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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

XIV *. COMPLEXES OF MONOCHLORODIORGANOANTIMONY(V) MOIETIES WITH DIANIONIC ONO TRIDENTATE LIGANDS

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Summary

Diorganoantimony(V) complexes of the type $R_2SbClTrid$ (R = Me, Ph) containing dianionic, potentially tridentate Schiff-base ligands with ONO donor atoms ($Trid^{2-}$) have been prepared and characterized. IR and NMR data suggest an octahedral coordination environment for the antimony atom with meridional arrangement of the ONO ligand atoms and a linear CSbC skeleton.

Introduction

In a previous paper from our laboratories the synthesis and structural studies of novel complexes formed by R_3Sb^V moieties (R = Me, Ph) and "planar" tridentate ligands ($Trid^{2-}$) having ONO and SNO donor atoms have been reported [1]. In these compounds the antimony atom attains the coordination number six as a result of chelation by the dianionic ligand which occurs in the Schiff-base form. The ligand donor atoms as well as the organic radicals assume meridional configurations in an octahedral structure around antimony, both in the solid state (as inferred, for example, from the crystal and molecular structure of Me_3SbSah, H_2Sah being 2,2'-(methylidynenitrilo)diphenol)) and in solution [1]

We have now extended these researches to corresponding complexes of R_2Sb^V with the $Trid^{2-}$ ligands Sah^{2-}, Bah^{2-} and Aah^{2-}, where $Trid^{2-}$ have ONO donor atoms [1,2].

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[*] For Part XIII see ref. 28.

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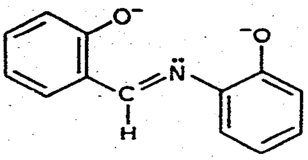
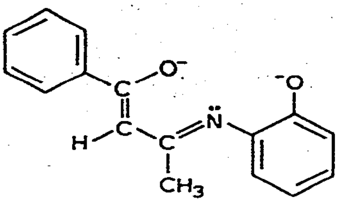
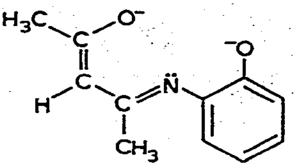


(Sah^{2-})



(Bah^{2-})



(Aah^{2-})

The novel complexes $R_2SbClSah$, $R_2SbClBah$ (R = Me and Ph) and $Ph_2SbClAah$ have been obtained via the metathetic reactions 1 and 2. These reactions

$$Me_3SbTrid + R_2SbCl_3 \rightarrow R_2SbClTrid + Me_3SbCl_2 \qquad (1)$$

$$Me_2SnTrid + R_2SbCl_3 \rightarrow R_2SbClTrid + Me_2SnCl_2 \qquad (2)$$

proceed to completion as a result of the greater Lewis acidity of R_2Sb^V as compared with Me_3Sb^V and Me_2Sn^{IV}. The complexes $R_2SbClTrid$ have been investigated by infrared spectroscopy in the solid state and PMR spectroscopy in solution. Results have been discussed mainly in connection with known spectroscopic characteristics of $R_3SbTrid$ and $R_2SnTrid$ complexes [1,2].

Experimental

The starting materials Me_2SbCl_3, $Ph_2SbCl_3 \cdot H_2O$, $Me_3SbTrid$ and $Me_2SnTrid$ have been prepared by literature methods [1-4]. Anhydrous Ph_2SbCl_3 has been obtained by distillation of the azeotropic mixture C_6H_6/H_2O from benzene solutions of the aquated derivative and subsequent recrystallization.

The preparation of complexes $R_2SbClTrid$ has been carried out in CH_2Cl_2

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR $R_2SbClTrid$ COMPLEXES

Compound (colour)	M.p. (°C)	Analyses, found (calcd.) (%)				
		C	H	N	Cl	Sb
$Me_2SbClSah$ (yellow)	218-220 (dec.)	45.56 (45.20)	3.86 (3.77)	3.72 (3.52)	8.22 (8.92)	30.38 (30.56)
$Ph_2SbClSah$ (yellow)	210-218 (dec.)	57.33 (57.45)	3.66 (3.64)	3.13 (2.68)	6.47 (6.80)	22.71 (23.30)
$Ph_2SbClSah \cdot CCl_4$ (yellow)	220-225 (dec.)	46.29 (46.16)	3.04 (2.83)	2.17 (2.07)	25.28 (26.20)	17.91 (18.00)
$Me_2SbClBah$ (orange)	185-190 (dec.)	48.79 (49.29)	4.47 (4.37)	3.16 (3.20)	8.66 (8.08)	27.21 (27.26)
$Ph_2SbClBah$ (orange)	220-225 (dec.)	59.21 (59.76)	4.35 (4.12)	2.33 (2.49)	6.58 (6.30)	21.56 (21.64)
$Ph_2SbClAah$ (green-yellow)	225-230 (dec.)	54.74 (55.18)	4.40 (4.23)	2.78 (2.80)	7.64 (7.08)	24.09 (24.32)

