobalt phthalocyanine [Co(pc)] obtained from glassy spectra with the electronegativity of the amine solvent. In the present study of α,β,γ,δ-tetra(*p*-methoxyphenyl)porphinatocobalt(II) [Co(*p*-OCH_3)TPP] it was found that the esr spectrum was extremely sensitive to the quality of the glass, and because of this a common solvent (toluene), which is known to form good glasses, was used for all samples, with various amounts of amines added as ligands. The purpose of this study was to determine the esr parameters ($g_{\|}$, $g_{\perp}$, $A_{\|}$, $A_{\perp}$, A_N) of a number of different cobalt–porphyrin complexes in a common medium in order to isolate the specific effects due to coordination from

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