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Preparation and ^{121}Sb Mössbauer Spectroscopy of Methylchlorostibines

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The synthesis and ^{121}Sb Mössbauer spectra are reported for CH_3SbCl_2 and $(CH_3)_2SbCl$. The Mössbauer spectroscopic data for the series $(CH_3)_xSbCl_{3-x}$ with $x = 0$–3 are discussed. The quadrupole coupling parameters of all four compounds can be explained qualitatively with a simple point charge model, assuming the bond angles between the ligands to be close to 90°. The isomer shift data indicate a decrease of s-electron density at the Sb nucleus with increase of x, which is ascribed to an increase of p character of the lone-pair electrons.

Introduction

A Mössbauer study of methylhalostibines has been reported by Devort et al.[1] However, the numerical data presented by these authors are not consistent with the spectra shown (e.g., the sign of the quadrupole coupling constants reported are reverse of that expected from the spectra shown), and the method of synthesis used is likely to result in the preparation of impure compounds. We report here on the preparation and the Mössbauer spectra of CH_3SbCl_2 and $(CH_3)_2SbCl$. These compounds together with $(CH_3)_3Sb$ and $SbCl_3$ are of interest because they represent a model series for the study of the effect of the replacement of halogen by organic groups on the lone-pair electrons. The structures of the methylchlorostibines are not known, but for the corresponding arsenic compounds, data are available.[2] In a first approximation the structures of all four compounds are based on a trigonal arrangement of the ligands with bond angles between 100 and 90° and with the lone-pair electron density along the "trigonal axis".

Experimental Section

Synthesis of Dimethylchlorostibine. In an atmosphere of dry nitrogen, $(CH_3)_2SbSb(CH_3)_2$[3] (1.9 g, 6.4 mmol) dissolved in 20 mL of methylene dichloride at −78 °C was chlorinated by dropwise addition of 10 mL of methylene dichloride containing 6.4 mmol of SO_2Cl_2. Meanwhile, the reaction mixture was vigorously stirred with a magnetic stirrer, after which methylene dichloride and SO_2 were evaporated at reduced pressure. $(CH_3)_2SbCl$ (1.5 g, bp ~20 °C (0.05 mmHg)) was distilled into a cold trap (−20 °C (yield 62%)). ^{1}H NMR spectroscopy revealed the product to be almost pure, containing only a trace (<1%) of $(CH_3)_3Sb$.

Synthesis of Methyldichlorostibine. In an atmosphere of dry nitrogen, $(CH_3)_2SbSb(CH_3)_2$[3] (1.2 g, 4.0 mmol), dissolved in 40 mL of methylene dichloride at −78 °C, was chlorinated by dropwise addition of 12 mmol of sulfuryl chloride to give 2.0 g of $(CH_3)_2SbCl_3$ as a colorless solid upon evaporation of the solvent.[3] Thermal cracking was effected by heating this sample for 10 min at 120 °C. So that thermal decomposition of the CH_3SbCl_2 formed could be minimized, the cracking product was twice rapidly distilled at reduced pressure (0.05 mmHg) into a cold trap. The first distillate yielded CH_3SbCl_2 containing 4 mol % of $(CH_3)_2SbCl_3$, as determined by ^{1}H NMR spectroscopy. Redistillation of this sample resulted in 0.9 g of spectroscopically pure CH_3SbCl_2, yield 54%.

Mössbauer Spectra. The methylchlorostibines are liquids at room temperature. The Mössbauer absorbers were made from freshly prepared samples in an oxygen-free dry-nitrogen atmosphere by putting a few drops of liquid between two boron nitride plates and cooling them immediately to liquid-nitrogen temperature. The spectra were measured with source and absorber at 4.2 K. The source was $Ni_{21}{}^{121m}Sn_2B_6$. All isomer shifts are given relative to InSb at 4.2 K. The spectra were fitted with use of a transmission integral analysis. Details of the experimental set up and analysis are given elsewhere.[4]

Results and Discussion

Preparation of Methylchlorostibines. In the literature three procedures have been reported for the preparation of methylhalostibines, viz., (1) thermal cracking of pentavalent halomethylantimony(V) compounds of the types $(CH_3)_3SbX_2$ and $(CH_3)_2SbX_3$,[5] (2) reaction of methyl halide, CH_3X, with antimony metal at elevated temperatures,[6] and (3) reaction of tetramethyldistibine, $(CH_3)_2SbSb(CH_3)_2$, with halogen.[3]

