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The Preparation of $(C_6H_{11})_3Sb(OH)Y$ and Their Infrared Spectra

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Tris(cyclohexyl)hydroxoantimony(V) compounds, $(C_6H_{11})_3Sb(OH)Y$, Y=Cl, Br, CH_3COO, and NO_3, were prepared by the hydrolysis of μ-oxo-bis[tris(cyclohexyl)haloantimony(V)], $[(C_6H_{11})_3SbX]_2O$, in a mixed solvent of acetone and water(7:3) or by a reaction of silver salts with $[(C_6H_{11})_3SbX]_2O$ in the same solvent. When Y=Cl and Br, the dehydration of the hydroxo compounds, giving the μ-oxo compounds, $[(C_6H_{11})_3SbY]_2O$, occurred readily. However, when Y=CH_3COO and NO_3, the hydroxo form is stable. In the IR spectra of these hydroxo compounds in dichloromethane solution, the ν(O–H) band was observed at *ca.* 3630 cm^{-1} and the ν(Sb–O) band, at 565—513 cm^{-1}. The hydrolysis of several μ-oxo compounds, $[R_3SbY]_2O$, R=CH_3, C_2H_5, *i*-C_3H_7, C_6H_5, and *p*-$CH_3C_6H_4$, Y=Cl, Br, CH_3COO, and NO_3, in a water-saturated dichloromethane solution was studied by using the IR spectra. All the compounds were hydolyzed in this solvent, but only the starting μ-oxo compounds were recovered from this solution.

There has been considerable confusion in the litrature regarding the structure of $R_3Sb(OH)Y$ and its dehydrated $[R_3SbY]_2O$ types of compounds. Several workers have reported a number of compounds which were formulated as hydroxo compounds, $R_3Sb(OH)Y$. The hydroxo structure, however, is mainly assigned on the basis of elemental analyses,[1–8] although some workers have obtained the $[R_3SbY]_2O$ type of compounds.[9–12] Therefore, Long and co-workers[13,14] have made a detailed study of these types of compounds. They could not obtain compounds which give elemental analyses corresponding to $R_3Sb(OH)Y$ and which show the hydroxo band in their infrared spectra. The compounds obtained were always $[R_3SbY]_2O$. Accordingly, they concluded that the $R_3Sb(OH)Y$ type of compound probably does not exist in the solid state, although the presence of such species has been assumed in an aqueous solution.[15,16] Recently, however, we have obtained the $R_3Sb(OH)Y$ type of compound when the Y group is a somewhat bulky ligand such as 8-quinolinolate and when R=CH_3, C_6H_5 and *p*-$CH_3C_6H_4$.[8] These compounds show the ν(O–H) band at *ca.* 3610 cm^{-1} and the ν(Sb–O) band at *ca.* 550 cm^{-1}. Therefore, we anticipated that, if the alkyl group is bulky enough, the $R_3Sb(OH)Y$ type of compound may be obtained even if the Y group is halogen. In fact, Hartmann and Kühl have reported the preparation of $(C_6H_{11})_3Sb(OH)Cl$ by the hydrolysis of $(C_6H_{11})_3SbCl_2$.[7] However, they relied only on elemental analysis to elucidate the hydroxo structure of this compound and did not report its infrared spectrum. Actually, there is an error in their calculation, and so their analytical value is much close to that of the μ-oxo compound, $[(C_6H_{11})_3SbCl]_2O$.

In this paper, the preparation of tris(cyclohexyl)-hydroxoantimony(V) compound, $(C_6H_{11})_3Sb(OH)Y$, Y=Cl, Br, CH_3COO, and NO_3, and their infrared spectra in the solid state and in a dichloromethane solution will be reported.

Experimental

*Preparation of μ-Oxo-bis[tris(cyclohexyl)haloantimony(V)], $[(C_6H_{11})_3SbX]_2O$, X=Cl(**1**) and Br(**2**).* To a benzene solution (70 ml) of tris(cyclohexyl)bis(halo)antimony(V) (10 mmol), sodium methoxide (10 mmol) in methanol (10 ml) was added. The mixture was heated at reflux for 1 h, after which the sodium halide thus precipitated was filtered off. The crystalline white compound obtained after distilling off a large portion of the filtrate was purified by recrystallization from dichloromethane.

