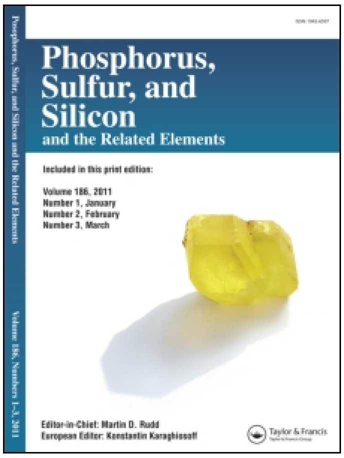

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VIBRATIONAL SPECTRA AND STRUCTURE OF ALKOXY AND CHLOROALKOXY DERIVATIVES OF ANTIMONY(V)

B. A. Arbuzov[a]; V. S. Vinogradova[a]; R. R. Shagidullin[a]; Yu. M. Mareev[a]; I. Kh. Shakirov[a]
[a] Butlerov Chemical Institute of the Kazan State University, USSR and Arbuzov Institute of Organic and Physical Chemistry, Kazan, USSR

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VIBRATIONAL SPECTRA AND STRUCTURE OF ALKOXY AND CHLOROALKOXY DERIVATIVES OF ANTIMONY(V)

B. A. ARBUZOV, V. S. VINOGRADOVA, R. R. SHAGIDULLIN, Yu. M. MAREEV, and I. Kh. SHAKIROV

Butlerov Chemical Institute of the Kazan State University, USSR and Arbuzov Institute of Organic and Physical Chemistry, Kazan, USSR

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Vibrational spectra of $(CH_3O)_nSbCl_{5-n}$. $n = 1$: **1**; $n = 2$: **2**; $n = 3$: **3**; $n = 4$: **4**; $n = 5$: **5**; have been recorded. According to ir and Raman data **1–5** are centrosymmetrical bridged dimers. The Raman spectra of **3–5** exhibit ν(Sb—O) doublets of terminal CH_3O at 530–541 and 550–570 cm^{-1}; vibrations of the 4-membered Sb_2O_2 ring, observed in the 500–517 cm^{-1} region of the ir spectra of 1–5, are absent. The ν(C—O) bands of bridged and terminal CH_3O are shifted to higher wave numbers (60 and 31 cm^{-1}, respectively) in the series **1** → **5**. The stability of the dimers increases in the series **1** < **2** < **3** < **4** ≪ **5**. At 100–120°C and in CH_3CN solutions dimers of **1–3** dissociate to monomers (ν(Sb—O) 537–540 cm^{-1}, ir data). The monochloride, **4**, is partially dissociated in CH_3CN. On solution of the tetrachloride, **1**, in benzene a dimer-monomer equilibrium has been observed, with the dimeric form being predominant.

INTRODUCTION

According to x-ray data, monomeric molecules of methoxytetraphenyl-, dimethoxytriphenylantimony[1] and alkoxy derivatives of tetramethylantimony (ir, Raman and ^{1}H-nmr data[2,3]) have a trigonal-bipyramidal (TBP) structure with axial arrangement of alkoxy moieties. Dimethyltrimethoxyantimony[4] and methoxy[5] and ethoxyantimony[6] tetrachlorides, both in the crystalline state and in solution[7] are dimers of bioctahedral structure. On the basis of ir and ^{1}H-nmr spectroscopic data a dimeric structure was established for pentaethoxyantimony.[6]

Chloroalkoxy derivatives of Sb(V) have been comparatively poorly studied due to difficulties in obtaining the compounds in pure form. Vibrational spectra of tetrachloroethoxyantimony have been recorded and assignment of bands according to crystallographic data has been carried out.[6,7] By comparing the Raman spectra of methoxy- and ethoxyantimony tetrachlorides, and of $SbCl_5$ in the low-frequency region ($\lesssim 500$ cm^{-1}), it has been established that the latter is monomeric at temperatures higher than 212 K and is dimeric below this temperature.[8] Recently we have reported the synthesis, ir spectra,[9] results of molecular weight determination[10] and the steric structure ^{1}H-nmr[11] of $[(CH_3O)_nSbCl_{5-n}]_2$; $n = 1–5$ (**1–5**), consisting of two tetragonal bipyramidal (TgBP) molecules. Vibrational spectra of the methoxy derivatives **2–5** have not been previously reported.

