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INVESTIGATIONS ON ORGANOANTIMONY COMPOUNDS

XI*. TRIORGANOANTIMONY(V) COMPOUNDS CONTAINING POTENTIALLY TRIDENTATE LIGANDS

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SUMMARY

Triorganoantimony(V) compounds of the types R_3Sb^VL, in which R = Me or Ph, and L represents a potentially tridentate dianionic Schiff base ligand of the ONO or SNO type, have been synthesized and investigated by spectroscopic (UV, IR, PMR) methods. Molecular weight determinations in benzene reveal the monomeric nature of these compounds. The free ligands, H_2L, used in this study are: 2,2′-(methylidynenitrilo)diphenol (H_2Sab), 2-(*o*-hydroxyphenyl)benzothiazoline (H_2Sat), 3-(*o*-hydroxyanilino)crotonophenone (H_2Bah), 4-(*o*-hydroxyphenylimino)-2-pentanone (H_2Aah) and 2-acetonyl-2-methylbenzothiazoline (H_2Aat).

Both the UV and the IR data suggest hexacoordinate molecular structures for the complexes R_3SbL in which the L^{2-} ligand coordinates to the R_3Sb^V moiety as a planar tridentate ligand. PMR spectroscopy indicates that at room temperature in solution the hexacoordinate organoantimony(V) compounds Me_3SbSab and Me_3SbSat are stereochemically non-rigid. An X-ray structure determination has revealed that in the crystalline state the antimony atom in Me_3SbSab possesses a distorted octahedral geometry.

Complexes of the type R_3Sb^VAat (R = Me, Ph) could not be isolated as a result of their spontaneous decomposition into triorganostibines, R_3Sb^{III}, and 2-acetyl-3-methyl-4*H*-1,4-benzothiazine.

INTRODUCTION

The coordination behaviour of the antimony atom in triorganoantimony(V) compounds has been the subject of a number of recent investigations. All compounds of the type R_3SbY_2 studied so far, in which Y represents a potentially bidentate ligand, *e.g.* a carboxylate[1] or nitrate[1,2] group, contain a pentacoordinate antimony atom. Recently, hexacoordination of the antimony atom has been observed for a number of

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[*] For Part X see ref 14

compounds of the type R_3SbXY in which R = phenyl, X = halogen and Y represents a potentially bidentate ligand, *e.g.* an acetylacetonate[3] or an oxinate[4] group. Hexacoordination as a result of dimerisation of triorganoantimony(V) compounds has been proposed by Okawara *et al.*[5] for triorganoantimony thioglycolates and glycolates.

The present paper deals with the preparation and coordination behaviour of triorganoantimony(V) compounds, R_3Sb^VL, in which L represents a potentially tridentate dianionic Schiff base ligand.

RESULTS AND DISCUSSION

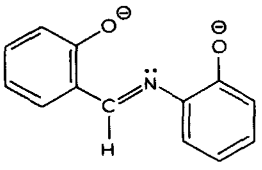
Preparation

Two reactions have been used to prepare the triorganoantimony (V) complexes, R_3SbL; *i.e.* treatment of triorganoantimony dichlorides with the sodium salt of the ligand in anhydrous methanol or reaction of triorganoantimony dimethoxides with the free ligand in benzene solution.

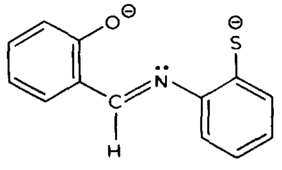
$$R_3SbCl_2 + Na_2L \xrightarrow{MeOH} R_3SbL + 2NaCl$$

$$R_3Sb(OMe)_2 + H_2L \xrightarrow{C_6H_6} R_3SbL + 2MeOH$$

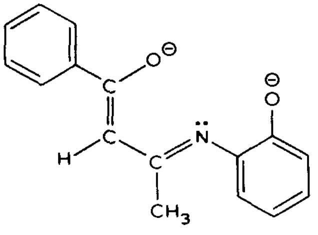
The potentially tridentate dianionic ligands of the ONO and SNO type used in this work were Sab^{2-}, Sat^{2-}, Bah^{2-}, Aah^{2-} and Aat^{2-}. These ligands have been previously used by Barbieri *et al.* in their study of diorganotin and diorganolead complexes of the type R_2ML (M = Sn, Pb)[6,7].



