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^{121}Sb Mössbauer Studies on Dialkylantimony(V) Compounds of the Types $R_2Sb(OMe)_3$, $R_2Sb(OAc)_3$ and $R_2Sb(O)OH$

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Mössbauer spectra of three series of dialkylantimony(V) compounds have been measured to study bonding and structural properties of these compounds. Trialkoxodialkyl and triacetatodialkylantimony(V) compounds have octahedral structure. The former are dimeric, containing bridging methoxo groups, the latter are monomeric, containing a bidentate acetato ligand, for which the bite angle is distorted from 90°. Dialkylstibinic acids, $R_2Sb(O)$-OH, have tetrahedral coordination around the antimony atom. The additive model for the Electric Field Gradient is used to interpret much of the quadrupole coupling data.

Introduction

So far very few dialkylantimony(V) compounds of the type R_2SbX_3 have been reported in the literature. The only known examples are the trihalo dimethylantimony compounds, Me_2SbX_3 (X = F, Cl, Br, I) [1–3] and a number of trialkoxo- and triacetatodialkylantimony compounds of the types R_2SbX_3 (R = Me, Et, Pr, Bu; X = OMe, OEt, OAc) reported by Meinema and Noltes [4]. Unlike the trihalodimethylantimony compounds, which gradually decompose at room temperature trialkoxo- and triacetatodialkylantimony compounds appear to be thermally stable. Dialkylstibinic acids, $R_2Sb(O)OH$ are formed upon hydrolysis of trialkoxodialkylantimony compounds. They are colourless, amorphous solids, which show a remarkable thermal stability. Based on IR, Raman and NMR measurements Meinema and Noltes [4] proposed a dimeric octahedral structure for $Me_2Sb(OMe)_3$ with the two Me-groups in *trans* position. For $Me_2Sb(OAc)_3$ a monomeric octahedral structure was proposed with two ester type and one bidentate acetato group in equatorial positions. In the present communication we report on results of a ^{121}Sb Mössbauer spectroscopy study of R_2SbX_3 (R = Me, Et; X = OMe, OAc) and $R_2SbO(OH)$ (R = Et, Bu, Ph).

Additive models for the Electric Field Gradient (EFG) have recently been applied successfully to interpret ^{121}Sb Mössbauer spectroscopic data of a variety of antimony(V) compounds [5–9]. Of interest for the present study are measurements of dimethylantimonytrichlorides [8, 10] and diphenylantimonytrichloride [5, 11] and a study of stibonic and stibinic acids containing phenyl groups [12].

Experimental

Apart from $Et_2Sb(OMe)_3$ all dialkylantimony(V) compounds described in this paper have been prepared according to the procedures described in reference [4]. The purity of R_2SbX_3 (R = Me, Et; X = OMe, OAc) was confirmed by PMR spectroscopy in benzene solution. The dialkylstibinic acids were analyzed for antimony, carbon and hydrogen. *Anal.* Calc. for $Et_2Sb(O)OH$: Sb, 57.27; C, 22.58; H, 5.17. Found: Sb, 58.81; C, 22.00; H, 5.04%. Calc. for $Bu_2Sb(O)OH$: Sb, 45.35%; C, 35.75%; H, 7.12%. Found: Sb, 45.96%; C, 35.16%; H, 7.18%.

The synthetic procedure for $Et_2Sb(OMe)_3$ has been very much improved using trichlorodiethylantimony, prepared in situ by chlorination of tetraethyldistibine as a starting material [3]. In an atmosphere of dry, oxygen free, nitrogen, sulfurylchloride (4.47 ml, 55.2 mmol) in methylene chloride was added dropwise to a stirred solution of tetraethyldistibine (6.6 g, 18.4 mmol) in methylene chloride (60 ml) kept at −78 °C. Initially the colour of the reaction mixture turns orange-red, subsequently Et_2SbCl_3 deposits from the solution as a colourless solid. The reaction mixture was allowed to warm to room temperature to give a clear colourless solution, which

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was evaporated to dryness at reduced pressure. Et_2SbCl_3 thus obtained was dissolved in 40 ml of absolute methanol. At 0 °C sodium methoxide (110.4 mmol) in absolute methanol (50 ml) was added dropwise to the stirred solution. NaCl deposited from the solution. The reaction mixture was evaporated to dryness. Hexane (50 ml) was added and the insoluble NaCl was removed by filtration under an atmosphere of dry nitrogen. Upon distillation at reduced pressure 7.4 g of $Et_2Sb(OMe)_3$ [b.p. 66–68 °C (0.1 mm)] was isolated, yield 74%.

The Mössbauer spectra were measured with the source and absorber at 4.2 K. The source was $Ni_{21}{}^{121}Sb_2B_6$ and all isomer shifts are given relative to InSb at 4.2 K. The isomer shift of InSb with respect to the source is −1.61 ± 0.05 mm/s at 4.2 K. The spectra were fitted using a transmission integral analysis. Detailed information on the experimental set-up and analysis is given elsewhere [13]. A typical spectrum is shown in Fig. 1 and the Mössbauer parameters for the complexes reported in this study are summarized in Table I.