In the present paper we describe the results of a study of the vibrational spectra of **1–5** in solid state, in the temperature range of 20–120°C and also in various solvents.

RESULTS AND DISCUSSION

We have already reported[10] on the difference in the ir spectra of the tetrachloride, **1**, obtained with a melting point higher than described.[12]

Table I presents the vibrational frequencies of **1** and their interpretation.

The ir bands of **1** given in Table I undoubtedly belong to the crystalline form. When "spraying" the tetrachloride from a CH_2Cl_2 solution on to a KBr plate the main absorption peaks (508 and 908 cm^{-1}) appear in the ir spectrum.

The fulfilment of the rule of mutual exclusion that is in conformity with the presence of a centre of symmetry in the dimer (x-ray data[5]) is clearly revealed by comparison of ir and Raman spectra of **1**. According to Ref. 5 the Sb—O and Sb—Cl bonds of bioctahedral **1** are nonequivalent, so in

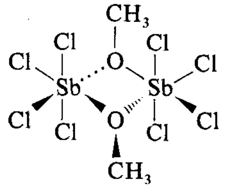
TABLE I

Vibrational spectrum of tetrachloromethoxyantimony (**1**), molecular dimer, C_1 symmetry

IR ν cm^{-1}	Raman ν cm^{-1}	Assignment	Vibration symmetry
—	35 (0)	Lattice vibrations	
—	37 (0)		
—	48 (0)		
—	51 (0)		
—	55 (0)		
—	58 (0, 1)		
—	62 (0)		
—	75 (0)		
—	77 (0)		
—	79 (0)		
—	86 (0, 1)	χ SbOC	A_g
—	120 (2)	δSb_2O_2, δ SbOC τCH_3, $\delta SbCl_n$	A_g
—	128 (1, 6)		A_g
—	144 (0, 3)		A_g
—	149 (1, 6)		A_g
—	167 (1, 1)		A_g
—	179 (2, 3)		A_g
210 w	—		A_u
—	212 (1, 2)		A_g
—	273 (0)		A_g
—	278 (0, 1)		A_g
303 mw	—		A_u
—	320 (2, 5)	ν Sb—Cl	A_g
—	327 (2, 2)		A_g
359 ms	—		A_u
—	369 (10)		A_g
385 s	—		A_u
—	413 (00)	$\nu Sb_2O_2 + \delta Sb_2O_2$	A_g
—	450 (0)	laser irradiation	
467 w	—	$\nu Sb_2O_2 + \delta Sb_2O_2$	A_u
514 vs	—	νSb_2O_2	A_u
532 w	—	514 + lattice	
572 w	—	$514 + \delta Sb_2O_2$ (A_u)	A_u
790 vw	—	910 — lattice	
910 vs	—	ν SbO—C	A_u
—	933 (00)	?	
—	960 (0)	ν SbO—C	A_g
981 w	—	910 + lattice vibrations (A_u)	
1020 vw	—		
1080 vw	—		
1145 w	—	ρCH_3	A_u
1180 vw	—	ρCH_3	A_u
1442 wm[a]	1443 (0, 1)	δ_s, $\delta_{as} CH_3$	A_g, A_u
[a]	2835 (00)	components and	A_g, A_u
[a]	2902 (00)	overtones 2 δ_s, 2 $\delta_{as} CH_3$	A_g, A_u
[a]	2954 (0, 1)	$\nu_s CH_3$	A_g, A_u
3000 w	—	$\nu_{as} CH_3$	A_u

[a] Superimposed on bands of vaseline oil.

Designation: ν, stretching; δ, deformational; χ, out-of-plane; τ, twisting; ρ, rocking bending vibrations.



