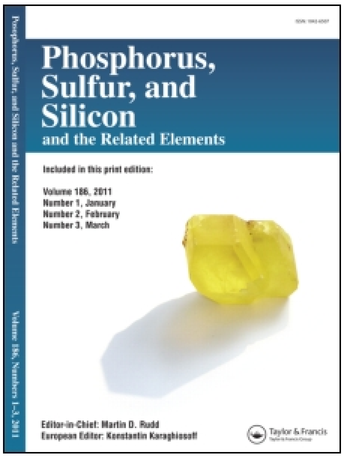

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POLYHEDRAL STEREOISOMERY OF DIMERIC ALKOXY- AND CHLOROALKOXYANTIMONY (V) DERIVATIVES

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The structure of dimers $[Cl_{5-n}Sb(OCH_3)_n]_2$ with $n = 1$–5 and their polyhedral stereoisomery have been studied on the basis of ^1H nmr data. It has been shown that in the case of $n = 1$ only one nondegenerate dimeric structure and with $n = 5$ only a single 25-fold degenerated structure formed by two tetragonal bipyramids are formed. The complicated spectra of compounds with $n = 2$, 3 and 4 may be explained as a superposition of resonance lines from different isomeric structures. In these structures the tetragonal-bipyramidal moieties have OCH_3 groups at different apical and equatorial positions. Solvent effects and temperature dependencies of spectra are discussed qualitatively.

INTRODUCTION

According to the X-ray data of crystalline tetrachloromethoxy- and tetrachloroethoxyantimony, the atoms of antimony are bonded with each other by an oxygen bridge, the equatorial Sb–Cl bonds of each of the antimony atoms being unequal in length. The crystals are characterized by a monoclinic structure.[1] The study of the tetrachloroethoxy- and pentaethoxyantimony by ^1H nmr[2] has resulted in the conclusion that the dimeric structures with hexa-coordinated Sb atoms are still to be found even when the compounds are dissolved. This is proved both by an essential difference of the proton chemical shifts and the form of the ethoxy group spectrum of the compound under study compared with that of ethyl alcohol. A cursory examination of the total nmr spectrum reveals that the proton resonance of the two equatorial-bridging groups is shifted downfield compared with the resonance position of four apical and four other equatorial ethoxy groups of dimers $[Sb(OC_2H_5)_5]_2$. The ^1H nmr investigation of methoxy derivatives of antimony $(CH_3)_4SbOCH_3$[3] and $R_2Sb(OR)_3$ with $R = CH_3$, C_2H_5 and $C(O)CH_3$[4] shows the existence of rapid positional exchange of the antimony bonds (pseudorotation), but at −80°C a rigid dimeric structure results since the CH_3 group shows two peaks.[4]

Up to now, however, the dependence of alkoxylic dimeric structures on temperature, nature of the solvent or consistent change of the number of Cl atoms from one ($n = 4$) to four has not been studied yet. However the electron-acceptor capacity of the antimony atom and, consequently, the lifetime of the dimers should depend on n.

This paper aims at a fuller consideration of the structure of compounds of the types $Cl_{5-n}Sb(OCH_3)_n$ and of pentaethoxyantimony $Sb(OC_2H_5)_5$. The syntheses of some of these derivatives has been previously published.[5] The configuration of dimeric structures formed from methoxy derivatives of $Cl_{5-n}Sb(OCH_3)_n$ in solutions with a given n will be derived in this paper by an analysis of ^1H nmr spectra.

RESULTS AND DISCUSSIONS

Part of the ^1H nmr spectra for $n = 1$, 2 and 5 is shown in the foot of Figure 1 (spectra **A**, **B**, **C**); chemical shifts are given on the δ-scale.