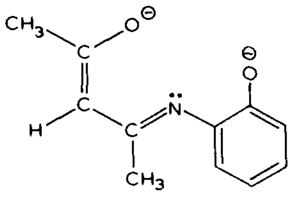
Sab^{2-}



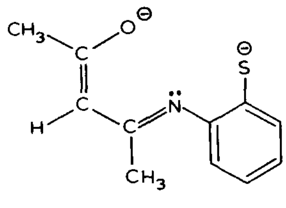
Sat^{2-}



Bah^{2-}



Aah^{2-}



Aat^{2-}

Physical and analytical data of the various complexes R_3SbL prepared are given in Table 1. Attempts to prepare Me_3SbBah and Me_3SbAah resulted in the isolation of viscous oils of obscure composition. Complexes of the type R_3SbAat (R = Me, Ph) could not be isolated as a result of their spontaneous decomposition, which will be discussed in greater detail below.

TABLE 1

PHYSICAL AND ANALYTICAL DATA OF R_3SbL COMPLEXES

Compound (colour)	*M p (°C)*	*Analysis found (calcd) (%)*						*Mol wt found (calcd)*
		C	*H*	*N*	*O*	*S*	*Sb*	
Me_3SbSab (yellowish orange)	188–190	50 77 (50 83)	4 80 (4 80)	3 60 (3 70)	8 33 (8 46)		32 03 (32 21)	382 (378)
Ph_3SbSab (yellow)	249–250	65 73 (65 98)	4 11 (4 29)	2 36 (2 48)	5 62 (5 67)		21 60 (21 58)	536 (564)
Me_3SbSat (yellow orange)	113–115[a]	48 88 (48 76)	4 69 (4 60)	3 74 (3 56)	3 98 (4 06)	8 27 (8 13)	30 67 (30 89)	399 (394)
Ph_3SbSat (yellow orange)	218–220[a]	64 14 (64 15)	4 18 (4 17)	2 67 (2 42)	2 56 (2 76)	5 50 (5 52)	21 15 (20 98)	568 (580)
Ph_3SbBah (orange)	217	67 47 (67 57)	4 75 (4 67)	2 52 (2 32)	5 20 (5 29)		20 20 (20 15)	573 (604)
Ph_3SbAAh (yellow)	195–196	64 01 (64 23)	4 93 (4 83)	2 60 (2 58)	5 83 (5 90)		22 48 (22 46)	544 (542)

[a] With decomposition

Molecular weight determinations show that all complexes are non-dissociating monomers in benzene solution (see Table 1).

Structure

All complexes are strongly coloured, varying from yellow to orange. Electronic spectra have been recorded in benzene solution and band maxima are tabulated in Table 2. As compared with the spectra of the free ligands the electronic spectra of the various complexes R_3SbL display new absorption bands at lower energy fully comparable to the previously reported spectra of R_2SnL complexes[6]. Similarly, comparison of the electronic spectra of H_2Aah and Ph_3SbAah reveals a new band at lower wavelength. The structure and coordination behaviour of H_2Sab, H_2Sat and H_2Bah (H_2L) has been extensively discussed by Barbieri *et al.*[6] who have proposed a five-

TABLE 2

ELECTRONIC ABSORPTION SPECTRA OF R_3SbL COMPLEXES[a] (in benzene)

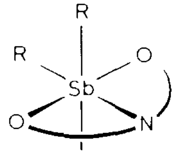
Compound	*λ*	*log ε*	*λ*	*log ε*	*λ*	*log ε*	*λ*	*log ε*	*λ*	*log ε*
Me_3SbSab	307	3 90	~350(sh)	3.70			~370(sh)	3 74	424	4 08
Ph_3SbSab	312	3 94	~323(sh)	3 85	~357(sh)	3 76	~372(sh)	3 81	423	4.11
Me_3SbSat	~320(sh)	3 89	352	3 62			~390(sh)	3 73	425	3 88
Ph_3SbSat	~320(sh)	3 95	367	3 80					428	3 79
Ph_3SbBah			340	3 81					423	4 17
Ph_3SbAah	320	3 69					390	3 97		
H_2Aah	306	4 04								

[a] λ (nm) and ε (M^{-1} cm^2) refer to band maxima and shoulders (sh)

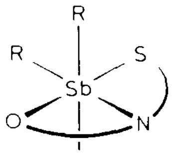
coordinate structure for the R_2SnL complexes*. Based upon their results we suggest that in our R_3SbL complexes L^{2-} coordinates to the R_3Sb^V moiety in the Schiff base form as a planar tridentate ligand.