(**1**)

designations we proceeded from the fact that it belongs to the point symmetry group, $C_i \equiv S_h$. The general theory[13] shows that the dimer of structure **1** has 54 normal modes dividing by symmetry types according to the sum of the irreducible representations $\Gamma = 27A_g + 27A_u$. Of the total number, due to differences in the corresponding atom masses, in the bond lengths and force constants, one can single out somewhat approximately, but correctly enough, 18 C—H, 6 O—C, 24 Sb—Cl and 6 vibrations of the Sb_2O_2 ring. We were unable to identify all vibrations due to coincidence of frequencies and low intensity. According to calculations[14] the vibrations of terminal equatorial X—Y groups, axial X—Y groups and the 4-membered bridge Sb_2O_2 are also considerably localized in dimeric X_2Y_{10} molecules (X = Nb, Ta; Y = Cl, Br).[14] However, on account of the coincidence of the regions of vibrational frequencies of differently constructed $SbCl_n$ groups (for example, two equatorial and two axial Sb—Cl bonds or three equatorial and one axial Sb—Cl bonds in $SbCl_n$)[8, 11, 15] we decided to restrict ourselves to general analysis, detailed interpretation must await a calculation. Table II shows the most characteristic frequencies of **1**–**5** spectra necessary for further discussion.

Analysis of vibrational spectra showed that compounds **1**–**5** at room temperatures are bridged dimers formed through oxygen atoms of CH_3O moieties. Comparison of ir and Raman spectra revealed ν(Sb—O) and ν(C—O) bands belonging to terminal and bridging CH_3O groups.

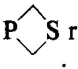
Figure 1 presents the ir spectra of **1**–**5** at room temperature and at 100–120°C. The simplest compound where ν(Sb—O) and ν(C—O) for a CH_3O bridge may be determined is the tetrachloride, **1** (see Table I).

The ir spectrum of **1** in vaseline oil displays a ν(C—O) band at 910 cm^{-1} (vs). The frequency is much lower than the usual one of X—O—C (X = "heavy" atom).[16] In the absorption region of the Sb_2O_2 ring a strong ir band is observed at 514 cm^{-1} (Figure 2). One could have expected a line of totally symmetrical "breathing" (ν_{br}) vibration of the 4-membered ring in the Raman spectrum. The low-frequency region of the tetrachloride Raman spectrum presented without interpretation, in a Figure from Ref. 8, completely coincides with our spectrum (see Figure 2, Table I). However, in our

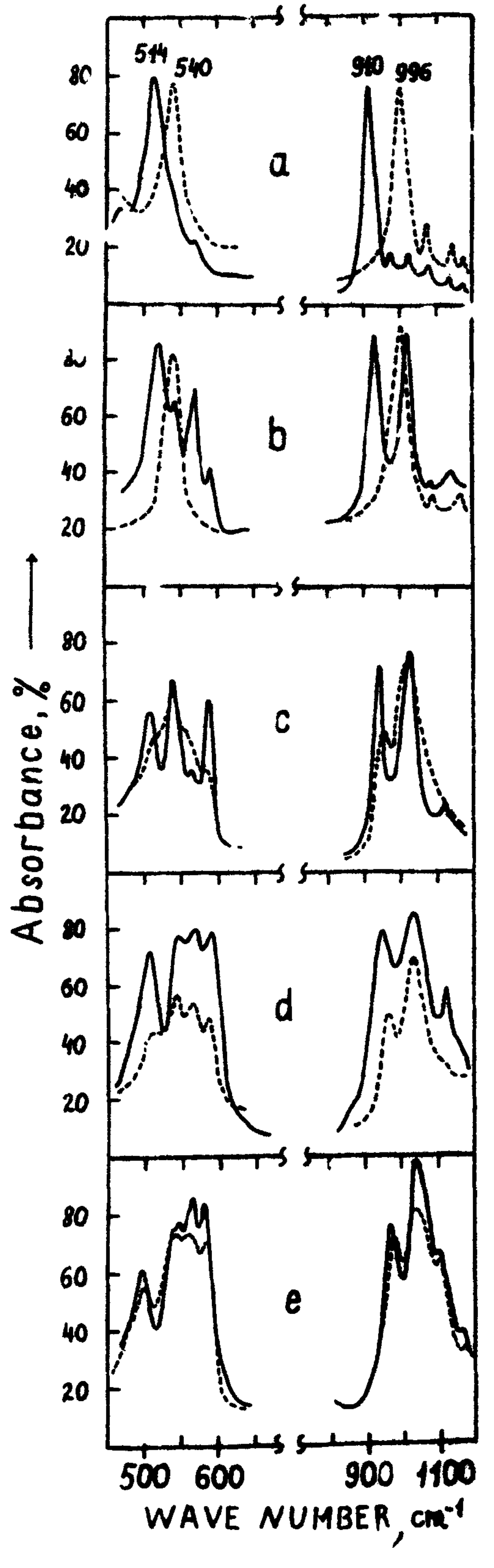
TABLE II
Most characteristic ir and Raman frequencies (cm^{-1})