or cyclohexane by reactions 1 and 2, operating under a N_2 atmosphere. The occurrence of the metathetic reaction has been studied by PMR spectroscopy on $CDCl_3$ solutions of solid residues obtained by evaporation to dryness of the reaction solutions. The formation of $Me_2SbClTrid$ (see Table 4), Me_3SbCl_2 ($\delta Sb(CH_3)$ 2.30 ppm) or Me_2SnCl_2 ($\delta Sn(CH_3)$ 1.20 ppm), and the disappearance of the reagent Me_2SbCl_3 (δ $Sb(CH_3)$ 2.90 ppm) have been detected in this way.

$Me_3SbTrid$ (about 3 mmol in 40 ml of CH_2Cl_2) or $Me_2SnTrid$ (about 3 mmol in 100 ml of cyclohexane) was added dropwise to an equimolar amount of R_2SbCl_3 in 30 ml of CH_2Cl_2 (or 100 ml of cyclohexane). The solvent

TABLE 2

INFRARED ABSORPTION BANDS OF $R_2SbClSah$ AND THE CORRESPONDING COMPLEXES IN THE REGIONS 4000-1500 cm^{-1} AND 620-250 cm^{-1} [a]

$Me_2SbClSah$	$Ph_2SbClSah$ [c]	Me_3SbSah	Ph_3SbSah	Assignments [b]
3050vw	3070w	3070vw	3050w(br)	ν(CH)
	3030vvw	3010vw	3020vw	
2920vw		2920vw		
1610vs	1610vs	1610s	1610s	ν(C=N)
	1595(sh)	1600s(sh)	1600s	*k*, *l* in mono- and disubstituted benzene
1590vs		1590s	1590s	
1540m(br)	1550s	1540m(br)	1550m	ν(C—O)
620m	620m	610m	615w	
		605m		
610s	610s	595m	600m	
585mw				$\nu_{as}(SbC_2)$
		550m		$\nu(SbC_3)$
	555s			
530vs	545vs	530vs	530s	
		520vs		$\nu(SbC_3)$
495mw		490vw	490w	
	485s		480s	*y* ?
	465s		465mw	*y* ?
475mw		455vw	455m	
	455s		445ms	*y* ?
445w	440vw	440w	435vw	
380m	380s	365mw	365s	
340m	340mw	325vw	335m	
305(sh) [d]	300(sh) [d]	310vw	305ms	
			280ms	*t*(+lig.?)
285s [d]				ν(SbCl) + lig.
275s [d]				
	285s [d]			ν(SbCl) + *t* + lig.
	275s [d]			
		270vw		
			260ms	*t*(+lig.?)

[a] Nujol mulls (nujol bands omitted); hexachlorobutadiene mulls in the 3100-2900 cm^{-1} region. Symbols for compounds as in the Introduction; s, strong; m, medium; w, weak; (br), broad; (sh), shoulder; v, very. [b] See text under Discussion and Refs. 5 and 6. Phenyl ring vibrations indicated by a letter refer to Whiffen's notation [6]. ν(C—O) according to Ref. 7. [c] Spectra of $Ph_2SbClSah$ and $Ph_2SbClSah \cdot CCl_4$ differ only in the 700-800 cm^{-1} region, as follows: $Ph_2SbClSah$: 785ms; 760s; 745s; 740s; $Ph_2SbClSah \cdot CCl_4$: a broad band (due to $\nu_{as}(CCl_4)$) with superimposed bands at 785vs; 780s; 760s; 745vs. [d] Components of a broad band.

was pumped off (totally for the CH_2Cl_2, partially for the cyclohexane-containing solutions). The solid residue (or the crystalline precipitate) obtained was recrystallized from CH_3OH or from CH_3OH/C_2H_5OH or $CHCl_3/CCl_4$ 1/1 solvent mixtures to give pure products.

