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The Preparation and Properties of Some Triorgano(oxinato)antimony Hydroxides

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Synopsis. Some new triorgano(oxinato)antimony hydroxides, $R_3Sb(L)OH$ (R=CH_3, C_6H_5 and p-$CH_3C_6H_4$: L=Ox, 2-Me-Ox, and 5-Cl-Ox), have been prepared, and the UV, IR, and NMR spectra of these compounds have been measured. These compounds have a hexa-coordinate configuration around antimony. The effects of the hydroxyl group on the IR and NMR spectra are discussed.

The preparation of the $R_3Sb(OH)X$ type of compounds have been reported by several workers.[1-8] These compounds, however, have been characterized only by chemical analysis, and no IR spectral data such as the O–H stretching band have been reported. Many authors[9-14] have reported that triorganoantimony dihalides, on hydrolysis or on treatment with appropriate silver salts, form stable oxybistriorganoantimony compounds of the $(R_3SbX)_2O$ type. Therefore, there is considerable confusion in the literature regarding the structure of these oxy compounds in the solid state *i.e.*, as to whether they should be regarded as hydroxy compounds, $R_3Sb(OH)X$, or as oxides, $(R_3SbX)_2O$. Doak *et al.*[12] have concluded that compound of the $R_3Sb(OH)X$ type probably do not exist in the solid state.

In the present paper we wish to report on the preparation and spectral data of some new triorgano(oxinato)antimony hydroxides, $R_3Sb(L)OH$.

Experimental

Preparation of $R_3Sb(L)OH$ (R=CH_3, C_6H_5, and p-$CH_3C_6H_4$; L=Ox, 2-Me-Ox and 5-Cl-Ox**).* All of these complexes were prepared in an essentially identical manner, so that only one typical procedure will be given. A benzene solution (70 ml) of trimethylantimony dibromide (10 mmol) was added to sodium methoxide (20 mmol) in methanol (about 10 ml), and the mixture was heated at reflux for 30 min. After distilling off a portion of the solvent, the precipitated sodium bromide was removed by filtration. To the filtrate we then added 8-quinolinol (10 mmol) in benzene (50 ml), and the mixture was heated at reflux for 1 h; the solvent was then removed by distillation under reduced pressure. A mixture of acetone (20 ml) and water (5 ml) was added to the residual, highly viscous yellow liquid. A yellow solid product was obtained by scratching the vessel with a glass rod. The complex was purified by recrystallization from acetone. The analytical data for this and similar compounds are shown in Table 1.

TABLE 1. ANALYTICAL DATA OF TRIORGANO(OXINATO)ANTIMONY HYDROXIDE

$R_3Sb(L)OH$		Mp (°C)	Analysis Found (Calcd) (%)		
R	L		C	H	N
CH_3	Ox	110—111	43.87 (43.94)	5.01 (4.92)	4.40 (4.27)
C_6H_5	Ox	108—109	63.00 (63.07)	4.68 (4.31)	2.65 (2.72)
C_6H_5	2-Me-Ox	129—131	63.49 (63.66)	4.66 (4.58)	2.61 (2.65)
C_6H_5	5-Cl-Ox	161—163	59.38 (59.12)	3.84 (3.86)	2.80 (2.55)
p-$CH_3C_6H_4$	Ox	170—171	64.56 (64.77)	5.10 (5.07)	2.67 (2.52)

* 2-Methyloxine.
** 5-Chlorooxine.

Spectral Measurements and Analysis of the NMR Spectra. The UV spectra were recorded on a Hitachi model 124 spectrometer with 1-mm quartz cells. The absorption maxima measured in methylene chloride are shown in Table 2. The IR spectra were measured on a Hitachi model 225 grating spectrometer in Nujol mulls or a 5 wt% methylene chloride solution. The NMR measurements were made with a JEOL model JNM-PS-100 spectrometer operating at 100 MHz. The chemical shifts were measured relative to tetramethylsilane as the internal standard. Methylene chloride was used as the solvent. The spectra for the 2-, 3-, and 4-protons of the oxinato ligand were analyzed as a first-order system, and those for the 5-, 6-, and 7-protons as an ABC system by using the method reported by Reilly *et al.*[16] The calculations were carried out on a NEAC 2200 model 700 computer at the Computer Center of Osaka University.

Results and Discussion

The absorption maxima of the longest wavelength for the triorgano(oxinato)antimony hydroxides are found in the region where the chelation of the oxinato ligand is expected.[17-19] From these result, it seems almost certain that the antimony atom is hexacoordinate, as has been reported for triorgano(oxinato)antimony halides.[20,21] The absorption maxima for the triaryl(oxinato)antimony hydroxides appear at longer wavelengths than those for the trimethylantimony analogs. Similar bathochromic shifts upon the substitution of methyl group by aryl groups have been noted for triorgano(oxinato)antimony halides.[15,20,21]

As has been shown in Table 2, in the solid state all the triorgano(oxinato)antimony hydroxides gave one very broad band, in some cases there was also an additional sharp band in the O–H stretching region. The broad band indicates a hydrogen-bonded hydroxyl group, and the sharp one, a free hydroxyl group. Two similar O–H stretching bands, one sharp and one broad, have been reported for tetraphenylantimony hydroxide.[22] In a methylene chloride solution, triorgano(oxinato)antimony hydroxides show only one sharp O–H stretching band at a somewhat higher wave number than is found for these compounds in the solid state. This result may be attributed to the absence of hydrogen bonding in the methylene chloride solution.