Compound	ν(Sb–O) ir	ν(Sb–O) Raman	ν(C–O) ir, 20°C	ν(C–O) ir, 100–120°C	ν(Sb–Cl) Raman
CH_3OSbCl_4	467 w	—			
(1)	514 vs	—	910 vs	—	322 m
	532 sh s	—	981 vw	996 vs	330 m
	572 vw		1073 w	1073 m	368 s
$(CH_3O)_2SbCl_3$	470 w	—			
(2)	517 vw	—	924 vs	—	318 w
	532 sh s	—	990 sh m	995 vs	362 s
	542 s	540 vs	1014 vs	1015 sh m	
	572 s	550 sh m	1075 w	1080 m	
	590 w				
$(CH_3O)_3SbCl_2$	475 w	—			
(3)	510 vs	—	937 vs	948 s	326 w
	517 vs	520 vw	990 sh m	—	
	540 vs	538 vs			356 s
	567 m	569 w	1010 s	1010 vs	
	590 vs	—	1018 vs	1020 vs	
			1075 w	1075 sh m	
$(CH_3O)_4SbCl$	470 m	—			
(4)	505 vs	—	944 vs	—	
	543 vs	537 vs	970 sh vs	969 m	322 m
	566 vs	563 s	1035 vs	1028 vs	347 m
	590 vs	—	1074 sh s	1075 w	
$(CH_3O)_5Sb$	470 w	—	970 s	980 s	
(5)	500 s	—		1030 vs	
	540 vs	530 vs	1045 vs	1040 vs	—
	545 vs	550 vs	1075 s		
	565 vs	—	1100 m	1100 s	
	585 vs	—			

Designations: vs, very strong; s, strong; w, weak; vw, very weak; m, medium; sh, shoulder.

conditions we were unable to observe the 514 cm^{-1} Raman line that (although not shown in the Figure), is given in the Table.[8] Therefore, according to our observations, the fully symmetrical ν_{br} vibrations of the dimer ring **1** are not revealed in the Raman spectrum. One can draw an analogy with the  ring 1,3-thiaphosphetanes which, according to experiment and calculations,[17] has a weak Raman-active ν_{br} line. This fact was qualitatively explained[17] by compensation of changes in ring polarizability due to electron shells of heavy easily-polarized atoms situated in opposite apices of the tetragon. The ir spectra of **2**–**5** become more complicated in the region of ν(Sb—O) and ν(C—O) stretchings with increase of the number of CH_3O moieties (see Figure 1). In the Raman spectra of **2** ~540 and 510 cm^{-1} lines appear. The effect, however, should not necessarily be attributed to the number of methoxy groups. It is quite probable that these lines correspond to the vibrations of the 4-membered ring, missing in Table I, that were activated by changes in the environment. Therefore, from comparison of the spectra of **1**–**5** it may be assumed that the Sb_2O_2 ring is characterized by frequencies $\approx$540, 410, 200 cm^{-1} (A_g) and $\approx$510, 460, < 100 cm^{-1} (A_u).

In dimer **2**, in addition to bridging [ν(Sb—O) 514, ν(C—O) 924 cm^{-1}], two terminal CH_3O groups are present. Correspondingly, the ir spectrum displays additional bands at 542 and 572 cm^{-1} and a very intensive ν(C—O) band at 1014 cm^{-1}, which have higher frequencies in conformity with published data.[7, 16] The difference in the frequencies of terminal and bridging CH_3O is $\Delta\nu$(C—O) = 90 cm^{-1}. In the spectrum of the trichloride, **2**, the ν(C—O) bands have approximately the same inten-



sities. When passing from **2** to **5** the Sb—O and C—O bands of terminal CH_3O gradually increase in intensity. The complexity of the multiplet in the ν(Sb—O) region and of the ν(C—O) band in **3–5** may be due to the axial terminal CH_3O in addition to equatorial bridging groups. ν(C—O) bands of bridging and terminal CH_3O are shifted toward higher wave numbers (by ~60 and 31 cm^{-1} respectively) when passing from **1** to **5**.