The ^1H nmr spectrum of tetrachloromethoxyantimony Cl_4SbOCH_3 (**I**) at room temperature shows a single line at $\delta = 4.50$ ppm. This kind of spectrum is easily accounted for, as $n = 1$ the only possible nondegenerated dimeric structure with Sb . . . O bond is the one formed by two octahedral complexes (OhC)† of type **A**. In this case the two methoxy groups are situated bridge-diequatorially and resonate at low field, as will be demonstrated below while analysing the case when $n = 5$. Possible dimeric structures with two Sb . . . Cl (**D**) bonds are not discussed in this paper, as the spectra of other compounds are interpreted without such structures. Conversely, at low temperatures (−80°C) pentamethoxyantimony $Sb(OCH_3)_5$

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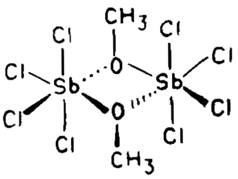
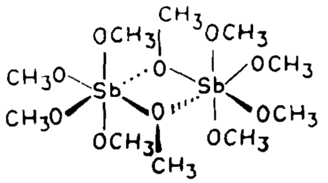
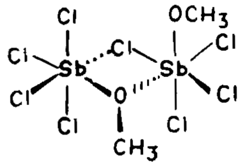
† Trigonal bipyramid being conventionally designated TBP, we abbreviate octahedral complexes by OhC.



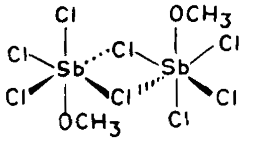
(A)



(B)



(C)



(D)

(**V**) shows a ^1H nmr spectrum consisting of two lines with a ratio of integral intensity of 1:4. For a dimeric structure of this compound a single 25-fold degenerated OhC structure (**B**) may be suggested in which the electronic environment of bridging methoxy groups differs from that of the two apical and two equatorial methoxyls. So far as the apical and equatorial positions should be nonequivalent, a broadened line with a relative intensity equal to 4 is split into two lines of equivalent intensities which one can see in the spectrum to the right (spectrum C). As is seen from our earlier paper[6] these lines may be assigned to the methoxy groups with a certain spatial position. In our previous paper we have shown both experimentally and by LCAO-MO EHT calculations that the protons of the apical methoxy group in phosphoranes when the pseudorotation of the trigonal bipyramid of phosphorus is restricted, resonate at higher field than the equatorial counterparts. Assuming that OhC structure with a Sb atom should be characterized by the same tendency we may suppose that the upfield component of the doublet in the ^1H nmr spectrum of compound **V** should belong to the apical methoxy group. At somewhat higher temperatures this ^1H nmr spectrum does not essentially change. This is suggestive therefore, of the presence of dimers and the absence of pseudorotation within the limits of the nmr time scale.

Thus, in accordance with the ^1H nmr spectrum of compound **V** it may be considered as working hypothesis that the resonance of α-protons shows a chemical shift to lower field, provided they are part of the bridging group.[2] This corroborates the interpretation of the spectrum and the structure of compound **I**.

The above-mentioned tendencies in the proton chemical shifts may be employed when assigning the rather complicated ^1H nmr spectrum of the compound $Cl_3Sb(OCH_3)_2$ (**II**). This compound may be found simultaneously in five different dimeric-isomeric structures $\mathbf{II}_1$-$\mathbf{II}_5$ as shown in Figure 1. If as a first approximation the effect of non-bonded atom-atom interactions are neglected and analysis of the probable structures is conducted only from a geometrical point of view, the dimeric OhC structures $\mathbf{II}_1$-$\mathbf{II}_4$ should appear to have a statistical weight of 2 and the structure $\mathbf{II}_5$ with a weight of 8. In structures $\mathbf{II}_1$, $\mathbf{II}_2$ and $\mathbf{II}_4$ the protons of the two bridging OCH_3 groups (**a** and **b**) must produce identical lines, but at every $\mathbf{II}_i$ a new chemical shift should be expected as the other two OCH_3 groups and chlorine atoms have mutually a different concrete spatial location and, consequently, different magnetic-anisotropic and electric influence on the screening constant. Likewise, due to the symmetric location of the methoxy groups **c** and **d** with respect to the rest of the dimer in structures $\mathbf{II}_1$-$\mathbf{II}_4$ their protons should also show identical lines as well. Schematically (cf. Figure 1) these lines of the given structures are shown by two vertical lines, the height of which in relative units corresponds to the statistical weight of OhC structures. In structure $\mathbf{II}_3$ the protons of the two bridging methoxy groups are not equivalent, the protons of group **b** being closer to the two adjacent equatorial groups (**c** and **d**) which are likely to be characterized by a flat conformation of the **W** type. Consequently the influence of the magnetic anisotropy of the lone pair orbitals of oxygen must shift the resonance of **b**-OCH_3 group to higher magnetic fields.[7] This is why the resonance of two bridging methoxy groups is shown in the scheme (Figure 1) as two lines **a** and **b**, the relative intensity of each line being equal to 1. In the dimeric structure $\mathbf{II}_5$ all four methoxy groups are nonequivalent, and the ^1H nmr spectrum accordingly comprises four lines, each of which should be characterized by an intensity of 4, the statistical weight of the structure being 8.