Examination of the IR spectra of the complexes R_3SbL and the free ligands H_2L reveals band shifts very similar to those observed[6] for the corresponding organotin complexes R_2SnL [*e.g.* ν(C=N) at 1630 vs and 1610 vs cm^{-1} for H_2Sab and Ph_3SbSab, respectively]. Such shifts, observed in a variety of metal complexes of these ligands, have been interpreted in terms of metal nitrogen coordination in a planar dianionic tridentate ligand (*cf.* ref. 6 and references cited therein).

Both the UV and the IR data suggest hexacoordinate structures (Ia) and (Ib) for the complexes R_3SbL.



(I a)



(I b)

PMR spectroscopy reveals that the structure in solution of the complexes R_3SbL, in which R = Me, is non-rigid. The PMR spectrum of Me_3SbSab recorded in CCl_4 solution at 25° displays one sharp singlet for Sb-Me protons at δ 1.15 ppm indicating a rapid exchange of equatorial and axial methyl group positions. In toluene-d_8 at $-65°$ this signal transforms into two signals with 2/1 intensity ratio at δ 1.26 and 1.06 ppm, respectively, as expected for structure (Ia). Me_3SbSat appears to be more stereochemically rigid as already at 25° the PMR spectrum in toluene-d_8 displays

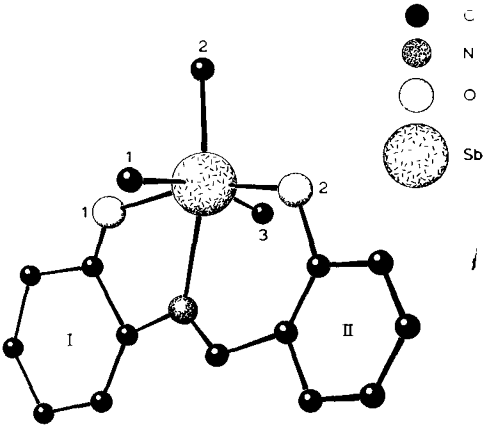


Fig 1 The structure of the Me_3SbSab molecule in the crystalline state

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* Very recently Tanaka *et al*[15] observed the presence of (Sn←N=C–^{1}H) coupling in the PMR spectrum of Me_2SnSab which confirms the tridentate nature of the Sab ligand in this complex

two broad signals (2/1 intensity) at δ 1.44 and 1.05 ppm. At −20° sharp signals are observed at 1.46 and 1.03 ppm in agreement with structure (Ib).

A detailed picture of the coordination geometry of the antimony atom in this type of complex cannot be presented in the absence of an X-ray structure determination. Therefore the molecular structure of Me_3SbSab in the crystalline state has been elucidated. Crystals of Me_3SbSab (from methanol) are monoclinic with $a=10.27$, $b=10.28$, $c=14.50$ Å, $\beta=93.45°$; space group Ic; $d_m=1.63$ g/cm^3, $d_c=1.65$ g/cm^3 for $Z=4$. Intensity data for 1727 independent reflexions were collected on an automatic four-circle diffractometer with Mo-K_α radiation. The molecular structure has been solved based on Patterson and Fourier techniques. R has converged to 0.046.

The structure of the molecule is presented in Fig. 1. The antimony atom, which is hexacoordinate as a result of Sb–N coordinative bonding, appears to possess a distorted octahedral geometry. The two aromatic rings (I) and (II) in the tridentate Sab ligand are slightly twisted from a planar position, the dihedral angle being 11°. Interatomic distances and bond angles are given in Table 3.