According to our experience, procedures 1 and 2, both applied by Devort et al., are not very suited to the synthesis of pure samples of methylhalostibines. At the elevated temperatures used in these reactions, the methylhalostibines formed are subject to redistribution reactions, leading to the formation of impure products. Thermal cracking of a sample of $(CH_3)_3SbCl_2$, for instance, leads to the formation of $(CH_3)_2SbCl$ contaminated with varying amounts of $(CH_3)_3Sb$ and CH_3SbCl_2 (5–10 mol %), dependent on the overall reaction procedure. The composition of such a reaction mixture can be easily determined by ^{1}H NMR spectroscopy. A separate methyl proton is observed for each compound. ^{1}H NMR chemical shift data [δ CH_3Sb in C_6H_6 ($CHCl_3$) solution] are as follows: $(CH_3)_3Sb$, 0.61 (0.98); $(CH_3)_2SbCl$, 0.94 (1.43); CH_3SbCl_2, 1.22 (1.90); $(CH_3)_3SbCl_2$, 1.88 (2.36); $(CH_3)_2SbCl_3$, 2.00 (2.92).

We have succeeded in preparing pure samples of $(CH_3)_2SbCl$ and CH_3SbCl_2 suitable for a reexamination of the ^{121}Sb Mössbauer data of these compounds. $(CH_3)_2SbCl$ was obtained following reaction procedure 3. A sample of pure CH_3SbCl_2 was obtained by careful thermal cracking of $(CH_3)_2SbCl_3$.

Methylchlorostibines are thermally unstable. When two samples of originally pure $(CH_3)_2SbCl$ and CH_3SbCl_2 had been stored in the dark at room temperature for a period of 2 months, a black solid (most likely antimony metal) had formed in both samples. ^{1}H NMR spectroscopy revealed that $(CH_3)_2SbCl$ had partially decomposed into a mixture containing 11% $(CH_3)_3Sb$, 74% $(CH_3)_2SbCl$, 14% CH_3SbCl_2, and 1% $(CH_3)_3SbCl_2$. Likewise, CH_3SbCl_2 had been transformed into a mixture of 3% $(CH_3)_2SbCl$, 91% CH_3SbCl_2, and 6% $(CH_3)_3SbCl_2$. These fractions refer only to the methyl–antimony species and have an estimated accuracy of 1%. No attempt has been made to determine the amount of $SbCl_3$ and Sb present. Obviously redistribution reactions (cf. ref 7) resulting in the formation of mixtures of $(CH_3)_xSbCl_{3-x}$ (x = 0–3) compounds have taken place. The occurrence of an

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Table I. Measured and Calculated Mössbauer Parameters of $(CH_3)_xSbCl_{3-x}$

		measd			calcd				
compd	ref	δ,[a] mm/s (±0.1)	e^2qQ, mm/s (±1.0)	η (±0.2)	e^2qQ,[b] mm/s	η[b]	Γ_a,[c] mm/s (±0.1)	10^3N_0,[d] c/ch	t_a[e] (±0.07)
$SbCl_3$	4	−5.9	13.3	0.17	15	0.0	1.6	183	0.77
CH_3SbCl_2	*f*	−4.2	31.0	0.35	29	0.3	1.6	36	2.97
$(CH_3)_2SbCl$	*f*	−2.5	−31.7	0.77	−28	0.6	1.7	21	3.39
$(CH_3)_2SbCl$	*f*	−2.6	−30.0	0.82	−28	0.6	1.05	100	1.00
$(CH_3)_3Sb$	1	+0.04	15.2		15	0.0			
$(CH_3)_3Sb$	9	−0.22	16.3		15	0.0			

[a] Isomer shift relative to InSb at 4.2 K. [b] See text. [c] Absorber line width and source line width kept at 1.15 mm/s. [d] Number of counts per channel far from resonance. [e] Effective absorber thickness. [f] This work.

oxidation/reduction reaction between trimethylstibine and antimony trichloride[8] accounts for the presence of $(CH_3)_3SbCl_2$ and antimony metal in the product mixtures:

$$3(CH_3)_2Sb + 2SbCl_3 \rightarrow 3(CH_3)_3SbCl_2 + 2Sb$$

In view of the instability of the compounds it is imperative to use freshly prepared or well-preserved samples. Samples for the Mössbauer effect were therefore stored at liquid-nitrogen temperature immediately after preparation.

Mössbauer Spectra. The measured spectra of CH_3SbCl_2 and $(CH_3)_2SbCl$ are given in Figure 1, together with the calculated spectrum which gives the best fit. The calculated spectrum of CH_3SbCl_2 is in excellent agreement with the measured data. For $(CH_3)_2SbCl$, however, the fit is not perfect. The reason for the discrepancy is not understood; $SbCl_3$ or $SbCl_5$ which cannot be recognized in the ^1H NMR spectra would result in deviations different from those present in Figure 1. A second measurement on a much thicker sample of newly prepared material resulted in practically the same Mössbauer parameters. The numerical data for all measurements are given in Table I, together with the value of e^2qQ of $SbCl_3$[4] and $(CH_3)_3Sb$.[9]

