Journal of Organometallic Chemistry, 348 (1988) 185–191
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis of tris(2,4,6-trimethylphenyl)hydroxoantimony carboxylates. Crystal structure of tris(2,4,6-trimethylphenyl)hydroxoantimony 1-adamantylcarboxylate

T. Westhoff, F. Huber and H. Preut

Fachbereich Chemie, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50 (Federal Republic of Germany)

(Received December 31st, 1987)

Abstract

The tris(2,4,6-trimethylphenyl)hydroxoantimony carboxylates $Mes_3Sb(OH)OOCR \cdot nH_2O$ ($n = 1$, $Mes = 2,4,6\text{-}Me_3C_6H_2$, $R = H$, CH_2F; $n = 0$, $R = CH_3$, $CHCl_2$, CF_3, $C_{10}H_{15}$ = 1-adamantyl) have been obtained by neutralization of tris(2,4,6-trimethylphenyl)antimony dihydroxide with the appropriate carboxylic acid. The crystal structure of tris(2,4,6-trimethylphenyl)hydroxoantimony 1-adamantylcarboxylate has been determined by single crystal X-ray diffraction. Antimony is in a slightly distorted trigonal bipyramidal environment, with the unidentate carboxylate group and OH being in apical positions. The Sb–O(H) bond length, 202.6(3) pm, is appreciably shorter than the usual value for Sb–O(carboxylate) bond, viz. 212.1(3) pm in tris(2,4,6-trimethylphenyl)-hydroxoantimony 1-adamantyl-carboxylate. From IR data analogous molecular structures are inferred for the other compounds $Mes_3Sb(OH)O_2CR \cdot nH_2O$. The water in $Mes_3Sb(OH)O_2CR \cdot H_2O$ ($R = H$, CH_2F) is assumed to be water of crystallization.

Introduction

The reactions of R_3SbO or $R_3Sb(OH)_2$ with sulfonic acids ($R'SO_3H$) give, depending on the nature of R and R′, various types of compounds: $R_3Sb(O_3SR')_2$ [1], $(R_3SbO_3SR')_2O$ [2,3], $(R'SO_3SbR_3O)_2SbR_3$ [4], $R_3Sb(OH)O_3SR'$ [3] and even, in the case of R = 2,4,6-trimethylphenyl (Mes) and $R' = CF_3$ or C_6H_5, hydrogen-bonded adducts of the type R_3SbOHX [5]. The formation of these adducts is due to some extent to the bulk of the mesityl groups and the low nucleophilicity of the sulfonate groups [5]. The factors which determine the formation of the other types of compounds are not well understood. In order to further examine the influence of the ligands we have begun a study of the reactions of R_3SbO and $R_3Sb(OH)_2$ with

0022-328X/88/$03.50

carboxylic acids (RCOOH), and describe here the first synthesis of tris(2,4,6-trimethylphenyl)hydroxoantimony carboxylates and their structural characterization.

Experimental

$Mes_3Sb(OH)_2$ was prepared as described in ref. 5. The carboxylic acids and solvents were commercial products (EGA, Fluka). The carboxylates were synthesized by stirring a mixture of 1 mmol of $Mes_3Sb(OH)_2$ and 1 mmol of the appropriate carboxylic acid in 20 ml of acetone at room temperature. After a few hours stirring, the volume of the solvent was reduced in vacuo to 5–10 ml and petroleum ether (b.p. 50–60 ° C) was added. The crystalline product was filtered off, washed with 5 ml of petroleum ether, and dried in vacuo. For the preparation of **6** chloroform was used as solvent. In the preparation of **1** the solvent was evaporated off in vacuo after 14 h and the residue recrystallized from $CHCl_3$/petroleum ether mixture. Analytical data are summarized in Table 1.

IR spectra (KBr disc) were recorded with a Perkin–Elmer grating spectrometer PE 580B, and ^1H NMR spectra in $CDCl_3$ with a Perkin–Elmer 90 MHz spectrometer R32 at 37 ° C. Molecular weights were determined osmometrically.