In the given scheme the relative position of lines on the δ-scale of chemical shifts is chosen keeping in mind the actual distribution of lines in the spectrum under study. Comparing this spectrum with the lines of the scheme and taking into consideration the algebraic sum of the integral intensities of superimposed lines in the ^1H nmr spectrum, a quantitative agreement is to be observed. The presence of non-assigned lines of some insignificant intensity in the region of the bridging OCH_3 group resonance (δ = 4.15–4.50 ppm) can be accounted for either by

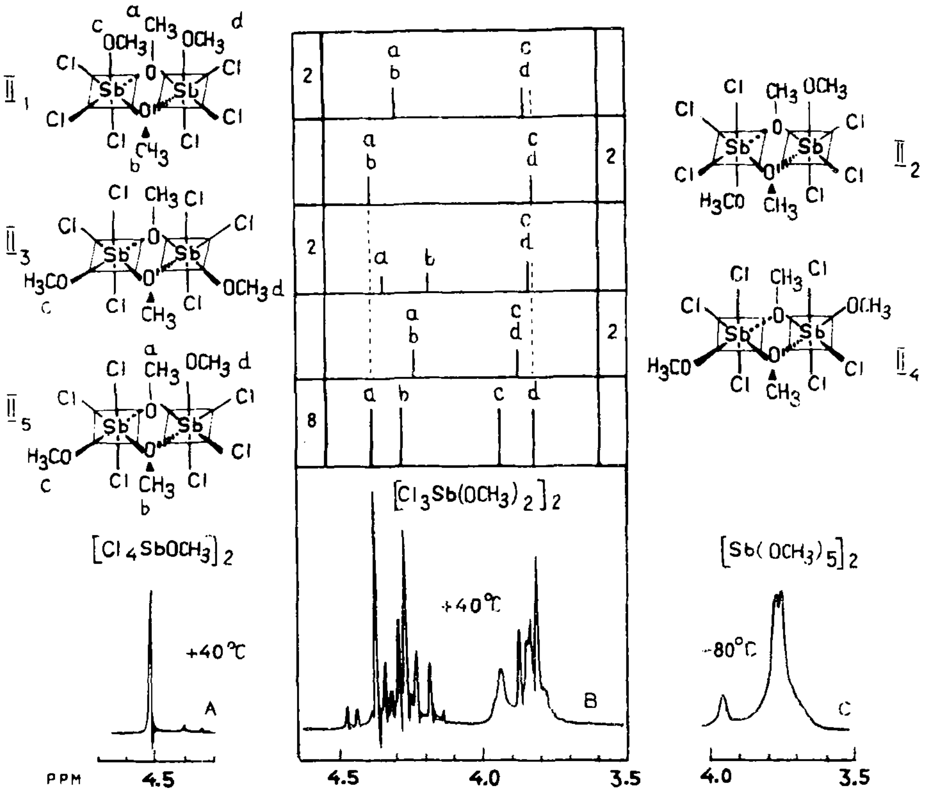


FIGURE 1 The scheme of the expected ^{1}H nmr spectra for the stereoisomeric structures II_1–II_5 and natural spectra of the compounds I, II and V.

impurities or by the presence of monomeric molecules.† The spectrum of compound **II** recorded at +40° shows that the lower limit of an average life time of isomeric structures II_1–II_5 at this temperature is more than $\tau = 1/(\nu_a - \nu_b) \sim 10^{-1}$ sec. If the temperature is raised the lines **a**, **b** and **c**, **d** start broadening. At +120° the lines of each group begin to coalesce and their maxima mutually begin approaching each other (Figure 2). This is suggestive both of the shortening of time τ and emergence of a pseudorotation of bonds in OhC or TBP structures. No attempt has been made to make these lines fully coalescence as it might have destroyed the reversible character of dimerization because of the decomposition of the compound.