*Prepartion of Tris(cyclohexyl)halohydroxoantimony(V), $(C_6H_{11})_3Sb(OH)X$, X=Cl(**3**) and Br(**4**).* μ-Oxo-bis[tris(cyclohexyl)haloantimony(V)] (2 mmol) in a mixed solvent of acetone (70 ml) and water (30 ml) was heated at reflux until the solid compound was dissolved (1 h). The crystalline white compound obtained after removing a large portion of the solvent under reduced pressure was recrystallized from a mixed solvent of acetone and water (7:3). The compound was dried in air for a few minutes and then store in a tight-capped bottle. When the compound was stored in a desciccator overnight, air-dried for long time, or recrystallized from acetone, it changed to the dehydrated μ-oxo compound, $[(C_6H_{11})_3SbX]_2O$.

*Preparation of Other Tris(cyclohexyl)hydroxoantimony(V) Compounds, $(C_6H_{11})_3Sb(OH)Y$, Y=CH_3COO (**5**) and NO_3(**6**).* **1** (5 mmol) and the corresponding silver salt (10 mmol) were added to a mixed solvent of acetone (70 ml) and water (10 ml). The mixture was then heated at reflux for 1 h, and the silver chloride thus precipitated was removed by filtration. The crystalline white compounds obtained after removing a large portion of the solvent under reduced pressure was recrystallized from acetone. The compound was then dried in air.

Attempted Preparation of Other $R_3Sb(OH)X$, R=CH_3, C_2H_5, i-C_3H_7, C_6H_5, and p-$CH_3C_6H_4$ and X=Cl and Br. A suspension of μ-oxo-[tris(organo)haloantimony(V)] in a mixed solvent of acetone and water (7:3) was heated at reflux for about 1 h. The hydroxo compound, $R_3Sb(OH)X$, was not obtained by removing the solvent, and only the starting materials were recovered in the case of the phenyl and *p*-tolyl compounds. In the case of the methyl and isopropyl compounds, tris(alkyl)bis(halo)antimony(V) was precipitated from the condensed solution.

*Deuteration of **3**.* **3** (50 mg) was dissolved in a mixture of acetone-d_6 (1 ml) and D_2O (0.3 ml), after which the solution was sealed in a glass ampule. This was heated at about 50 °C for 2 h. After removing the solvent under reduced pressure, the crystalline white compound was obtained. Relevant IR spectral data in Nujol mull; 2520 cm^{-1} (ν(O–D)), 800 cm^{-1} (δ(Sb–O–D)), and 565 cm^{-1} (ν-(Sb–O)).

*Reaction of **5** with Picric Acid.* To an acetone solution of **5** (2 mmol), picric acid (2 mmol) was added, after which the mixture was stirred for 30 min at room temperature. A crystalline yellow compound of acetatotris(cyclohexyl)picratoantimony(V) was obtained when the solution had been

TABLE 1. ANALYTICAL DATA OF μ-OXO-BIS[TRIS(CYCLOHEXYL)HALOANTIMONY(V)] AND TRIS(CYCLOHEXYL)-HYDROXOANTIMONY(V) COMPOUNDS

	Mp[a] θ_m/°C	Yield %	Found(Calcd) (%) C	H	N
1	198—199	70	51.92 (52.14)	8.19 (8.02)	
2	197—198	88	46.93 (47.09)	7.28 (7.24)	
3	188	61	50.96 (51.03)	8.24 (8.09)	
4	195—196	80	46.29 (46.18)	7.47 (7.32)	
5	135—138	55	53.31 (53.71)	8.40 (8.34)	
6	156—157	25	47.86 (48.02)	7.65 (7.65)	3.10 (3.11)

a) Decomposition occurs gradually before melting.

left to stand at room temperature. This was recrystallized from acetone. Mp 160—171 °C (decomp). Found: C, 47.08; H, 5.93; N, 6.43%. Calcd for $C_{26}H_{38}N_3O_9Sb$: C, 47.43; H, 5.82; N, 6.38%.