The frequencies of bridging Sb–O decrease by 14 cm^{-1} in the same series, while frequencies of terminal Sb—O remain unchanged. Together with bridging ν(Sb—O) the frequency of ν(Sb—Cl) decreases. The data obtained are in complete agreement with the structure of **1–5** established by the method of ^{1}H-nmr spectroscopy.[11] Presumably, in the series **1–5** with decrease of the number of chlorine atoms the strength of the bridging bonds increases, while the strength of Sb—O and Sb—Cl drops in accordance with the change of electron density at O and Sb.

Comparison of ir and Raman spectra of **1–5** revealed a distinct difference in the region of ν(Sb—O). Raman spectra of **3–5** display highly intensive doublets at 530–541 and 550–570 cm^{-1} (Figure 2) corresponding to terminal Sb—O, whereas the Sb_2O_2 frequencies, observed in the 500–517 cm^{-1} region of the ir spectra, are absent in all compounds. This may be due to the retention of the rule of mutual exclusion for all the compounds studied, i.e. with the centrosymmetrical structure of the molecules.

The highly intense ν(Sb—Cl) Raman lines (~360 cm^{-1}) appear (see Figure 2) directly when it is possible for an Sb atom to have two equivalent Sb—Cl bonds on passing from the monochloride, **4**, to the dichloride, **3**; they are also present in the spectra of tri-, **2**, and tetrachlorides, **1**. Whereas, the similar ν(Sb—O) Raman line (~530 cm^{-1}) appears on passing from the trichloride, **2**, to the dichloride, **3** and is displayed also in the spectra of the monochloride, **4** and pentamethoxyantimony (**5**). This fact may be very important for determining the conformations of the molecules and will be the subject of further studies. Possibly the terminal CH_3O group occupies an axial position in the trichloride, **2**. From this may be deduced the structure of other members of the series. However, final conclusions should be based on calculations.

FIGURE 1 Ir absorption spectra of $(CH_3O)_nSbCl_{5-n}$ (in vaseline oil). (a) $n = 1$ (**1**); (b) $n = 2$ (**2**); (c) $n = 3$ (**3**); (d) $n = 4$ (**4**); (e) $n = 5$ (**5**). (———), 20–25°; (– – – –), 100–120°.