Single crystals of $Mes_3Sb(OH)OOCC_{10}H_{15}$ (**6**) were obtained by crystallization from methanol/water. A crystal of dimensions 0.13 × 0.26 × 0.61 mm was mounted on a glass fibre.

Crystal data: $C_{38}H_{49}O_3Sb$, $M = 675.56$, monoclinic, space group $P2_1/n$, a 1518.3(18), b 1240.2(9), c 1875.4(20) pm, β 108.9(7) °, V 3340.4 × 10^6 pm^3, $Z = 4$, D_x 1.343 Mg m^{-3}, $F(000) = 1408$, $\mu(Mo\text{-}K_\alpha)$ 0.86 mm^{-1}, graphite monochromated Mo-K_α radiation, λ 71.07 pm, temperature 291(1) K, lattice parameters from least-squares fit with 25 reflexions up to 2θ 27.6 °, CAD4 diffractometer, $\omega/2\theta$ scans, scan speed 2.5–10.0 ° min^{-1}, six standard reflexions recorded every 2.5 h showed up to 18% intensity loss; 12575 reflexions measured in the range $1.5 \leq \theta \leq 25.0$ °, $-18 \leq h \leq 18$, $0 \leq k \leq 14$, $-22 \leq l \leq 22$; after averaging 6166 unique reflex-

Table 1

Analytical data for tris(2,4,6-trimethylphenyl)hydroxoantimony carboxylates

Compound		Yield (%)	M.p. (° C)	Microanalytical (Found/calcd.) (%))		Molecular weight, (in $CHCl_3$ (calcd.))
				C	H	
$Mes_3Sb(OH)OOCH \cdot H_2O$	**1**	78	161	57.3	6.1	555
$C_{28}H_{37}O_4Sb$				(60.12)	(6.67)	(559)
$Mes_3Sb(OH)OOCCH_3$	**2**	61	191	62.9	6.4	534
$C_{29}H_{37}O_3Sb$				(62.72)	(6.72)	(555)
$Mes_3Sb(OH)OOCCHCl_2$	**3**	57	182	55.6	5.6	604
$C_{29}H_{35}O_3Cl_2Sb$				(55.80)	(5.65)	(624)
$Mes_3Sb(OH)OOCCH_2F \cdot H_2O$	**4**	67	170	58.1	6.2	586
$C_{29}H_{38}O_4FSb$				(58.90)	(6.48)	(591)
$Mes_3Sb(OH)OOCCF_3$	**5**	38	101	56.1	5.3	617
$C_{29}H_{49}O_3F_3Sb$				(57.16)	(5.62)	(609)
$Mes_3Sb(OH)OOCC_{10}H_{15}$	**6**	62	218	67.3	7.2	653
$C_{38}H_{49}O_3Sb$				(67.56)	(7.31)	(675)

ions, 3812 with $I \geq 1.96\sigma(I)$. The following corrections were applied: Lorentz-polarization correction and absorption correction by ψ-scans; max/min transmission 1.00/0.91; systematic absences $(h0l)$ $h+1=2n+1$, $(0k0)$ $k=2n+1$. Space group: $P2_1/n$ (No. 14). The structure was solved by direct methods, ΔF synthesis and full matrix least squares on F with 3812 observed $I \geq 1.96\sigma(I)F_0$ values and refined 380 parameters; all non-H atoms were refined anisotropically and a common isotropic temperature factor was used for all H-atoms, which were placed in calculated positions (C–H 95 pm); weighting scheme $w^{-1} = 4F_o^2/(\sigma^2(F_o^2) + (0.07F_o^2)^2)$; $S = 1.01$, R(unweighted) = 0.044, R(weighted) = 0.060, max. $\Delta/\sigma = 0.02$, largest peak in final F map = $\pm 1.3(2) \times 10^{-6}$ e pm^{-3}; complex neutral-atom scattering factors from ref. 6; Programs: Enraf–Nonius Structure Determination Package [7], MULTAN 80 [8], PARST [9], SHELXTL PLUS [10].