TABLE 3

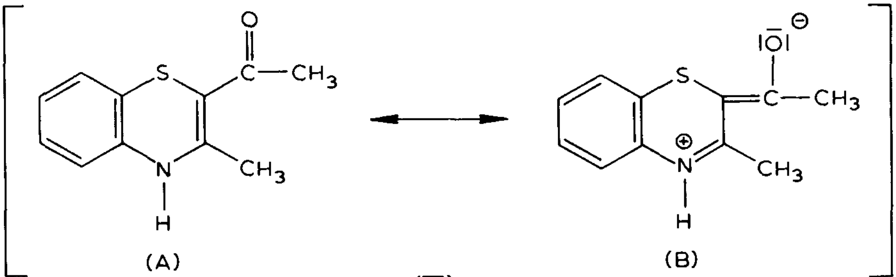
INTERATOMIC DISTANCES AND BOND ANGLES AROUND ANTIMONY FOR Me_3SbSab

Distances (*Å*)		*Bond angles* (°)			
Sb–C(1)	2.10	C(1)–Sb–C(2)	96.8	C(3)–Sb–O(1)	88.0
Sb–C(2)	2.14	C(1)–Sb–C(3)	165.3	C(3)–Sb–O(2)	95.3
Sb–C(3)	2.19	C(1)–Sb–O(1)	82.2	C(3)–Sb–N	80.2
Sb–O(1)	2.06	C(1)–Sb–O(2)	90.2	O(1)–Sb–O(2)	159.8
Sb–O(2)	2.07	C(1)–Sb–N	85.8	O(1)–Sb–N	66.6
Sb–N	2.34	C(2)–Sb–C(3)	95.5	O(2)–Sb–N	94.3
		C(2)–Sb–O(1)	98.7		
		C(2)–Sb–O(2)	100.7		
		C(2)–Sb–N	164.7		

Isolation of 2-acetyl-3-methyl-4H-1,4-benzothiazine from the attempted preparation of R_3SbAat

Upon reaction of R_3SbCl_2 (R = Me, Ph) with Na_2Aat or of $R_3Sb(OMe)_2$ (R = Me, Ph) with H_2Aat the corresponding complex R_3SbAat could not be isolated. Instead a crystalline orange-red coloured product (m.p. 194–195°; electronic absorption spectrum in ethanol solution λ_{max} 264, 433 nm; log ε 4.22 and 3.48, respectively) was obtained which analysed for $C_{11}H_{11}NOS$. The PMR spectrum in acetone-d_6 shows two sharp methyl group signals at δ 2.18 and 2.28 ppm, one broad N-H signal at δ 7.85–8.05 ppm and a multiplet of four aromatic proton signals at δ 6.80–7.00 ppm. The mass spectrum shows a molecular ion at m/e 205. The base peak at m/e 162 originates from the molecular ion by elimination of an acetyl group. The fragment ion observed at m/e 130 results from further loss of a sulfur atom. Based upon the PMR and mass spectroscopic data we conclude the reaction product to be 2-acetyl-3-methyl-4*H*-1,4-benzothiazine (II). Similar orange-red coloured N-substituted 2-benzoyl-4*H*-1,4-benzothiazines have been reported by Friedrich *et al.*[8].

The IR spectrum of (II) displays several strong absorption bands in the region 1600–1500 cm^{-1}, but between 1800 and 1600 cm^{-1} no absorptions are present. The absence of a C=O stretching vibration in the usual region is not surprising, because as a result of resonance the carbonyl stretching vibration is expected to occur at low frequency (*cf.* refs. 8—10).



(II)

The formation of (II) can be rationalised in terms of the previously observed instability of triorganoantimony dimercaptides, $R_3Sb(SR)_2$, which spontaneously decompose with the formation of R_3Sb and RSSR[11,12]. It is assumed that a similar decomposition occurs for R_3SbAat, with the important difference that instead of dimerisation, the Aat fragment undergoes intramolecular cyclisation followed by an allyl rearrangement.

EXPERIMENTAL

General

The ligands 2,2'-(methylidynenitrilo)diphenol (H_2Sab; from salicylaldehyde and *o*-aminophenol)[6], 2-(*o*-hydroxyphenyl)benzothiazoline (H_2Sat; from salicylaldehyde and *o*-aminobenzenethiol)[6], 3-(*o*-hydroxyanilino)crotonophenone (H_2-Bah; from benzoylacetone and *o*-aminophenol)[6], 4-(*o*-hydroxyphenylimino)-2-pentanone (H_2Aah; from acetylacetone and *o*-aminophenol)[13] and 2-acetonyl-2-methylbenzothiazoline (H_2Aat; from acetylacetone and *o*-aminobenzenethiol)[6] were prepared as previously described in the literature. H_2Aah was prepared according to ref. 13, the observed m.p. after recrystallization from ethanol being 197–199° (lit. 186–187°).