TABLE 2. UV AND IR DATA OF TRIORGANO(OXINATO)ANTIMONY HYDROXIDE

$R_3Sb(L)OH$		λ_{max}[a] (nm)	ν (O–H)		ν (Sb–O) solid	ν (Sb–O)(Ox) solid
R	L		CH_2Cl_2	solid		
CH_3	Ox	350 (2380)	3627 sh[b]	3240 br[c]	540	508
C_6H_5	Ox	376 (2200)	3608 sh	3555 br	561	512
C_6H_5	2-Me-Ox	352 (2430)	3613 sh	3605 sh 3350 br	558	506
C_6H_5	5-Cl-Ox	386 (3030)	3609 sh	3595 sh 3380 br	568	514
p-$CH_3C_6H_4$	Ox	375 (1900)	3605 sh	3580 br 3370 br	562	515

a) Value in parentheses is extinction coefficient. b) sh: Sharp. c) br: Broad.

TABLE 3. PROTON CHEMICAL SHIFTS OF $(CH_3)_3Sb(Ox)X$[a] (δ value)

X	NO_3	Cl	Br	OAc	OH	Ox^{-b}	H_2Ox^{+c}
2-H	8.86	8.74	8.76	9.05	8.69	8.47	9.26
3-H	7.52	7.43	7.39	7.39	7.39	7.12	8.12
4-H	8.28	8.19	8.22	8.12	8.18	7.90	9.19
5-H	7.31	7.22	7.24	7.15	7.14	6.56	7.66
6-H	7.49	7.44	7.44	7.41	7.46	7.00	7.75
7-H	7.11	7.02	7.04	6.96	6.93	6.37	7.66
CH_3–Sb	1.84[d]	1.91[d]	2.07[d]	1.64[d]	1.42	—	—

a) Coupling constants, J_{23}, J_{24}, J_{34}, J_{56}, J_{57} and J_{67}, were found to be 4.2 ± 0.2, 1.5 ± 0.2, 8.0 ± 0.2, 8.1 ± 0.2, 1.1 ± 0.2 and 7.6 ± 0.2 Hz, respectively. b) Sodium oxinate in HMPA (Ref. 26). c) 8-Quinolinol hydrochlordie in HMPA (Ref. 26). d) Ref. 15.

The frequency of the O–H stretching band for triorgano(oxinato)antimony hydroxides is not affected to a large extent by the substituent on the oxinato ligand, but the value is somewhat small for trimethyl(oxinato)antimony hydroxide.

A strong but somewhat broad band in the region of 540—570 cm^{-1} is assigned to the Sb–O stretching band between the hydroxyl group and the antimony atom, because triorgano(oxinato)antimony complexes, $R_3Sb(Ox)X$, $X=NO_3$, Cl, Br, and OAc show no band in the region. The frequencies observed are almost the same as those assigned to the Sb–O stretching bands in trialkyl-bis(ethoxy)antimony,[23] $R_3Sb(OC_2H_5)_2$ (562, 547, 545, and 540 cm^{-1} for $R=CH_3$, C_2H_5, n-C_3H_7, and n-C_4H_9 respectively), and $(SbF_5OH)^-(NR_4)^+$ (560 and 554 cm^{-1} for $R=C_2H_5$ and n-C_4H_9 respectively,[24] but the values are larger than that reported for tetraphenylantimony hydroxide (528 cm^{-1}). [22]Zingaro *et al.*[25] estimated the Sb–O stretching frequency to be 550 cm^{-1} by using Gody's rule.

The Sb–O stretching bands between the oxinato group and the antimony atom for some trimethyl(oxinato)antimony complexes, $(CH_3)_3Sb(Ox)X$, are found to be 525, 520, 520, 516, and 508 cm^{-1} for $X=NO_3$, Cl, Br, OAc, and OH respectively. The corresponding value for tetramethyl(oxinato)antimony has been reported to be 497 cm^{-1}.[20] The Sb–O bond in the hydroxide complex, therefore, is weaker than those in the nitrate and halide complexes.

Except for the 2-proton of trimethyl(oxinato)antimony acetate, the chemical shifts of the ring protons show a general drift of the low-field shift in the order: $NO_3 > Cl \gtrsim Br > OAc > OH$. This order is the same as that for the high-frequency shifts of the Sb–O stretching band between the oxinato group and the antimony atom. These results may indicate that the electron-withdrawing effect of the hydroxyl group is smaller than that of the nitrato group and the halogens.

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