Discussion

Trialkoxodialkylantimony Compounds

The positive sign of the quadrupole coupling constants for these compounds implies a greater charge concentration along the principle axis than in a direction perpendicular to this axis. In addition there is trigonal or higher order symmetry about this axis, as the asymmetry parameters are zero. Two structures can be inferred for these compounds. One is a monomeric structure, *i.e.* a trigonal bipyramid with the alkyls in the axial positions and the methoxy groups in the equatorial plane, and the other a dimeric complex consisting of two octahedrally coor-

TABLE I. ^{121}Sb Mössbauer Parameters of Dialkylantimony(V) Compounds.

Compound	δ^a mm/s (±0.1)	e^2qQ mm/s (±1.0)	η (±0.2)	Γa^b mm/s (±0.1)	No^c 10^3ckh	Ta^d (±0.07)
$Me_2Sb(OMe)_3$	+4.7	+22.5	0.1	1.12	90	1.71
$Et_2Sb(OMe)_3$	+4.0	+24.6	0.0	1.40	24	5.9
$Me_2Sb(OAc)_3$	+3.0	+27.7	0.3	1.26	87	2.21
$Et_2Sb(OAc)_3$	+2.7	+22.9	0.2	1.45	96	1.84
$Et_2Sb(O)OH$	+5.0	±10.5	1.0	1.20	108	1.54
$Bu_2Sb(O)OH$	+5.4	±10.7	1.0	1.05	92	1.90
$Ph_2Sb(O)OH$	+5.8	±9.3	1.0	1.06	124	1.37

[a] Isomer shift relative to InSb at 4.2 K. [b] Absorber linewidth, source linewidth kept at 1.15 mm/s. [c] Number of counts per channel far from resonance. [d] Effective absorber thickness.

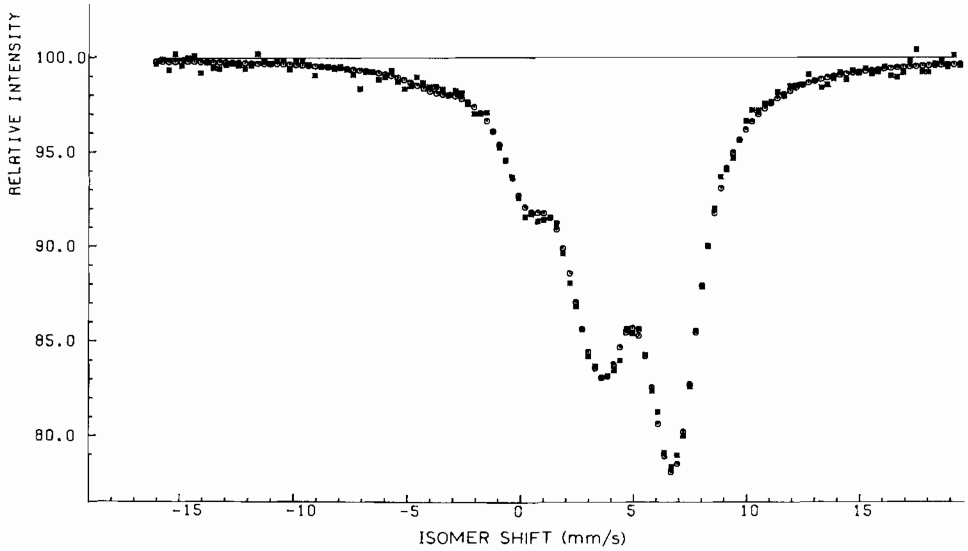

Fig. 1. ^{121}Sb Mössbauer spectrum of $Me_2Sb(OMe)_3$ at 4.2 K.

dinated antimony atoms joined by two oxygen bridges, also with the alkyls in the axial positions.

A bipyramidal structure of the suggested configuration, however, conflicts with the Gillespy–Nyholm electron pair repulsion theory which would predict an equatorial position for the alkyl groups in these compounds [14, 15]. For a dimeric octahedral structure two additional specifications must be met to assure $\eta \approx 0$. The bite angle at the antimony formed by the bridging oxygens must be close to 90° and the bridging oxygens and the oxygens of the non-bridging methoxo groups must each have a similar effect on the EFG. Mössbauer data cannot distinguish between the two structures. However, previous NMR data and molecular weight measurements support the dimeric structure [4].

The additive model for the QS [16] can be used to further evaluate our Mössbauer data. Using experimental quadrupole coupling data given in a recent paper by Bertazzi *et al.* [10], we determined the differences in Partial Quadrupole Splitting (PQS) values for a number of ligand pairs for the antimony octahedral geometry. Taking averages of data for sets of ligand pairs gives the results summarized in Table II.

TABLE II. Differences in PQS Values for Antimony Ligand Pairs Used in an Octahedral Coordination.

Ligand Pairs (A, B)	PQS Difference[a] (mm/s)
(Ph, F)	6.2
(Ph, Cl)	5.2
(Ph, Br)	5.3
(Ph, N_3)	5.2
(Ph, NCS)	6.6
(Ph, O)	5.8
(R, O)	6.8

[a] PQS differences derived from data in reference 16 except last two values. See text for explanation of these last two values.