Analytical grade reagents were used; solvents were dried on molecular sieves, and all reactions were performed in an atmosphere of dry N_2

Electronic spectra were recorded on benzene solutions, using Beckman DK-2A and Cary 15 spectrometers, equipped with 1 cm optical path cells. The results are shown in Table 2.

Infrared absorption spectra were run on nujol and hexachlorobutadiene mulls, using a Perkin–Elmer 457 spectrometer.

PMR spectra were recorded on a Varian Associates HA-100 NMR spectrometer

The mass spectrum of 2-acetyl-3-methyl-4*H*-1,4-benzothiazine was recorded on a AEI-MS 902 spectrometer with an electron impact energy of 70 eV, at the Laboratory for Analytical Chemistry of the State University of Utrecht.

Molecular weights have been measured on benzene solutions at 37°, with a Mechrolab 301 A vapor pressure osmometer.

Analytical and melting point data are given in Table 1. Analyses were performed by Mr. W J. Buis at the Institute for Organic Chemistry TNO

Preparation of triorganoantimony(V) complexes R_3SbL

Triorganoantimony(V) complexes, Ph_3SbL (L = Sab^{2-}, Sat^{2-}, Bah^{2-} and Aah^{2-}) and Me_3SbL (L = Sab^{2-}) were prepared by addition of a methanolic solution of the sodium salt of the ligand, Na_2L (5 mmoles in 50 ml of methanol; prepared from $H_2L + 2$ NaOMe) to a stirred suspension of an equimolar amount of R_3SbCl_2 in 30 ml of methanol. The volume was such as to avoid precipitation of NaCl. Solid complexes deposited from the reaction mixture, which analysed for compounds R_3-SbL (see Table 1). Yield 63 to 68%.

The attempted preparation of Me_3SbSat by a similar reaction procedure resulted in the deposition of a yellow crystalline solid, m.p. 160–165°, which analysed for the disulfide $(HSat)_2$ (Found: C, 68.42; H, 4.46; N, 6.11; S, 14.09. $C_{26}H_{20}N_2O_2S_2$ calcd.: C, 68.42; H, 4 38; N, 6.14; S, 14.05%.) Mol. wt. found 445, calcd. 456.

Me_3SbSat has been prepared by a 1/1 molar reaction of the free ligand H_2Sat with $Me_3Sb(OMe)_2$ in benzene solution The yellow-coloured benzene solution was evaporated, and recrystallisation of the remaining solid from cyclohexane afforded analytically pure Me_3SbSat. This product appeared to be thermally instable; after a month at room temperature decomposition had taken place

Attempted preparation of complexes R_3SbAat. Isolation of 2-acetyl-3-methyl-4H-1,4-benzothiazine

Attempted preparation of Me_3SbAat H_2Aat (1.65 g, 8 mmoles) in benzene (50 ml) was added dropwise to a stirred solution of $Me_3Sb(OMe)_2$ (1.83 g, 8 mmoles) in benzene (50 ml). Upon evaporation of the yellow benzene solution the colour of the reaction mixture changes to orange-red. Recrystallisation of the reaction residue from methanol results in the isolation of 1.1 g of 2-acetyl-2-methyl-4*H*-1,4-benzothiazine as orange-red needlelike crystals with m.p. 194–195°. Yield 69%. (Found: C, 64.54; H, 5.48; N, 6.71; S, 15.76. $C_{11}H_{11}NOS$ calcd.: C, 64.40; H, 5 36; N, 6.83; S, 15.61%.)

Upon addition of bromine to the evaporated volatiles which had been collected in a cold trap, a colourless solid deposited which was identified as Me_3SbBr_2.

Similarly, reaction of R_3SbCl_2 (R = Me, Ph) with the sodium salt of the ligand, Na_2Aat, in anhydrous methanol results in the formation of 2-acetyl-3-methyl-4*H*-1,4-benzothiazine.

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