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STUDIES ON STABLE ADDUCTS OF DIORGANOANTIMONY TRICHLORIDES

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SUMMARY

The properties of the adducts of diorganoantimony trichlorides, R_2SbCl_3L ($R=CH_3$, C_2H_5, C_6H_5; L=DMSO, HMPA, TPPO, PyO), and the acceptor behavior of the antimony atom in these adducts are described and compared with the similar adducts of antimony pentachloride. All of these compounds are stable in air at room temperature. They are monomeric in $C_6H_5NO_2$ and contain hexacoordinated antimony. The probable configurations of these adducts are discussed on the basis of IR and NMR data.

INTRODUCTION

Dialkylantimony(V) halides, R_2SbX_3, are thermally unstable and decompose easily even at room temperature[1]:

$$R_2SbX_3 \rightarrow RSbX_2 + RX$$

We have succeeded[2] in isolating stable derivatives of these chlorides by substituting one chlorine atom by one acetylacetonate group or by adding an oxygen donor molecule, such as dimethyl sulfoxide. At the same time, Meinema and Noltes reported independently the preparation of stable dialkylantimony dichloride acetylacetonates[3], and mono- and dialkylantimony chloride oxinates[4].

The present paper reports the structures, as indicated by IR and NMR studies, of the stable adducts, R_2SbCl_3L, isolated from the reaction of diorganoantimony trichlorides with several oxygen donors. The acceptor behavior of the antimony atom in these adducts also will be discussed in comparison with the similar adducts of antimony pentachloride.

EXPERIMENTAL

Preparation of R_2SbCl_3L ($R=CH_3$, C_2H_5; *L=DMSO, HMPA, TPPO, PyO*)

Details of only a typical experiment will be given, since all of the adducts have been prepared by practically the identical procedure.

A solution of dimethylchlorostibine (1.88 g, 0.01 mole) in methylene chloride (50 ml) was cooled to −70° under a nitrogen atmosphere. A solution of sulfuryl chloride (1.36 g, 0.01 mole) in dry methylene chloride (10 ml) and then a solution of dimethyl sulfoxide (DMSO) (0.78 g, 0.01 mole) in methylene chloride (10 ml) were added dropwise with stirring. The mixture was allowed to stand at room temperature, and the solvent was distilled off under reduced pressure. The white residue was dissolved in dry methanol. The solution was evaporated to approximately one half of its original volume under reduced pressure. When it was cooled, white crystals of $(CH_3)_2SbCl_3(DMSO)$ were precipitated.

Preparation of $(C_6H_5)_2SbCl_3L$ *(L=DMSO, HMPA)*

To a solution of diphenylantimony trichloride (2.00 g, 0.0050 mole*) in dry methanol (50 ml) was added a slight excess of DMSO (0.41 g, 0.0052 mole) or hexamethylphosphoric amide (HMPA) (0.93 g, 0.0052 mole).

TABLE 1

PROPERTIES OF THE ADDUCTS

Adduct		M.p. (°C)	Analysis found (calcd.) (%)			Mol.wt.[a] found (calcd.)
R	L		C	H	N	
R_2SbCl_3L						
CH_3	DMSO	147.5	14.46	3.84		348
			(14.29)	(3.60)		(336)
C_2H_5	DMSO	79–81	19.45	4.48		352
			(19.78)	(4.43)		(364)
C_6H_5	DMSO	214	36.55	3.44		441
			(36.52)	(3.50)		(460)
CH_3	HMPA	118–119	21.70	5.83	9.60	420
			(21.97)	(5.53)	(9.61)	(437)
C_2H_5	HMPA	86–87	25.02	6.12	8.89	483
			(25.81)	(6.06)	(9.03)	(465)
C_6H_5	HMPA	241 (dec.)	38.45	5.17	7.53	[b]
			(38.50)	(5.03)	(7.48)	
CH_3	TPPO	145	44.63	3.92		553
			(44.78)	(3.95)		(537)
CH_3	PyO	157	23.49	3.28	3.94	365
			(23.80)	(3.14)	(3.96)	(353)
$SbCl_5L$						
	DMSO	138–139	6.42	1.69		372
		135[c]	(6.37)	(1.60)		(377)
	HMPA	158 (dec.)	15.43	3.91	9.03	440
			(15.07)	(3.79)	(8.79)	(478)
	TPPO	200–201	36.52	2.56		598
		196–197[d]	(37.45)	(2.62)		(577)
	PyO	193–194	15.81	1.41	3.62	378
			(15.24)	(1.28)	(3.55)	(394)