Difficulties have been encountered in the attempted preparations of R_2Sb-XTrid by the reaction of $R_2Sb(OR')_3$ with H_2Trid, as well as of R_2SbCl_3 with Na_2Trid. Solids of obscure composition were isolated.

Compounds recrystallized from $CHCl_3/CCl_4$ mixtures reveal a strong affinity for the solvent, as demonstrated by high Cl and low C content, even after extensive pumping in a vacuum line (0.1 Torr). This is particularly true for Ph_2SbCl-Sah, which on recrystallization from CCl_4 affords an adduct which analyzes perfectly for a 1/1 composition.

Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO under the supervision of Mr. W.J. Buis. Results are given in Table 1.

Molecular weights have been determined with an AEI-MS 902 Mass Spectro-

TABLE 3

RELEVANT INFRARED ABSORPTION BANDS OF R_2SbClTrid AND OF THE CORRESPONDING Ph_3SbTrid COMPLEXES (Trid = Bah AND Aah) IN THE REGIONS 4000-1500 cm^{-1} AND 640-250 cm^{-1} [a]

Me_2SbClBah	Ph_2SbClBah	Ph_3SbBah	Ph_2SbClAah	Ph_3SbAah	Assignments [b]
3070w	3050m(br)	3060m(br)	3060w	3070m(br)	ν(CH)
			3000vw	3000vw	
2930vw	2930vw		2930vw	2920vw	
1590vs	1590vs	1590s	1585s	1590vs(br)	ν(C=N), ν(C=O), ν(C=C); *k*,*l*,*m*
1570vs	1575vs	1565s	1575s	1575(sh)	
1500(sh)	1500(sh)	1500vs	1505vs	1505vs	
1475vs(br)	1475vs(br)	1475vs(br)	1470vs	1470vs	
			640w	635w	
625m	620m	620m	620m	620m	
575mw					$\nu_{as}(SbC_2)$
565m	565s	560s	575mw	570w	
555s	555m	550s	565mw	560m	
			525s	520s	
475w					
	465vs	465vs	470m	465vs	*y* ?
			465m		
		445vs	455m	445vs	*y* ?
420s	425mw	415s	390mw	385m	
		400w			
390m	405ms	385mw	365m	365s	
	355m	355mw	330mw	330s	
		290vs(br)		295vs	*t*
				280s	
			300vs		ν(SbCl) + *t*
285s	295vs		290(sh)		
280s	285vs		275(sh)		
	265mw	255mw	260w	260vs	*t*

[a,b] See footnotes of Table 2.

TABLE 4

PMR SPECTRAL DATA FOR COMPLEXES $R_2SbClTrid$ IN $CDCl_3$ AT 27°C

Compound	Chemical shifts, δ (ppm) [a]			
	CH_3—(Sb)	$=\overset{\mid}{C}-CH_3$	$=\overset{\mid}{C}-H$	Aromatic-H
$Me_2SbClSah$	2.02		8.45	6.50—7.60
$Ph_2SbClSah \cdot CCl_4$			8.38;8.26	6.60—8.10
$Me_2SbClBah$	2.05	2.52	6.06	6.60—8.00
$Ph_2SbClBah$		2.39	5.82	6.60—8.00
$Ph_2SbClAah$		2.02;2.25 [b]	5.12	6.50—8.00

[a] Downfield from TMS. [b] Assigned to $CH_3-C\genfrac{}{}{0pt}{}{=C-}{-O^-}$ and $CH_3-C\genfrac{}{}{0pt}{}{=\bar{N}}{-}$, respectively, based on the comparison with the spectrum of $Ph_2SbClBah$.

meter at the Laboratory for Analytical Chemistry of the State University of Utrecht.

The infrared spectra have been measured with Perkin—Elmer Mod. 457 and 577 instruments in nujol and hexachlorobutadiene mulls between CsI windows in the 4000-250 cm^{-1} range. Selected data are reported in Tables 2 and 3 which for purposes of comparison also present IR spectra data for the corresponding $R_3SbTrid$ complexes.

The PMR spectra were determined by a Jeol C-60 as well as by a Varian Associates HA-100 NMR spectrometer (see Table 4).