Spectral Measurement. The infrared spectra were recorded on a Hitachi 215 spectrometer (4000—650 cm^{-1}) and on a Hitachi EPI-L spectrometer (700—200 cm^{-1}) in Nujol mulls or a dichloromethane solution. The concentration of the solution was 3 wt% or a saturated solution for not very soluble compounds. CaF_2 windows were used for obtaining the solution spectra of the O–H stretching region while KRS-5 plates were used for other region. The cell length used was 0.1 or 0.5 mm.

Conductivity Measurement. The molar conductances of **3**, **5**, and **6** in dichloromethane were measured by using a TOA digital conduct meter, model CM-15A, at 25±0.1 °C. The molar conductances of these compounds at 1×10^{-3} mol dm^{-3} were found to be less than 0.5 Ω^{-1} cm^2 mol^{-1}, indicating that these compounds are non-electrolytes in this solvent.

Solvent. Dichloromethane was dried over P_2O_5 and distilled before use. To dried dichloromethane, water was added and the mixture was shaken vigorously. The amount of water in dichloromethane was determined by referring to the signal strength of the known amount of hexamethylbenzene in the ^1H NMR spectra. The concentration of water was found to be 0.0095 mol dm^{-3}.

Results and Discussion

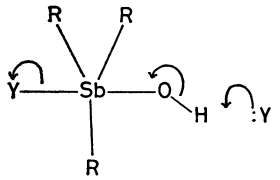
μ-Oxo-bis[tris(organo)antimony(V)] compound, $[R_3SbY]_2O$, show a characteristic band at around 790—740 cm^{-1} in the IR spectra,[12-14] which is attributed to the presence of the Sb–O–Sb skeleton. Compounds **1** and **2** have given a strong band at 720 cm^{-1}, also indicating the Sb–O–Sb skeleton, this is in accordance with the results of elemental analyses. Such a band, however, was not observed in **3**—**6**, these compounds showed a ν(O–H) band at around 3400—3300 cm^{-1} and ν(Sb–O) band at around 610—560 cm^{-1} in the solid state. Therefore, these compounds were assumed to be hydroxo compounds, $(C_6H_{11})_3Sb(OH)Y$. This is also consistent with the results of elemental analyses.

TABLE 2. RELEVANT IR DATA OF μ-OXO-BIS[TRIS(CYCLOHEXYL)HALOANTIMONY(V)] AND TRIS(CYCLOHEXYL)-HYDROXOANTIMONY(V) COMPOUNDS IN THE SOLID STATE AND IN SOLUTION[a]

	ν(O–H) cm^{-1}	ν(Sb–O) cm^{-1}	ν(Sb–O–Sb) cm^{-1}
1	—	—	720
2	—	—	720
3	3420 br (3630 sh)	572 (531)	—
4	3420 br (3628 sh)	569 (538)	—
5	3360 br (3640 sh) (3380 br)	563 (513)	—
6	3340 br (3625 sh) (3400 br)	609 (565)	—

a) Values in parentheses are observed in a dichloromethane solution.

The frequency of the ν(O–H) band is lower than that of the normal one, indicating the presence of an intermolecular hydrogen bond.[17] The frequency of the ν(Sb–O) band in the solid state is a little higher than those reported for $R_3Sb(OH)$(8-quinol) (570—540 cm^{-1}),[8] $(C_6H_5)_4Sb(OH)$ (528 cm^{-1}),[17] and $[F_5Sb(OH)]^-$ (560 cm^{-1}).[18] Upon the deuteration of the hydroxo group of **3**, the ν(O–D) band appeared at 2520 cm^{-1}, and the ν(Sb–O) band, at 565 cm^{-1}. The latter band does not show any large shift upon deuteration. In the dichloromethane solution, the ν(O–H) band of **3**—**6** shifts to a higher frequency and becomes