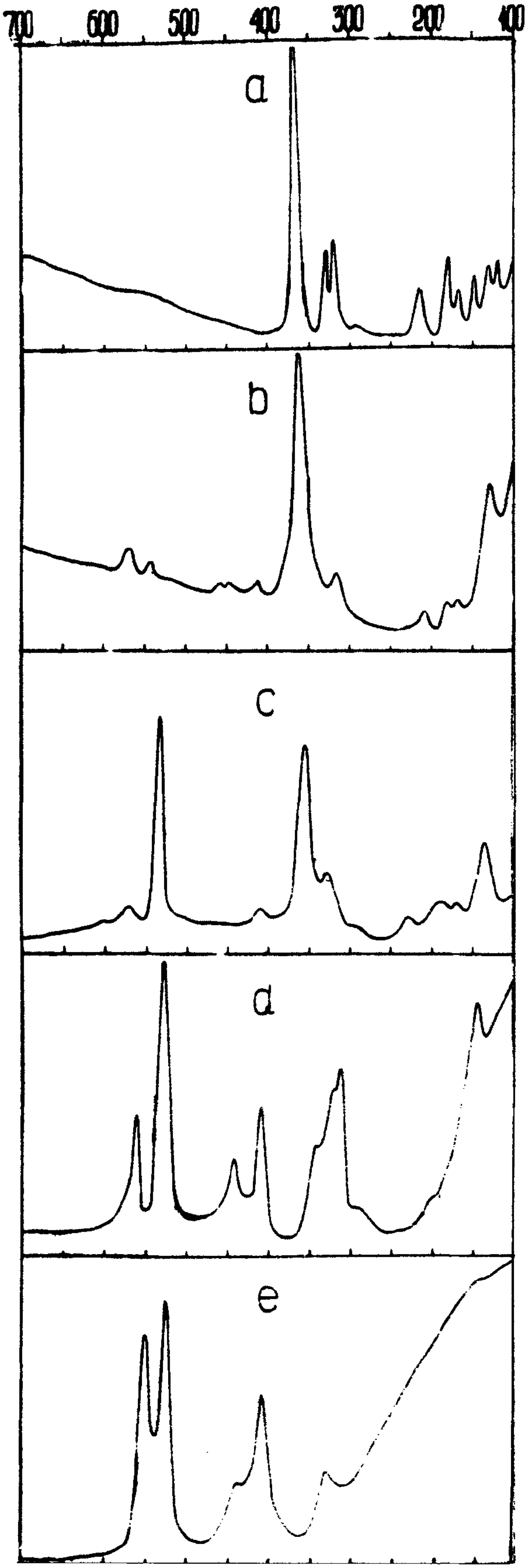


FIGURE 2 Raman spectra of $(CH_3O)_nSbCl_{5-n}$ (crystals). (a) $n = 1$ (**1**); (b) $n = 2$ (**2**); (c) $n = 3$ (**3**); (d) $n = 4$ (**4**); (e) $n = 5$ (**5**).

It is of interest to study the relative stability of **1**–**5** dimers depending on the number of chlorine atoms in the molecule and to determine the effect of heating and of various solvents.

The Effect of Heating

Heating of the tetrachloride, **1**, in vaseline oil to 80°C does not bring about any noticeable changes in the ir spectra. At 90°C new bands ν(Sb—O) 540 and ν(C—O) 996 cm^{-1} appear and the intensities of the dimer bands (514 and 910 cm^{-1}) decrease due to partial dissociation of **1**. At 100°C the dimer bands disappear completely. Therefore, the difference between ν(Sb—O) of the monomer (TBP) and ν(Sb—O) bonded in the dimeric form (TgBP) is 26 cm^{-1}. The difference between ν(C—O) in the monomeric form and bridging in the dimeric tetrachloride, **1**, is much greater, $\Delta\nu = 86$ cm^{-1}. Similar changes are observed in the ν(Sb—O) and ν(C—O) regions of the ir spectra the tri-, **2** and dichloride, **3**: at 100–105°C dimer bands disappear in the spectra of the trichloride, **2** and are substantially reduced in the dichloride, **3** [ν(Sb—O) 514, 567 and ν(C—O) 937 cm^{-1}]. At the same time the intensity of the ν(Sb—O) 540 and ν(C—O) 1000 cm^{-1} bands increases (see Figure 1 and Table II). In similar conditions the dimer is considerably less dissociated in chlorotetramethoxyantimony (**4**) and the spectra of pentamethoxy (**5**) (Figure 1) and pentaethoxyantimony (**6**) remain practically unchanged. At higher temperature (140–150°C) **5** and **6** decompose. Pentaethoxyantimony is converted to triethoxyantimony. On cooling to 20°C of the heated methoxychlorides **1**–**4** their initial ir spectra are not reproduced. Apparently, dissolution (by heating) in vaseline oil hinders dimerization. The absence of the chemical change of **2** and **6** was established by the high-temperature experiments of the ^{1}H-nmr spectra.[11] The reverse conversion of monomers into dimers was observed in the ir spectra for antimony methoxychlorides, **2** and **3**, in C_6H_6 and CH_3CN solutions, respectively, after removal of the solvents (see below). Therefore, according to the relative ir intensities, the most readily dissociated is dimer **1**. The stability of the dimer increases with reduction of the number of chlorine atoms in the following order: $Cl_4SbOCH_3 < Cl_3Sb(OCH_3)_2 < Cl_2Sb(OCH_3)_3 < ClSb(OCH_3)_4 \ll Sb(OCH_3)_5, Sb(OC_2H_5)_5$.

At first sight this conclusion is at variance with the conclusion about the weakening of Sb···O bonds in this series. However, one should bear in mind that the dissociation constant is determined as the difference of internal energies which depend not only on the strength of bonds, but also on other effects including steric and entropy factors.