The inductive effect of oxygen in expected to be between those of F and Cl, consequently a PQS difference of 5.8 mm/s for a (Ph, O) pairs is reasonable. The replacement of the Ph with an alkyl group usually increases the PQS difference by about an additional 1.0 mm/s [5, 7, 17] giving an estimated→(R, O)→PQS difference of approximately 6.8 mm/s. For an octahedral environment with alkyls in transposition the quadrupole coupling constant is four times the PQS difference [16] which gives $e^2qQ = 27 \pm 2$ mm/s. This value compares favourable with the experimental values found for these compounds.

Triacetatodialkyl Antimony Compounds

As for the trimethoxodialkyl antimony compounds the positive quadrupole coupling constant observed for triacetatodimethyl- and triacetato diethylantimony requires a charge concentration along the principle axis, but in this case $\eta \neq 0$ although it is small. The acetate ligand can be monodentate or bidentate. From IR and Raman spectral data it is concluded that these compounds possess an octahedral structure in which two methyl groups occupy axial positions and two monodentate ester-type and one bidentate acetato ligand occupy the equatorial positions. The Mössbauer data are in accordance with the proposed octahedral structure of this compound, but cannot differentiate between the trigonal bipyramide and octahedral geometries. Data for determining the PQS values for the acetato group are not available, therefore it is not possible to calculate a value for e^2qQ. Even though the antimony bonds directly with the oxygens, as it does in the trialkoxyantimony complexes, e^2qQ values are different. There are, however, no apparent differences in the isomer shifts. The small values for η can be explained by a slight deviation from 90° in the bite angle at the Sb formed by the coordination of the bidentate acetate [18, 19].

Dialkylstibinic Acids, $R_2Sb(O)OH$

The most striking Mössbauer result for these compounds is that η has a value of one for all three compounds studied. The other known examples of $\eta \approx 1$ are for antimony(III) compounds [13, 20, 21], but the isomer shift values observed in this study are indicative of Sb(V). The only large asymmetry values ($0.6 < \eta < 0.9$) previously reported for Sb(V) compounds have been for a series of arylstibonic acids ($RSbO_3H_2$) and for one arylstibinic acid ($(p\text{-}CH_3Ph)_2$-Sb(O)OH) [12].

The usual coordination structures for Sb(V) are either the trigonal bipyramid or the octahedron. Very special distortions of these geometries would be necessary for $\eta \neq 0$.

The effect of changing one bond angle in the octahedral geometry has previously been considered [18, 19]. It is possible to obtain $\eta = 1$, but only for angle distortions on the order of 20°, and η is so sensitive to the angle that small changes from the unique angle which gives $\eta = 1$ will result in an immediate decrease in the value of η. It is therefore highly improbable that such a specific distorted structure is found for all three compounds in this study. In a similar compound, Bowen and Long [12] have interpreted the Mössbauer isomer shift and quadrupole coupling data for $(p\text{-}CH_3Ph)_2Sb(O)OH$ in terms of a trigonal bipyramid like structure in which bridging oxygens are in the equatorial plane. They consider the bonding of the hydroxyl and bridging oxygens not to be very different. For this to be so, the asymmetry values would have to be quite small, but they are not ($\eta = 0.9 \pm 0.2$). In our opinion a more plausible structure is the tetrahedral coordination of the SbA_2B_2 where A = Et, Bu, or Ph and B = oxygen. This structure would give $\eta = 1$ (and requires distortions to give small values of η [16]). Added evidence for this structure are the crystal structure determinations for two dialkyl arsinic acids, $R_2As(O)OH$, with R = Me [22] or n-Bu [23]. In both cases the ligand–arsenic–ligand bond angles are tetrahedral within experimental error.

While PQS values are not available for use in the additive model for tetrahedrally coordinated antimony, they are available for trigonal bipyramid complexes [7]. Such values can, to a first approximation, be converted for use in tetrahedral coordination using the ratios: $[L]^{tet}:[L]^{tbe}:[L]^{tba} = 9:8:6$ [16]. This results in a range of possible values between 12.4 and 16.6 mm/s for e^2qQ which is larger than the experimental results (9.3 to 10.7 mm/s). If there is indeed an actual difference; it can be corrected by either smaller PQS values for the alkyl and phenyl groups (indicative of less p electron density in the alkyl/phenyl directions than expected) or a larger PQS value for the oxygen (more p electron in the oxygen direction than expected). The isomer shift values are quite large (>5 mm/s) for organo-antimony(V) complexes [10, 17, 24], but are consistent with those of the previously reported stibonic and stibinic acids [12]. This means that the s electron density at the antimony is less than expected in these compounds.

Conclusion

The Mössbauer data for $R_2Sb(OMe)_3$ and $R_2Sb(OAc)_3$ are in agreement with earlier proposed structures. For $R_2Sb(O)OH$ the Mössbauer data indicate a tetrahedral structure.

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