Discussion

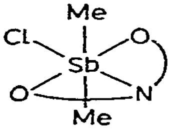
The analytical data (Table 1) reveal for the compounds under investigation the stoichiometry $R_2SbClTrid$. Molecular ion and degradation patterns observed in the mass spectra were in accordance with the presence of monomeric R_2SbCl-Trid complexes. The too high chlorine content observed in the elemental analyses was found to be the result of the presence of $CHCl_3$, CCl_4 in the solid products.

Apart from vibrations inherent to the organic groups bound to antimony and tin corresponding $R_2SnTrid$, $R_3SbTrid$ and $R_2SbClTrid$ compounds show essentially analogous infrared spectra in the range 4000-600 cm^{-1}. Conclusions drawn from earlier discussions concerning infrared data of coordinated $Trid^{2-}$ ligands, especially around 3000 cm^{-1} and in the 1620-1450 cm^{-1} range, would seem to hold true also for $R_2SbClTrid$. Based on the IR data reported in Tables 2 and 3 and those in ref. 2 the $Trid^{2-}$ ligands occur in the Schiff-base form and act as a tridentate ligand by Sb—ONO coordination. Taking into account that these $Trid^{2-}$ ligands according to X-ray and spectroscopic investigations assume a planar configuration when acting as a tridentate ligand [1,2,8-10], it is reasonable to assume a meridional arrangement of chelating ONO atoms also in R_2Sb-ClTrid.

Vibrations associated with Sb—Cl bonds and modes inherent to SbC_2 groups in Me_2Sb^V derivatives provide information concerning the configuration of R_2Sb-ClTrid complexes. On the basis of a thorough comparison of the spectra of R_3-SbTrid and $R_2SbClTrid$ and of the spectra of Me_2SbCl_3 [11-13], Me_3SbCl_2 [14-

16], Ph_2SbCl_3 and $Ph_2SbCl_3 \cdot H_2O$ [17], and Ph_3SbCl_2 [14,18,19], ν(SbCl) modes in R_2SbClTrid, reported in Tables 2 and 3, have been assigned. The observed decrease of ν(SbCl) in the R_2SbClTrid complexes with respect to R_2SbCl_3 can be interpreted in terms of increased ionicity of the metal—halogen bond. The order of magnitude of ν(SbCl) in R_2SbClTrid corresponds to values detected in complexes $R_2SbCl_2L_2$ and R_2SbCl_3L (L_2 = bidentate, L = monodentate ligand) [11, 13,20,21]. Two of the three $\nu(SbC_3)$ bands expected in Me_3SbSah for an ideal C_{2v} symmetry [1] have been identified with reasonable certainty (Table 2). These are in a frequency range usual for Me_3Sb^V derivatives [14-16,21-26]. Only $\nu_{as}(SbC_2)$ (usually found around 560-585 cm^{-1}) are IR active in Me_2SbClSah and Me_2SbClBah, no evidence being obtained for $\nu_s(SbC_2)$ (expected in the range 502-530 cm^{-1}) [12,13,20,21,27].

The infrared data discussed above strongly suggest an octahedral type of configuration for Me_2SbClTrid in the solid state, with meridional ONO ligand atoms, and a linear CSbC skeleton (structure I). The latter structure seems reasonable, also for the Ph_2Sb^V complexes.



(I)

PMR spectra for complexes R_2SbClTrid were run in $CDCl_3$ solution at room temperature. Data are given in Table 4. The signals are easily assigned on the basis of intensity ratios.

PMR spectra of Me_2SbClTrid complexes (Trid = Sah, Bah) point to the presence of only one isomer in solution as only one =C—H singlet is observed. The presence of a singlet for the Me—Sb protons points to structure I in which the methyl groups occupy *trans* positions. This is in accordance with the conclusion drawn from IR data.

The appearance of two =C—H singlets in the PMR spectrum of Ph_2SbCl-Sah · CCl_4 points to the presence in solution of two isomeric structures, possibly a *trans*-diphenyl and a *cis*-diphenyl isomer (cf. ref. 21). The occurrence of interchange between these isomers has not been observed. Both =CH singlets were observed in freshly prepared solutions and the intensity ratios did not change markedly in the range 25-70°C.

The PMR spectra of Ph_2SbClBah and Ph_2SbClAah point to the presence of only one isomer in $CDCl_3$ solution at 27°C as only one =C—H singlet has been observed.

The spectrum of Ph_2SbClAah shows an interesting feature in that the singlet at 2.25 ppm is broadened with respect to that at 2.02 ppm suggesting nonrigid behaviour for the part of the Aah ligand.

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