Quadrupole Interaction. A large value for the quadrupole coupling constant e^2qQ and the asymmetry parameter η is a feature that the methylchlorostibines have in common with other asymmetrical Sb(III) compounds such as $(C_6H_5)_2SbCl$[10] ($|e^2qQ|$ = 25.6 mm/s, η = 0.8), $(C_6H_5)_2Sb[S_2CN(C_2H_5)_2]$[4] ($e^2qQ$ = 20 mm/s, η = 1), and $[(C_6H_5)_2Sb]_2O$[11] (e^2qQ = 20 mm/s, η = 0.95). These values indicate that there is a large difference in inductive effect between organic ligands (methyl and phenyl) and inorganic ligands such as Cl, S, and O. However, the values for e^2qQ of $SbCl_3$ and $(CH_3)_3Sb$ are very similar. This result can only be reconciled with the results obtained on the asymmetric compounds if the bond angles in $SbCl_3$ and $(CH_3)_3Sb$ deviate considerably from the tetrahedral angles. For a bond angle of 90°, for instance, the value of e^2qQ is given solely by the lone-pair electron density. Indeed, for $SbCl_3$ the bond angle is 95°.[12] For $(CH_3)_3Sb$ the structure is not known, but in analogous compounds of Bi[13] and P[14] the bond angles are 96.7 and 98.9°, respectively. It is possible to explain qualitatively the quadrupole coupling constants measured in the series $(CH_3)_xSbCl_{3-x}$ by using what is known as partial quadrupole splitting constants.[15] In this method the electron-charge distribution along a Sb–ligand axis is replaced by an equivalent point charge. The electric field gradient (EFG) and resulting quadrupole coupling constants are expressed in these point charges. For the compounds under study, the lone-pair electron density is treated as a ligand. It is assumed that the equivalent point charge of a ligand within the series is independent of the other ligand coordinated to the Sb atom.[16] As discussed below, this is actually not the case, but the method leads, nevertheless, to a qualitative understanding of the measured parameters. For the trigonal configuration shown in diagram I with equivalent point charges *A* (corresponding with the lone pair) and *B* and *C* (corresponding with CH_3 and Cl respectively in CH_3SbCl_2 and with Cl and CH_3 respectively in $(CH_3)_2SbCl$), the principal components of the EFG, V_{ii}, are given by eq 1 and 2, where α is a proportionality constant and θ is the angle between the lone

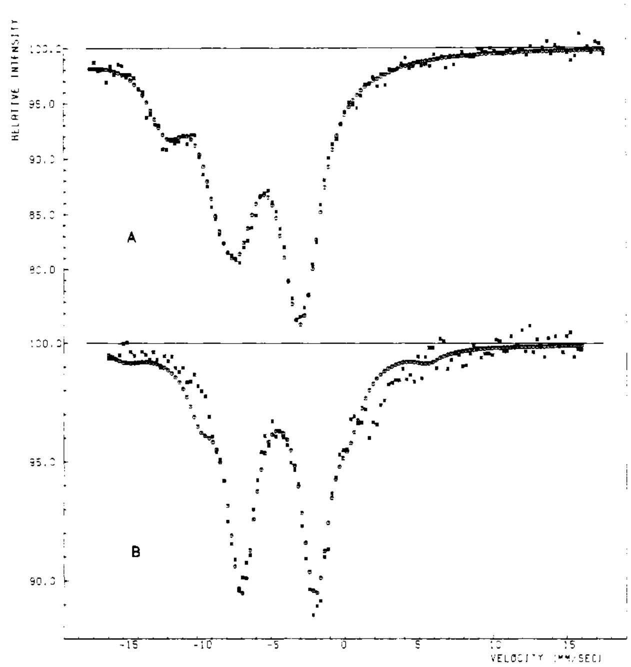

Figure 1. ^{121}Sb Mössbauer spectra of (A) CH_3SbCl_2 and (B) $(CH_3)_2SbCl$. Asterisks are measured intensities. Open circles are intensities calculated with (A) δ = −5.8 mm/s, e^2qQ = 31.0 mm/s, η = 0.35, Γ_a = 1.6, and t_a = 2.97 and (B) δ = −4.2 mm/s, e^2qQ = −30.0 mm/s, η = 0.82, Γ_a = 1.05, and t_a = 1.00. Isomer shifts are with respect to the $Ni_{21}Sn_2B_6$ source.

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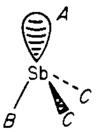

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$$V_{11} = -\alpha(A + B + 2C - \tfrac{9}{2}C \sin^2 \theta) \tag{1}$$

$$V_{22} - V_{33} = 3\alpha[[A - (B + \tfrac{1}{2}C) \sin^2 \theta + (B + 2C) \cos^2 \theta]^2 + 4(B - C)^2 \sin^2 \theta \cos^2 \theta]^{1/2} \tag{2}$$

pair and the respective Sb–ligand bond axis. Together with the sum rule $V_{11} + V_{22} + V_{33} = 0$, all three components can be calulated separately and renamed such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$.