[a] Determined cryoscopically in $C_6H_5NO_2$ at concentrations 1–3 wt%. [b] Not determined because of the limited solubility. [c] Ref. 6. [d] Ref. 7.

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* Calculated as the monohydrate[5].

Precipitated $(C_6H_5)_2SbCl_3(DMSO)$ and $(C_6H_5)_2SbCl_3(HMPA)$ were recrystallized from methylene chloride/petroleum ether and acetonitrile, respectively, as colorless crystals.

Preparation of $SbCl_5L$ (L=DMSO, HMPA, TPPO, PyO)

The adducts of DMSO and triphenylphosphine oxide (TPPO) were prepared as reported[6,7], and those of HMPA and pyridine *N*-oxide (PyO) were also prepared by a similar procedure.

These adducts are non-hygroscopic, stable crystalline compounds and can be handled in the air at room temperature. They are listed in Table 1 together with some physical properties.

Infrared spectra

The IR spectra were obtained in Nujol mulls in the 4000–400 cm^{-1} region, using a Hitachi EPI-2G or 225 spectrophotometer equipped with gratings and in the region of 700–200 cm^{-1}, using a Hitachi EPI-L spectrophotometer equipped with gratings. The results are given in Table 2.

TABLE 2

RELEVANT IR STRETCHING FREQUENCIES OF R_2SbCl_3L AND $SbCl_5L$ IN NUJOL MULL (IN cm^{-1})

Compound	ν(Sb–C)	ν(Sb–Cl)	ν(Sb–O)	ν(X–O)[a]	Δν(X–O)[a]
$(CH_3)_2SbCl_3$	567, 504	342			
	(565, 502)[b]	(328)[b]			
$(C_2H_5)_2SbCl_3$	512, 483	329			
L = DMSO				1045[c]	0
$(CH_3)_2SbCl_3L$	572, 513	295	438	930	−115
$(C_2H_5)_2SbCl_3L$	519, 493	280	439	918	−127
$(C_6H_5)_2SbCl_3L$	[d]	280	440	916	−129
$SbCl_5L$		355	497	878	−167
L = HMPA				1212[e]	0
$(CH_3)_2SbCl_3L$	579, [d]	290	[d]	1086	−126
$(C_2H_5)_2SbCl_3L$	525, [d]	270	[d]	1089	−123
$(C_6H_5)_2SbCl_3L$	[d]	260	[d]	1056	−156
$SbCl_5L$		357	[d]	1019	−193
L = TPPO				1192	0
$(CH_3)_2SbCl_3L$	572, [d]	283	[d]	1065	−127
$SbCl_5L$		367	[d]	1032	−160
		357			
L = PyO				1265[f]	0
$(CH_3)_2SbCl_3L$	[d]	280	357	1194	− 71
$SbCl_5L$		350	402	1192	− 73

[a] X=S, P, N. [b] Ref. 8. [c] Ref. 9. [d] Obscured by the strong bands of the ligands. [e] Ref. 10. [f] Ref. 11.

NMR spectra

The NMR spectra were measured on a Japan Electron Optics JNM-3H-60 spectrometer or HNM-3H-60 spectrometer at 60 MHz and 20°. The results are tabulated in Table 3.

