Antimony-121 Mössbauer Spectra of Six-co-ordinate Di- and Tri-organoantimony(v) Compounds

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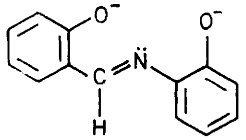
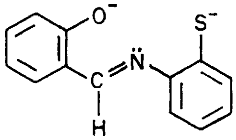
The ^{121}Sb Mössbauer spectra are reported for a series of organoantimony(V) compounds of the type $[SbR_3(trid)]$ and $[SbClR_2(trid)]$ (R = Me or Ph, trid = tridentate ligand with ONO or ONS donor atoms). The compounds have an effective octahedral geometry with a meridionally disposed tridentate ligand and a T-shaped SbR_3 or *trans*-SbR_2 moiety. The observed parameters are fully consistent with a simple point-charge interpretation.

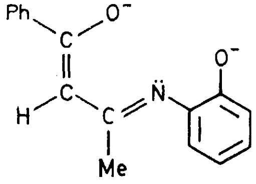
A STUDY by ^{121}Sb Mössbauer spectroscopy of a series of anionic six-co-ordinate mono- and di-organoantimonate(V) halogeno- and pseudohalogeno-compounds was reported in an earlier paper.[1] These measurements have now been extended to include a series of recently synthesized [2,3] neutral organoantimony(V) compounds of the type $[SbR_3(trid)]$ and $[SbClR_2(trid)]$ ($trid^{2-}$ = a tridentate Schiff-base ligand having ONO or ONS donor atoms, R = alkyl or aryl). The ligand anions used have the following structures:



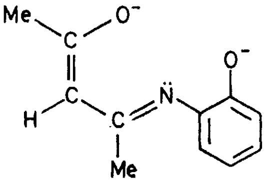
sah^{2-}



sat^{2-}

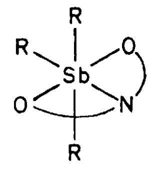


bah^{2-}

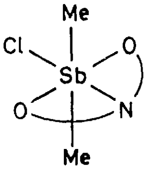


aah^{2-}

The molecular structure of one of the compounds studied, $[SbMe_3(sah)]$, has been determined.[2] The compound has essentially octahedral co-ordination about Sb [structure (1)] and represents the best substantiated example of a six-co-ordinate triorganoantimony species. Structure (1) may also reasonably be assumed for the other $[SbR_3(trid)]$ compounds. The meridional configuration adopted to the $trid^{2-}$ ligands on co-ordination to tin in a number of compounds of formula $[SnR_2(trid)]$ has also been confirmed by *X*-ray diffraction studies.[4-6] Available data on the $[SbClMe_2(trid)]$ compounds [3] suggest the six-co-ordinate structure (2) with *trans*-methyl groups both in the solid and solution phases, but the corresponding diphenyl species have not been so well characterized.



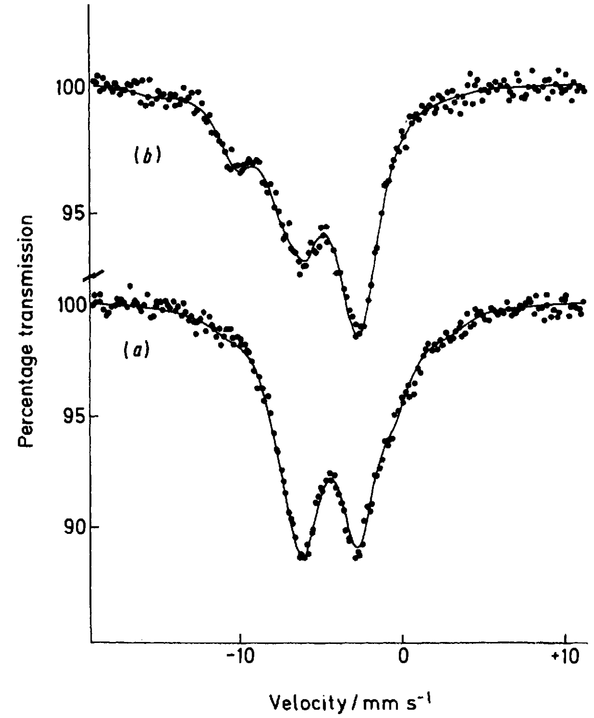
(1)