I

sharp. The ν(Sb–O) band, on the other hand, shifts to a lower frequency (see Table 2). One of the reasons for the high-frequency shift of the ν(Sb–O) band in the solid state may be an intermolecular hydrogen bond, as is shown in I. As a result of hydrogen bond, the Sb–O bond gains a partial double-bond character and the Sb–Y bond becomes a little ionic (*vide infra*). In a proton-accepting solvent such as *N*,*N*-dimethylformamide, the ν(Sb–O) band appears at a higher frequency (545 and 607 cm^{-1} for **5** and **6** respectively) than that in dichloromethane. In dichloromethane, this type of hydrogen bond is lost and the partial double-bond character of the Sb–O bond is diminished. The high-frequency shift of the ν(O–H) band in the dichloromethane solution is consistent with the above explanation. Chremos and Zingaro estimated, by using Gordy's formula, the frequencies of the ν(Sb–O) and ν(Sb=O) bands to be 550 and 803 cm^{-1} respectively.[19] In trimethyloxoantimony(V), $(CH_3)_3SbO$, the ν(Sb=O) band was observed at 645 cm^{-1}.[20]

The influence of the Y group on the ν(O–H) and ν(Sb–O) bands of $(C_6H_{11})_3Sb(OH)Y$ observed in the dichloromethane solution is not large. The ν(O–H) band, however, has a tendency to decrease frequency

Table 3. Relevant IR data of CH_3COO group of some trisorganoantimony compounds, $R_3Sb(X)O_2CCH_3$ in the solid state[a)]

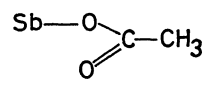
R	X	ν_{asym}(O-C-O) / cm^{-1}	ν_{sym}(O-C-O) / cm^{-1}	Δ
c-C_6H_{11}	OH	1600	1380	220
		(1625)	(1375)	250
	O_2CCH_3	1652	1298	354
	pic	1675	1292	383
CH_3	$O_{1/2}$	1622	1374	248

a) Values in parentheses are observed in a dichloromethane solution.

in the following order; NO_3<Cl, Br<CH_3COO. The ν(Sb–O) band, on the other hand, decreases in the reverse order.

The δ(M–O–H) band has been reported to appear in the region of 1200—700 cm^{-1}.[21] In $R_4Sb(OH)$, the band has been reported to be 995 cm^{-1} for R=CH_3[22] and 795 cm^{-1} for R=C_6H_5.[17] Since the IR spectra of **3** and **4** are quite similar to those of **1** and **2** in this region, this band could not be identified, although the deuterated compound of **3** shows the band at 800 cm^{-1}. In **5** and **6**, this band could not be identified unambigously.

In Table 3, some relevant IR data of acetato compounds of tris(cyclohexyl)antimony(V) are shown. In acetato–hydroxo compound, **5**, the frequency of $\nu_{asym}(CO_2)$ is rather low and that of $\nu_{sym}(CO_2)$ is high and the differnce between these frequencies (Δ=$\nu_{asym}(CO_2)-\nu_{sym}(CO_2)$) is the smallest among the compounds shown in Table 3. One of the reasons for small Δ value of **5** in the solid state is the intermolecular hydrogen bond, as is shown in I. The Δ value of **5** in the dichloromethane solution approaches that of $[(CH_3)_3Sb(O_2CCH_3)]_2O$, but it is still smaller than that of diacetate or acetato–picrate. This suggests that, in the acetato–hydroxo compound, **5**, the Sb–$OC(O)CH_3$ bond is more ionic, or the contribution of the Type-III mode to the bond is large, compared with that of diacetate or acetato–picrate, in which the Type-II mode is more predominant.



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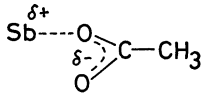

III

The frequencies of the $\nu_{asym}(NO_2)$, $\nu_{sym}(NO_2)$, and ν(N–O) bands of some nitrato compounds of trisorganoantimony(V) are shown in Table 4. The difference (Δ=$\nu_{asym}(NO_2)-\nu_{sym}(NO_2)$) is also shown in this table. These frequencies are characteristic of a nitrato group with essentially a C_{2v} symmetry. Ferraro[23] found that the Δ value is a measure of the covalent character between the metal-nitrato bond of several transition-metal complexes. On the other hand, Gatehouse *et al.*[24] used the frequency of the ν(N–O) band as a criterion of the covalent character of the metal-nitrato bond. As can be seen from Table 4, the Δ value of nitrato–hydroxo compound, **6**, is the smallest, and the frequency of the ν(N–O) band is