^{1}H nmr spectra of compounds **III** ($n = 3$) and **IV** ($n = 4$) resemble on the whole those of compound **II** (Figure 3), the difference being that while the ratio of intensities of the downfield group lines to those of the upfield group for compound **III** is, as is expected, 1 : 2, in the case of compound **IV** it is 1 : 3. Naturally, the kind of spectrum for each case is peculiar, the magnetic-anisotropic and electronic environment of each of OCH_3 group being different in each of a given degenerate structure. Still, as is seen from Figure 3, when n increases the spectrum is likely to simplify as OCH_3 groups, with the exception of bridging OCH_3 groups, are, more or less, distributed in approximately the same environment. The main contribution to the intensity of the lines is made by a dimeric structure with an equatorial-axial (IV_1) distribution of Cl atoms (statistic weight of 8), the other four IV_2–IV_5 probable structures have a statistical weight of 2, but are characterized by fragments having something in common with the environment IV_1. For this reason when $n = 4$ the complete spectrum of compound **IV** closely resembles in shape that of the spectrum of compound **V**. When $n = 3$ there may emerge six stereoisomeric structures, out of which structures with di-axial and di-equatorial distribution of chlorine atoms of each dimer fragments are realized with a statistical weight equal to 1, while others are characterized by their statistical weight of 4. As a

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† At high temperatures (+80°–+120°) these lines merge with basic peaks. This makes it possible to assert that they are the result of the contribution of monomeric structures.

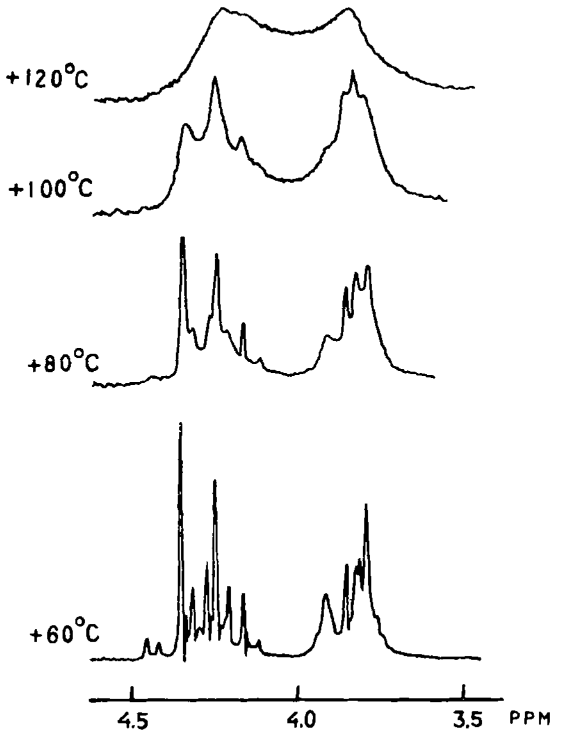

FIGURE 2 The temperature dependence of ^1H nmr spectrum of $Cl_3Sb(OCH_3)_2$; 10% CCl_4 solution.