(2)

EXPERIMENTAL

The preparation and characterization of the compounds have been described elsewhere.[2,3] The ^{121}Sb Mössbauer spectra were recorded at 4.2 K using the apparatus and



Antimony-121 Mössbauer spectra at 4.2 K of (*a*) $[SbMe_3(sah)]$ and (*b*) $[SbClMe_2(sah)]$

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[1] N. Bertazzi, T. C. Gibb, and N. N. Greenwood, *J.C.S. Dalton*, 1976, 1153.

[2] F. Di. Bianca, E. Rivarola, A. L. Spek, H. A. Meinema, and J. G. Noltes, *J. Organometallic Chem.*, 1973, **63**, 293.

[3] H. A. Meinema, J. G. Noltes, F. Di. Bianca, N. Bertazzi, E. Rivarola, and R. Barbieri, *J. Organometallic Chem.*, 1976, **107**, 249.

[4] H. Preut, H. J. Haupt, F. Huber, R. Cefalù, and R. Barbieri, *Z. anorg. Chem.*, 1974, **407**, 251.

[5] H. Preut, F. Huber, H. J. Haupt, R. Cefalù, and R. Barbieri, *Z. anorg. Chem.*, 1974, **410**, 88.

[6] H. Preut, F. Huber, R. Barbieri, and N. Bertazzi, *Z. anorg. Chem.*, 1976, **423**, 75.

procedures described previously.[1] The spectra were curve-fitted using a transmission-integral method,[2] with seven variable parameters: the ground-state quadrupole coupling constant e^2qQ_g, the asymmetry parameter η, the chemical isomer shift δ relative to the $Ca^{121m}SnO_3$ source, the line-width 2Γ, the thickness T_A, and values for the intensity scaling and baseline. The final values for e^2qQ_g, η, and δ are listed in the Table and typical spectra for [$SbMe_3$(sah)] and [$SbClMe_2$(sah)] are shown in the Figure.

Mössbauer data at 4.2 K

Compound	e^2qQ_g / mm s^{-1}	η	δ * / mm s^{-1}
[$SbMe_3$(sah)]	−20.65(22)	0.76(2)	−4.41(2)
[$SbPh_3$(sah)]	−17.52(29)	0.88(3)	−3.97(2)
[$SbPh_3$(aah)]	−16.64(21)	0.78(2)	−3.82(2)
[$SbPh_3$(sat)]	−14.02(20)	1.01(3)	−4.40(2)
[$SbClMe_2$(sah)]	26.98(21)	0	−5.03(2)
[$SbClMe_2$(bah)]	24.81(14)	0	−4.86(2)
[$SbClPh_2$(sah)]·CCl_4	23.22(18)	0	−4.51(2)
[$SbClPh_2$(bah)]	21.70(18)	0	−4.41(2)
[$SbClPh_2$(aah)]	22.26(15)	0	−4.52(2)

* Chemical isomer shift relative to the source, $Ca^{121m}SnO_3$.

DISCUSSION

Electric-field Gradient and Structure.—The numerical data in the Table show that the triorgano- and diorgano-antimony(V) derivatives differ considerably in their Mössbauer parameters. The [SbR_3(trid)] compounds have an electric-field gradient (e.f.g.) at the ^{121}Sn nucleus with e^2qQ_g negative in sign (Q_g is negative for ^{121}Sb) and a large value of η. The [$SbClR_2$(trid)] compounds show a larger, positive, value for e^2qQ_g and a negligible asymmetry parameter.

These observations are in accord with the proposed structures (1) and (2), provided that the e.f.g. at the ^{121}Sb nucleus is dominated by contributions from the Sb–C bonds. The values of e^2qQ_g and the zero value of η for the [$SbClR_2$(trid)] compounds are essentially the same as those observed in the corresponding [$SbCl_4R_2$]$^-$ species (R = Me or Ph).[1] This is strong evidence that the methyl or phenyl groups of [$SbClR_2$(trid)] are in the *trans* positions of an approximately octahedral co-ordination.