If the bond angle is 90°, $\theta = 125.26°$, and eq 1 and 2 reduce to

$$V_{11} = -\alpha(A + \Delta) \tag{3}$$

$$V_{22} - V_{33} = \alpha[(-3A + \Delta)^2 + 8\Delta^2]^{1/2} \tag{4}$$

where $\Delta = B - C$. When $B - C = 0$, which applies to the cases of $SbCl_3$ and $(CH_3)_3Sb$, we find

$$e^2qQ = eV_{zz}Q = 2A{\cdot}\alpha{\cdot}eQ \tag{5}$$

and the value of quadrupole coupling constant is given by the lone pair only. From the Mössbauer spectra, e^2qQ is determined in mm/s. For this reason it is convenient to express the equivalent point charges also in mm/s, which means that the proportionality constant $\alpha{\cdot}eQ = 1$. These numbers are known as the partial quadrupole splitting (pqs) associated with the ligands.

For a more realistic bond angle of 95°, $\theta = 121.6°$, and with $B = C$

$$e^2qQ = 2A - 0.53B \tag{6}$$

The dominant contribution to the QS is, thus, still due to the lone pair.

For our model calculation we use eq 3 and 4. The value of e^2qQ for $SbCl_3$ and $(CH_3)_3Sb$ is then given by the lone pair. Averaging the measured values of e^2qQ gives $A = 7.5$ mm/s. Good agreement between measured and calculated values (see Table I) of e^2qQ and η is found for $B - C = 13$ mm/s, where B is the pqs of methyl and C that of the chlorine; the positive difference between the pqs of the methyl and Cl is in agreement with the electron-donating character of the methyl ligand and the greater covalency of the methyl–antimony bond.

We emphasize once more that the model presents only a qualitative explanation: the bond angle is not 90°, the lone-pair electron distribution is not constant through the series (see below), and in the mixed-ligand complexes the bond angles do not necessarily all have the same values. Nevertheless the conclusion that the bond angles must be considerably smaller than the tetrahedral angle remains valid.

Isomer Shift. The increase of the isomer shift when electronegative Cl is replaced by less slectronegative methyl indicates a decrease in s-electron density on the Sb nucleus. This is in contrast to the trend observed in the trigonal compounds SbX_3 (X = Cl, Br, I) and Sb_2O_3: for these compounds the isomer shift increases with the increasing electronegativity of the ligands.[17] The increase in isomer shift is also in contradiction with the conclusion drawn from the quadrupole coupling parameters that the methyl forms the more covalent bond. Since this conclusion would seem to be correct, we believe that the change in isomer shift reflects a change in the s and p character of the lone pair: bonding of methyl to antimony induces an increase in p character of the lone pair with a simultaneous decrease in s character as would be expected according to Bent's rule.[18] Another indication for a change in the nature of the lone pair on replacing chlorine by methyl or other organic ligands can be found in the structure of the arsenic compounds $(C_6H_5)_2AsBr$[19] and $(C_6H_5)_2AsCl$.[20] In these compounds the C–As–C bond angle is larger (105°) than the C–As–halogen bond angle (~97°). With reference to eq 6, this implies that the pqs A increases on going from $SbCl_3$ to $(CH_3)_3Sb$. For $(CH_3)_3Sb$ this increase in A is compensated for by an increased coefficient for B due to a larger bond angle.

Conclusions

Our model differs somewhat from that of Hedges and Bowen,[21] in which they use hybrid orbitals. These require that the lone pair be made up of only s electrons when the ligand–antimony–ligand bond angle is 90°. We conclude from our data that there is considerable amount of p contribution to the lone pair at the angles from 90 to 100°. Preliminary extended Hückel calculations which we have done on this system reinforce this conclusion. The details of these are being investigated and will be reported later.

The quadrupole interaction data for the series $(CH_3)_xSbCl_{3-x}$ (x = 0–3) indicates that for all compounds in this series the bond angles are considerably smaller than the tetrahedral angle. Consequently the quadrupole coupling constant in $SbCl_3$ and $(CH_3)_3Sb$ is dominated by the lone-pair electron distribution. The isomer shift data on the other hand indiate that the lone-pair character changes throughout the series with increasing p character for increasing x.

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Registry No. $(CH_3)_2SbCl$, 18380-68-2; CH_3SbCl_2, 42496-23-1; $(CH_3)_2SbCl_3$, 7289-79-4; $(CH_3)_2SbSb(CH_3)_2$, 41422-43-9; SO_2Cl_2, 7791-25-5.

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