The Effect of Solvents

On the basis of electroconductivity measurements and differences in the ir spectra of $(C_2H_5O)_nSbCl_{5-n}$ ($n = 1, 4$) in $CHCl_3$, C_6H_6 and CH_3CN an ionic structure was assumed in CH_3CN.[18] Interpretation of the ir spectra was not carried out by the authors. A subsequent attempt[7] to obtain ethoxychlorides ($n = 2$–4) in pure form[18] so as to study the vibrational spectra failed. From the electroconductivity in nitrobenzene the covalent structure of tetrachlorotrifluoroethoxyantimony was established.[19] According to x-ray data the structure of $SbCl_5 \cdot CH_3CN$ is covalent.[20] We obtained interesting results while studying ir spectra of methoxy derivatives of antimony in different solvents (cyclohexane, CCl_4, $CHCl_3$, C_6H_6 and CH_3CN). It was established that dimers **1**–**5** differ substantially in solubility. Pentamethoxy (**5**) and pentaethoxyantimony (**6**) readily dissolve in nonpolar solvents and poorly in CH_3CN, whilst the tetrachloride, **1**, is insoluble in cyclohexane and poorly soluble in $CCl_4 \cdot CH_3CN$, solubility noticeably increases in the order **5** → **1**. Ir spectra of **1**–**5** do not change when passing from vaseline oil to $CHCl_3$ and CCl_4 solutions. Therefore, in the conditions indicated the compounds mainly retain the dimer form and the strength of dimerization does not determine solubility.

The ability of antimony alkoxides for complex formation is known. Introduction of chlorine atoms into the alkoxy moiety decreases the degree of association and enhances the acceptor strength of Sb.[21] Hence, the reverse order of solubilities in CH_3CN should be explained by energy surplus due to complexation with CH_3CN. We observed formation of yellow needle-like crystals during interaction of **1** with CH_3CN (in a 1 : 1 ratio) in CCl_4 solution.

In the ir spectrum of the product obtained the bands of the initial compounds were absent: ν(Sb—O) in the 500–540 region characteristic of the dimeric and monomeric forms of **1**, ν(C—O) of dimer **1** (910 cm^{-1}) and ν(C≡N) of CH_3CN (2255 cm^{-1}). Bands of medium intensity appeared in the ν(C≡N) region at 2290 and 2320 cm^{-1}. Formation of a complex between **1** and CH_3CN, a similar shift of ν(C≡N) has been reported in Ref. 22 and formation of the $SbCl_5 . CH_3CN$ complex in Ref. 23. We were unable to observe the ν(Sb—O) band of the complex obtained presumably shifted by complex-