It is significant that η remains essentially zero in compounds where different atoms (O, N, O, and Cl) are co-ordinated in the equatorial plane, and furthermore where the chelating ligand may be presumed to impose a considerable distortion from regular 90° bond angles. Within the scope of the point-charge model, this implies that contributions to the e.f.g. tensor from O, N, O, and Cl donor atoms are nearly equivalent and substantially smaller than those from the organic ligands. Accordingly, the values of e^2qQ_g and η for [SbR_3(trid)] (trid^{2-} has ONO donor atoms) should be derived essentially from the **T** configuration assumed by the SbR_3 unit. Point-charge calculations for such a structure with 90° bond angles predict $\eta = 1$ and a value of $|e^2qQ_g|$ in the ratio 3 : 4 with respect to that for compounds featuring a *trans*-SbR_2 moiety. However, the $SbMe_3$ unit in [$SbMe_3$(sah)] is known to be distorted from a perfect **T** shape, thus accounting for the value of $\eta < 1$ which is observed, and as shown below the negative sign of e^2qQ_g is consistent with the known bond angles.

The observed e^2qQ_g values in the Sb^VR_3 derivatives may be rationalized using a similar point-charge formalism to that employed elsewhere[7] to explain ^{119}Sn quadrupole splittings in distorted $Sn^{IV}Me_2$ structures. The partial field gradient (p.f.g.) of Me relative to Cl in octahedral structures [p.f.g. (Me) — p.f.g. (Cl)], derived from data for [$SbCl_4Me_2$]$^-$ species,[1] is −6.72 mm s^{-1} (expressed in units of the quadrupole coupling constant). Making the assumption that $\frac{1}{3}$p.f.g.(sah) − p.f.g.(Cl) = 0, which implicitly assumes that the e.f.g. is solely determined by the methyl groups, and using the known bond angles of [$SbMe_3$(sah)], it is possible to obtain 'predicted' values of $e^2qQ_g = -19.97$ mm s^{-1} and $\eta = 0.95$ for this compound. (The principal z axis is directed perpendicularly to the SbC_3 plane.) If the same bond angles for the SbC_3 unit are assumed for [$SbPh_3$(sah)], then using the value of p.f.g.(Ph) = −6.03 mm s^{-1} derived from data[1] for [$SbCl_4Ph_2$]$^-$, one obtains $e^2qQ_g = -17.92$ mm s^{-1} and $\eta = 0.95$.

Despite the crudity of the calculation the agreement with observation is encouraging. The overestimation of η is probably the result of neglecting contributions to the e.f.g. from the other donor atoms. In the case of [$SbMe_3$(sah)] for instance, if the value of $\frac{1}{3}$p.f.g.(sah) = p.f.g.(Cl) is allowed to have a finite negative value [keeping p.f.g.(R) − $\frac{1}{3}$p.f.g.(sah) equal to −6.72 mm s^{-1}] then e^2qQ_g becomes more negative and η decreases. For example, the value $e^2qQ_g = -20.65$ mm s^{-1} as observed can be reproduced by using p.f.g.(Me) = 12.92 mm s^{-1} and $\frac{1}{3}$p.f.g.(sah) = −6.20 mm s^{-1}, the corresponding value of η being 0.84. However, it would be unwise to place undue emphasis on these values.

In the examples above, no attempt was made to distinguish between partial field gradients assigned to the different points of ligation of an ONO chelate. However, this would seem to be appropriate for the sat^{2-} (ONS) ligand. Using the known structure of [$SbMe_3$(sah)] as a model for the structure of [$SbPh_3$(sat)] (the biting angles of sah^{2-} and sat^{2-} in the corresponding [$SnPh_2$(trid)] species are not very different[4,6]) point-charge calculations show that when the p.f.g. assigned to the appropriate oxygen-donor atom becomes more negative (in order to simulate the higher donor ability of S with respect to O) the calculated asymmetry parameter first increases, reaches the value of unity, and then decreases. At the same time e^2qQ_g decreases steadily and changes sign. These results give a satisfactory interpretation of the trend in the observed parameters for [$SbPh_3$(sah)] and [$SbPh_3$(sat)] and show that care must be exercised in using averaged p.f.g. values for multi-dentate ligands.