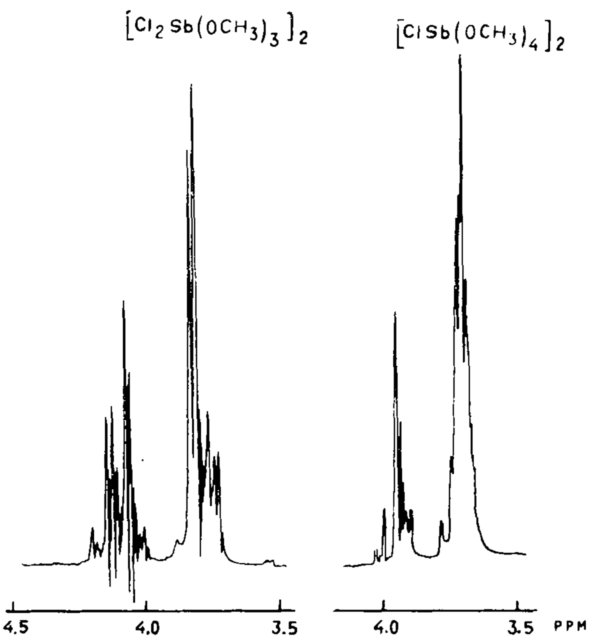

FIGURE 3 ^1H nmr spectra of the compounds III and IV, $t° = +28°C$.

result of superposition of ^1H nmr spectra of each structure, there comes into being a complete spectrum which closely resembles that of compound II.

The role of solvent nature. In the paper of Meinema *et al.*[8] ^1H nmr solvent shifts $\Delta\delta = [\delta(CCl_4) - \delta(C_6D_6)]$ have been measured for β-diketonate group protons of isomeric hexacoordinate dichloro-2.2′-biphenyleneantimony (V) β-diketonates Ph_2SbCl_2 Acac and p-Tol_2SbCl_2 Acac. The steric influences of bulky substituents in the β-diketonate ligand on the benzene–ligand interaction has been clearly shown. The configuration of the compounds has a comparatively small influence on the value of shifts $\Delta\delta(CH)$. The authors[8] accentuated the fact that the observed solvent shifts may be interpreted on the basis of a nonspecific tangential approach of the benzene molecules to the electron-deficient sites of the solute.[9]

The compounds I–V both in nonpolar (CCl_4, C_6H_6) and polar ($CHCl_3$, CH_3CN) solvents have been investigated so that additional information might be received concerning the structure and durability of dimers in the solution. Benzene used as a solvent for compounds III and IV generates a slight transformation of the spectrum. In compound V it results in downfield shifts ($\Delta\delta > 0$) for apical ($\delta = 3.83$ ppm) and equatorial ($\delta = 3.90$ ppm) methoxy groups, however the line of the equatorial-bridging methoxy protons actually does not change its position. Such a tendency of chemical shifts is consistent neither with a rupture of bridging bonds nor a structure of a complex of compound V with benzene molecules in which methyl groups get into a region of the diamagnetic effect of the aromatic rings. We may suppose that in this case the interaction of benzene molecules with solutes is realized in an unspecific way as is shown in the above-mentioned model.[9]

The influence of the polar solvents on the spectra is almost unnoticeable with the exception of compound I. For example in the case of the compound $ClSb(OCH_3)_4$ (IV) the line of the equatorial-bridging methoxyl groups does not change its position, but the centre of the weight of the peaks of other methoxyl groups experiences an upfield shift ($\Delta\delta = 0.04$ ppm) which may suggest some contribution of monomeric structures. However when we deal with the compound Cl_4SbOCH_3 (I) both benzene and acetonitrile bring about a considerable upfield shift of $\Delta\delta = 0.84$ and 0.70 ppm, respectively. Furthermore, when compound I is dissolved in acetonitrile there appears a complex band of lines with the centre $\delta = 4.20$ ppm, the nature of which we leave open for discussion.

Pentaethoxyantimony **(VI)**. *The dependence of ^1H nmr spectrum on the solvent and temperature.* The dimeric structure of pentaethoxyantimony $[Sb(OC_2H_5)_5]_2$ **(VI)** based on the ^1H nmr data and ir spectra is discussed in a previous paper.[2] At the time no concrete assignment of the lines to apical and equatorial groups was attempted. Downfield lines were correctly assigned on the qualitative basis to the two bridging ethoxy groups. A fuller experimental study of compound **VI** as compared with triethoxyantimony $Sb(OC_2H_5)_3$ **(VII)** has been carried out since then.