TABLE 3

PROTON CHEMICAL SHIFTS (ppm)[a] OF THE ADDUCTS IN C_6H_6 AND CH_2Cl_2 (5 wt.%)

Adduct		τ		$\Delta\tau$[b]
		In C_6H_6	In CH_2Cl_2	
L = DMSO				
$(CH_3)_2SbCl_3L$	$Sb{-}CH_3$	[c]	7.18	
	$S{-}CH_3$	[c]	7.05	
$(C_2H_5)_2SbCl_3L$	$Sb{-}CH_2{-}$	6.71	6.77	−0.06
	$Sb{-}C{-}CH_3$	8.28	8.37	−0.09
	$S{-}CH_3$	8.11	7.08	+1.03
$(C_6H_5)_2SbCl_3L$	$S{-}CH_3$	[c]	7.32	
$SbCl_5L$	$S{-}CH_3$	8.58	6.83	+1.75
L = HMPA				
$(CH_3)_2SbCl_3L$	$Sb{-}CH_3$	7.04	7.14	−0.10
	$N{-}CH_3$	7.88	7.34	+0.54
		7.71	7.17	
$(C_2H_5)_2SbCl_3L$	$Sb{-}CH_2{-}$	6.64	6.78	
	$Sb{-}C{-}CH_3$	8.17	8.37	−0.14
	$N{-}CH_3$	7.86	7.35	−0.20
		7.69	7.19	+0.51
$(C_6H_5)_2SbCl_3L$	$N{-}CH_3$	[c]	7.75	
			7.58	
$SbCl_5L$	$N{-}CH_3$	7.80	7.28	+0.53
		7.63	7.10	
L = TPPO				
$(CH_3)_2SbCl_3L$	$Sb{-}CH_3$	7.17	7.30	−0.13
L = PyO				
$(CH_3)_2SbCl_3L$	$Sb{-}CH_3$	[c]	7.43	

[a] Internal reference TMS. [b] τ(in C_6H_6)−τ(in CH_2Cl_2). [c] Not measured in C_6H_6 because of the limited solubility.

RESULTS AND DISCUSSION

The cryoscopic determination of the molecular weights of these adducts in nitrobenzene gives monomeric values (Table 1). This indicates the presence of hexacoordinated antimony as is also the case with the stable mono- and diorganoantimony(V) halide acetylacetonates[3,12] and oxinates[4].

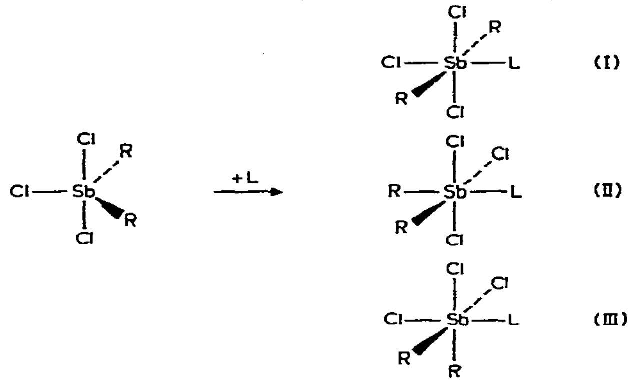
In the above complexes the frequency of the S–O, P–O or N–O stretching vibration is appreciably lower than that of the free ligand, and a characteristic strong band due to the Sb–O stretching mode is observed (Table 2). As expected, the frequency shift is related to the strength of the antimony–oxygen bond and the acid strength of the acceptor, which increases in the fllowing order:

$$(CH_3)_2SbCl_3 \approx (C_2H_5)_2SbCl_3 < (C_6H_5)_2SbCl_3 < SbCl_5$$

Stereochemistry of the adducts

It is generally accepted* that dialkylantimony trichlorides have a geometry of a trigonal bipyramid with the two alkyl groups and one chlorine atom in equatorial positions. In adduct formation the antimony atom increases its coordination number to six, and for our hexacoordinated adducts, three geometrical isomers [I], [II] and [III] can be considered based on a probable octahedral arrangement**.