Previous studies[1,8] have shown the existence of a linear relation between the e^2qQ parameters of corresponding octahedral mono- and di-organo-tin(IV) and

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[7] T. K. Shan and G. M. Bancroft, *Inorg. Chem.*, 1975, **14**, 2281.

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

-antimony(V) species and trigonal-bipyramidal triorgano-derivatives. It is more difficult to extend the relation to compounds with tridentate ligands. Compounds of the type $[SnR_2(trid)]$ do exist, but have a different structure and stoicheiometry[4-6] from the $[SbClR_2(trid)]$ compounds considered here. The triorganotin(IV) derivative $[SnPh_3(Hsah)]$ has been characterized by Mössbauer spectroscopy,[9,10] and has been tentatively assigned a *mer*-octahedral configuration analogous to (1); the corresponding ^{119}Sn parameters are a quadrupole splitting of $\Delta = \frac{1}{2}e^2qQ[1 + (\eta^2/3)]^{\frac{1}{2}} = -2.88$ mm s^{-1} and $\eta \sim 0.9$. If it is assumed that the contributions to the e.f.g. tensor of sah^{2-} and the protonated form $Hsah^-$ are the same, then using the ratio[1] $(e^2qQ_g)_{Sb}/(e^2qQ)_{Sn} = 3.19$ and the ^{121}Sb parameters for $[SbPh_3(sah)]$ the 'predicted' ^{119}Sn parameters for $[SnPh_3(Hsah)]$ are $\frac{1}{2}e^2qQ = 2.74$ mm s^{-1} and $\eta = 0.88$ (Δ −2.96 mm s^{-1}). The agreement with observation is noteworthy and consistent with the assigned *mer*-octahedral structure.

Chemical Isomer Shift.—In each series of six-coordinate organoantimonate(V) species with two and three Sb–C bonds the chemical isomer shift (δ) becomes less negative as the electron-withdrawing ability of atoms (or groups) bonded to Sb increases, indicating a decrease in *s*-electron density at the ^{121}Sb nucleus. For instance, in the related *trans*-SbR_2 species so far investigated,[1,11] δ increases in the order $[SbCl_4R_2]^-$ $(Cl_4) < [SbCl_2Ph_2(pd)]$ $(Cl_2O_2) < [SbClR_2(trid)]$ $(ClNO_2)$ and phenyl species show a larger δ value than corresponding methyl species (pd = pentane-2,4-dionate). The smaller value of δ for $[SbPh_3(sat)]$ with respect to $[SbPh_3(sah)]$ parallels the lower electronegativity of S with respect to O. Thus it appears that in each series the *s*-electron density at the ^{121}Sb nucleus is essentially governed by the loss of valence-shell electrons from the 5*s* orbital, and an appreciable antimony 5*s* character is used in bonds other than Sb–C.

Substitution of Cl for the less electronegative R to give $[SbClR_2(trid)]$ increases δ as expected.[1] The corresponding decrease in *s*-electron density at the antimony nucleus must originate in either a net loss of *s* electrons from the valence shell or in a substantial increase in *p*-electron shielding. Although a net loss of *s* electrons from the valence shell may appear improbable, various concomitant electronic processes may be envisaged analogous to the organotin(IV) case,[12] and a substantial redistribution of the antimony bonding orbitals remains a possibility.

A recent paper[13] has given a detailed analysis of data for several organoantimony(V) compounds in terms of orbital populations. However, the treatment described embodies several major assumptions and approximations, and it is considered that similar calculations are unlikely to add to our present understanding of the compounds under discussion.

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[6/1811 *Received, 27th September*, 1976]

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[9] J. N. R. Ruddick and J. R. Sams, *J. Organometallic Chem.*, 1973, **60**, 233.

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

[11] J. N. R. Ruddick and J. R. Sams, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 229.

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

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