In comparison with the ^1H nmr spectrum of triethoxyantimony [$\delta(OCH_2) = 4.05$ (quadruplet), $\delta(CH_3) = 1.23$ ppm (triplet), 10% solution in CCl_4] the resonance of the corresponding proton-containing groups of compound **VI** both in $CHCl_3$ and in C_6H_6 is shifted slightly downfield. As is seen from Figure 4, the quadruplet of the methylene protons and the triplet of the methyl group (characterized by integral intensities) corresponding to two ethoxy groups are shifted considerably downfield compared with that of compound **VII**. This makes it possible, (as in the series of compounds **I-V**) to assign these downfield lines to the two bridge ethoxy groups. This conclusion is further substantiated by the temperature dependence of the spectrum. When the temperature of the sample steadily increased up to +120°C (see Figure 4) the downfield lines merge with the other lines. This is suggestive of a rapid pseudorotation of the bonds to the antimony atoms in the dimeric structure. In boiling toluene (+110.6°) the molecular weight corresponds to the dimeric form. The values of chemical shifts remain practically unchanged when the solvent is varied from C_6H_6 to $CHCl_3$, but the anisochronity of apical and equatorial methyl protons in benzene becomes considerably larger. As in the case of the lines of compound **V** we have assigned the upfield lines to the four apical ethoxy groups of the dimeric structures.

EXPERIMENTAL SECTION

All samples were examined on a Varian HA-100D nmr spectrometer supplied with variable temperature accessories; 5–10% solutions were used with TMS as internal reference. The samples were prepared in a dry box (over P_2O_5 and dry nitrogen). The compounds under study had the following melting points:[5] **(I)** 178–179° (with decomposition); **(II)** 142–143° (with decomposition); **(III)** 97–98°; **(IV)** 100–102°; **(V)** 74–76°; **(VI)** 37–38°; **(VII)** bp 94–95° (10 mm), $n_D^{20} = 1.4935$, $d_4^{20} = 1.5233$.[10]

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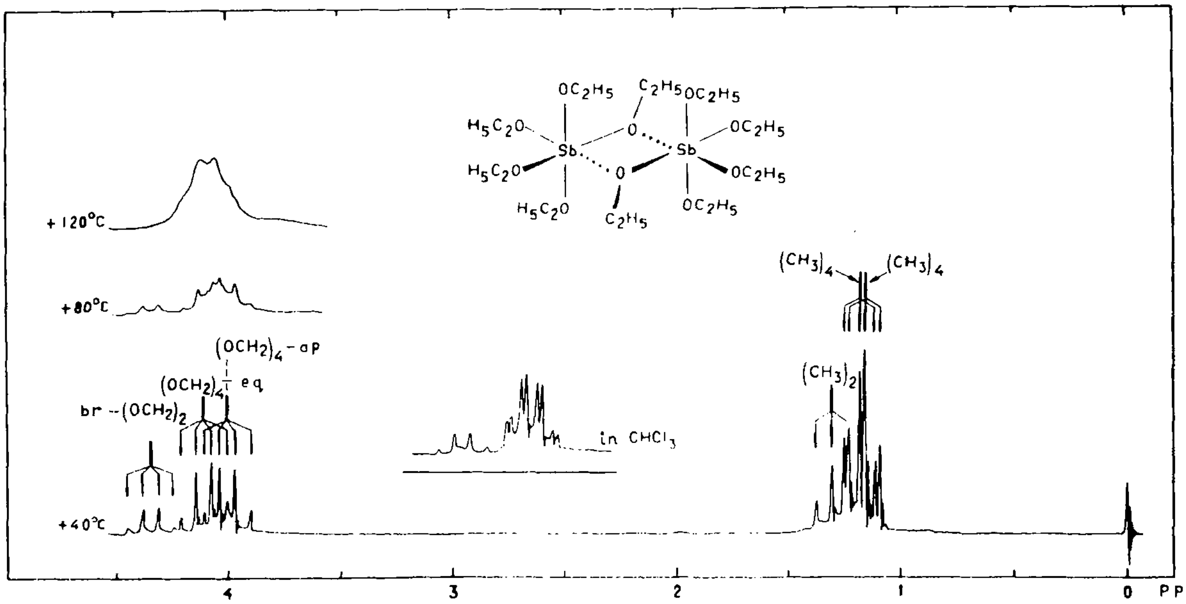

FIGURE 4 ^1H nmr spectrum of the pentaethoxyantimony (VI). The basic spectrum corresponds to the 10% benzene solution.

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