Table 4. Relevant IR data of the NO_3 group of trisorganoantimony compounds, $R_3Sb(X)NO_3$, in the solid state[a)]

R	X	$\nu_{asym}(NO_2)$ / cm^{-1}	$\nu_{sym}(NO_2)$ / cm^{-1}	ν(N-O) / cm^{-1}	Δ
c-C_6H_{11}	OH	1420	1305	1037	115
		(1450)	(1295)	(1020)	155
	NO_3	1533	1288	982	245
		1513			
CH_3	$O_{1/2}$	1455	1290	1005	165

a) Values in parentheses are observed in a dichloromethane solution.

Table 5. ν(O–H) and ν(Sb–O) data of $[R_3SbX]_2O$ in dichloromethane saturated with water

R	X	ν(O-H) / cm^{-1}	ν(Sb-O) / cm^{-1}
CH_3	O_2CCH_3	3638, 3420 br	542
	Cl	3625, 3480 br	552
	Br	3620	555
C_2H_5	Br	3632, 3460 br	544
	NO_3	3625, 3500 br	568
i-C_3H_7	Cl	3640, 3460 br	535
	Br	3640, 3475 br	536
c-C_6H_{11}	Cl	3630	531
	Br	3628	538
C_6H_5	O_2CCH_3	3615	535
	Cl	3615	540
	Br	3615	540
	NO_3	3600	568
p-$CH_3C_6H_4$	Br	3610	545

the highest. If the above criterions could be applied to the antimony compounds, the Sb–ONO_2 bond of **6** may have the largest ionic character. The differences in the Δ values and the frequencies of the ν(N–O) bands of **6** in the solid state and in solution may also be explained by the presence of the intermolecular hydrogen bond in the solid state, as in **5**.

Table 5 summarizes the frequencies of the ν(O–H) and ν(Sb–O) bands observed for several μ-oxo compounds, $[R_3SbY]_2O$, in a water-saturated dichloromethane solution, where R=CH_3, C_2H_5, i-C_3H_7, c-C_6H_{11}, C_6H_5, and p-$CH_3C_6H_4$ and Y=Cl, Br, CH_3COO, and NO_3. In isopropyl and cyclohexyl compounds, the two ν(O–H) bands of water disappeared completely, and only one ν(O–H) band due to the hydroxo group bound to the antimony atom was observed at 3640—3630 cm^{-1}. The ν(Sb–O) band appeared at around 535 cm^{-1}. The frequencies of the ν(O–H) and ν(Sb–O) bands of the cyclohexyl compounds in this solvent are similar to those of the hydroxo compounds, **3** and **4**, shown in Table 2. On the other hand, the solubility of the methyl, ethyl, and aryl compounds to this solvent is poor, and so the saturated solutions were used for the spectral measurements. Therefore, the water molecule in dichloromethane was not completely consumed, and the ν(O–H) bands of the water remained. The ν(O–H) band

of the hydroxo group bound to the antimony atom was found at the position of the ν_{sym}(O–H) band of water; *i.e.*, the intensity ratio of $I[\nu_{sym}(O–H)]/I[\nu_{asym}(O–H)]$ becomes large in the $[R_3SbY]_2O$-saturated solution. From the above results, the hydrolysis of the μ-oxo compounds to the hydroxo compounds was found to occur in the dichloromethane. However, the attempted isolation of the hydroxo compounds from this

$$[R_3SbY]_2O + H_2O \overset{CH_2Cl_2}{\rightleftarrows} 2R_3Sb(OH)Y$$

solution failed, and only the starting materials were recovered.

As has been mentioned in the Experimental part, tris(cyclohexyl)halohydroxoantimony(V) is readily dehydrated, giving the μ-oxo compounds in the solid state, although the latter compounds were hydrolyzed easily by a small amound of water in the solvent. In the acetato and nitrato compounds, however, the hydroxo form is stable in air.

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