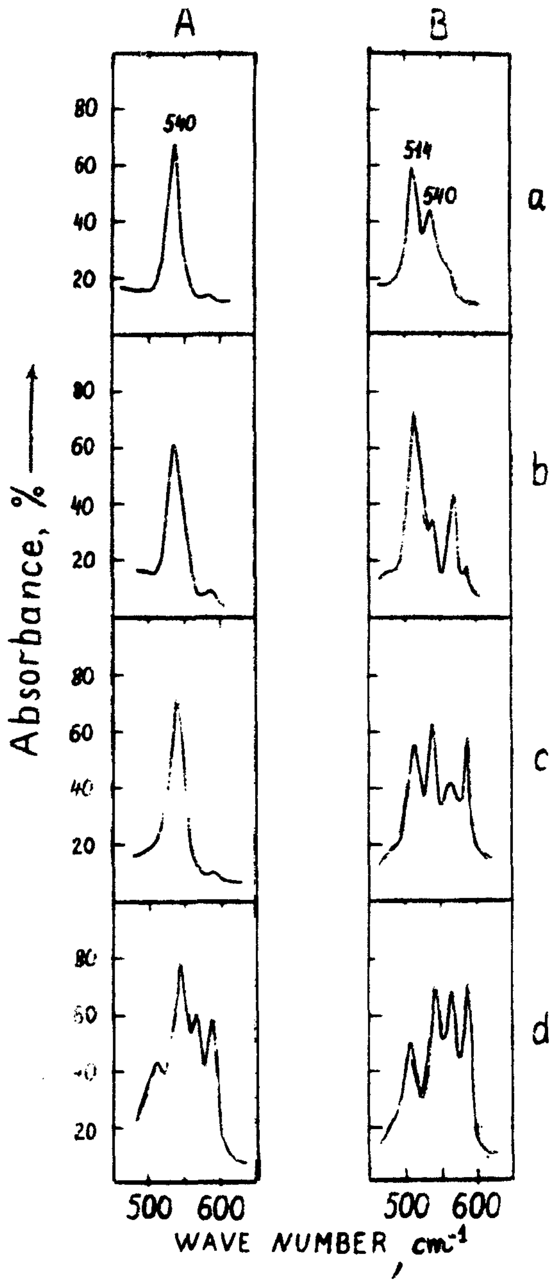


FIGURE 3 Ir absorption spectra of $(CH_3O)_nSbCl_{5-n}$ in the ν(Sb—O) region. (a) $n = 1$ (**1**); (b) $n = 2$ (**2**); (c) $n = 3$ (**3**); (d) $n = 4$ (**4**). A, in CH_3CN; B, in C_6H_6.

ation into the low-frequency region.[12] In the same conditions we failed to obtain a trichloride, **2**, complex, its formation was also not observed in the ir spectrum. Dimers **1–3** dissociate in CH_3CN solutions of ~10 wt.% concentrations. Twenty to thirty minutes after dissolution dimer bands gradually disappear and are replaced by symmetrical ν(Sb—O) bands at 537–540 cm^{-1} of monomeric forms (see Figure 3).

The Raman spectrum of **1** in CH_3CN solution shows a ν(Sb—O) band at 560 cm^{-1} of the terminal CH_3O moiety. According to ebulioscopic data tetrachloroethoxyantimony also exists as a monomer in acetonitrile.[18] On removal of CH_3CN, dichloride, **3**, is recovered in the form of white crystals with unchanged mp and ir spectrum. The monochloride dimer, **4** is in equilibrium with the monomeric form in CH_3CN. The ir spectra of pentamethoxy (**5**) and pentaethoxyantimony do not change significantly in CH_3CN solutions. Thus, the ir spectra of **1–5** in CH_3CN solutions in the ν(Sb—O) region are similar to spectra obtained at 100–120°C in vaseline oil and clearly indicate dissociation of dimers **1–3** to monomeric forms.

Benzene solutions of **1** and **2** acquire a light-orange color directly after dissolution. Ir spectra indicate partial dissociation of dimer **1** in C_6H_6: ν(Sb—O) band for the monomer appears at 540 cm^{-1} the intensity of which gradually increases during one hour, while that of the dimer band (514 cm^{-1}) diminishes (Figure 3). The equilibrium is shifted towards the dimer. Rather unexpectedly the equilibrium is not shifted by heating the benzene solution of **1** to 60–70°C. On removal of C_6H_6 in vacuo the trichloride **2** solution decolorizes and **2** is recovered without any changes in the mp and ir spectrum. All this points to weak π-type interaction of **1** and **2** with benzene. Dissolution of **3**, **4** and **5** in C_6H_6 does not lead to coloration and dissociation of the dimeric forms. The results obtained while studying ir spectra of **1–5** in CCl_4 and C_6H_6 solutions are in complete agreement with results of molecular weight determinations published in our previous report.[10]

EXPERIMENTAL

Ir spectra in the 400–3600 cm^{-1} region were recorded on a UR-10 spectrophotometer, in the 200–400 cm^{-1} region on an IKS-22V instrument. Crystalline samples of **1–5** were recorded in vaseline oil mulls between KBr plates (Tables I and II and Figure 1). Melts of **1–5** and **1** in the form of a crystalline film obtained by CH_2Cl_2 evaporation from solution interact with KBr plates. Changes of the initial spectrum of **1** were observed 15–20 min after beginning the recording. Vaseline oil mulls were placed on CsJ plates covered with polyethylene film when recording the 200–400 cm^{-1} region. Raman spectra were obtained with a PHO Coderg spectrophotometer; a LG-36A He–Ne laser was used. Crystalline samples and solutions were studied in capillaries (diameter 2 mm). Preparation and mp of the compounds studied: (**1**) 179–180°C (with decomposition); (**2**) 142–144°C (with decomposition); (**3**) 97–98°C;[9] (**4**) 102–104°C:[10] (5) 74–76°C; (**6**) 38–40°C.[9]

Due to the high sensitivity of (**1–6**) to the moisture of air, samples were prepared in a dry box over P_2O_5. The concentration of CH_3CN (Figure 3A) and C_6H_6 (Figure 3B) solutions of (**1–4**) was ~10 wt.%.

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