SCHEME 1



It has been assumed[15] that the addition of a base L to the central atom in a trigonal bipyramidal molecule takes place in the trigonal plane and steric and electrostatic factors play an important role in determining the position of entry of L. In view of the above idea the nucleophilic attack at the position between the two methyl groups to produce structure [I] appears to be most favorable, since R is less electronegative than Cl. The data from the far-IR and NMR spectra are consistent with this tentative conclusion.

As shown in Table 2, on the formation of an adduct, marked changes are observed in the far-IR spectra. For example, in the spectrum of $(CH_3)_2SbCl_3(DMSO)$, the frequencies of the Sb–C asymmetric and symmetric stretch shift up to 572 and 513 cm^{-1}, respectively. On the other hand, the Sb–Cl stretching frequency decreases to 295 cm^{-1}. These changes could be rationalized by assuming that the *s* character of the antimony orbitals directed to the carbons is greater in the adduct than in the trigonal bipyramidal $(CH_3)_2SbCl_3$. Then the Sb–Cl bond weakening in the complex might be explained by increased *p* and *d* character of those bonds. We presently prefer this interpretation and propose that the essentially linear CH_3–Sb–CH_3 structure [I] (L = DMSO) is most likely. However, some kind of distortion from this simple structure could be expected, since the scarcely observed very weak symmetric Sb–C stretching frequency at 513 cm^{-1} shows that the CH_3–Sb–CH_3 angle might not be 180°.

Similar changes in the far-IR spectra are observed for the other DMSO and HMPA dialkylantimony trichloride adducts shown in Table 2, and the same structure

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* See for example ref. 13.

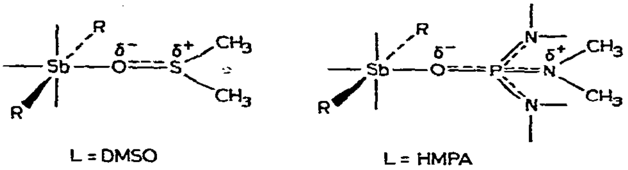
** X-ray structure determinations have been carried out on many adducts of $SbCl_5$ with neutral bases, and an octahedral configuration around the Sb atom has been established for each complex[14].

[I] is suggested for these compounds*. For organotin and organolead adducts of the type R_3MClL (M=Sn, Pb; L=TMSO, DMA), an analogous discussion has been given[16].

The NMR spectra of the adducts are rather simple, and the observation of only one sharp signal of the $Sb-CH_3$ protons (Table 3) supports the conclusion described above**.

With the assumption of structure [I] for these adducts, R_2SbCl_3L, it is relatively easy to explain the solvent effects on the NMR spectra. The signals of the methyl protons of the donor ligands (DMSO and HMPA) appear at higher magnetic field in C_6H_6 than in CH_2Cl_2 solution. On the other hand, the signals of the alkyl protons attached to antimony are at lower field in C_6H_6 solution (Table 3). These changes are in agreement with the expectation that the alkyl groups attached to antimony are *cis* to L and that the dipoles are oriented as shown below.

SCHEME 2



It is generally accepted that protons near the electron deficient center of the solute are shielded and those near the negative end of the dipole are deshielded in C_6H_6 solution[18]. Such an aromatic shift effect has been applied in structural studies of several organotin compounds[19].

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* The stereochemistry of the diphenyl analogues can not be explained in the similar way because of difficulty of obtaining the anhydrous diphenyl antimony trichloride. However, an X-ray diffraction study[5] of the monohydrated compound has demonstrated an octahedral geometry with the essentially linear C–Sb–C structure.

** The barriers to intramolecular rearrangement in hexacoordinate complexes are intrinsically relatively high[17], and a rapid pseudo-rotation of the ligands may be excluded.

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