Results and discussion

The tris(2,4,6-trimethylphenyl)hydroxoantimony carboxylates $Mes_3Sb(OH)OOCR'$ (**1** to **6**) listed in Table 1 were readily obtained by neutralization of $Mes_3Sb(OH)_2$ with the appropriate carboxylic acid R'COOH in acetone according to eq. 1:

$$Mes_3Sb(OH)_2 + HO_2CR' \rightarrow H_2O + Mes_3Sb(OH)OOCR' \qquad (1)$$

All these new compounds are colourless; they are soluble in methanol and chloroform, but insoluble in nonpolar solvents. Molecular weight measurements indicate that they are monomeric in chloroform (see Table 1).

The structure of a molecule of **6** as determined by X-ray diffraction is shown in Fig. 1 along with the atom numbering scheme. Final fractional atomic coordinates

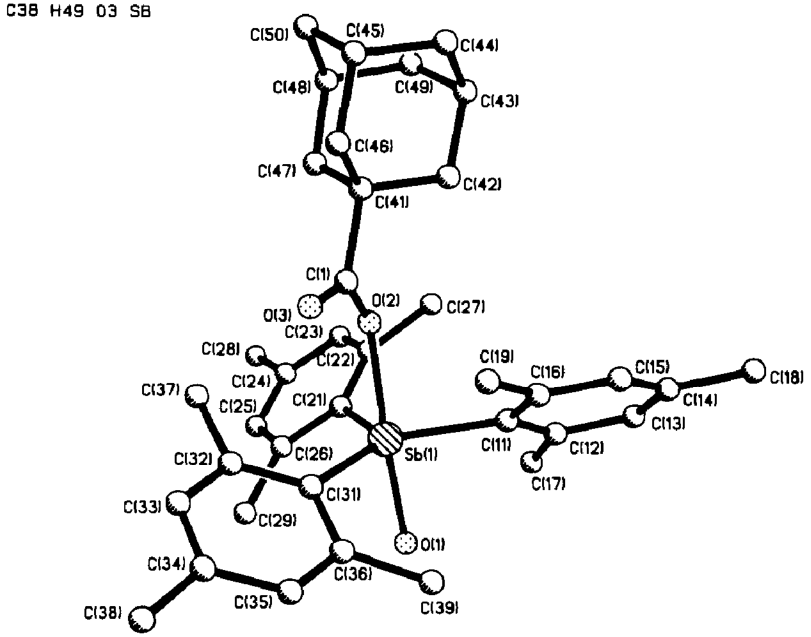

Fig. 1. Molecular structure of **6**.

Table 2

Atomic coordinates and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for non-hydrogen atoms in tris(2,4,6-trimethylphenyl)hydroxoantimony 1-adamantylcarboxylate ($U_{eq} = 1/(6\pi^2)\Sigma_i\Sigma_j\beta_{ij}a_ia_j$)

	x	y	z	U_{eq}
Sb(1)	0.02764(2)	0.15027(3)	0.22701(2)	44
O(1)	0.0624(3)	−0.0080(3)	0.2383(2)	62
O(2)	−0.0114(2)	0.3144(3)	0.2058(2)	52
O(3)	0.0221(5)	0.4109(5)	0.3124(3)	126
C(1)	−0.0046(5)	0.4002(7)	0.2412(4)	87
C(11)	0.1395(3)	0.1859(5)	0.1845(3)	51
C(12)	0.1486(4)	0.1267(5)	0.1246(4)	55
C(13)	0.2193(4)	0.1570(5)	0.0947(4)	68
C(14)	0.2811(4)	0.2406(4)	0.1264(4)	69
C(15)	0.2714(4)	0.2929(5)	0.1859(4)	67
C(16)	0.2031(4)	0.2688(5)	0.2176(3)	56
C(17)	0.0883(4)	0.0324(5)	0.0874(4)	80
C(18)	0.3544(5)	0.2705(7)	0.0926(5)	104
C(19)	0.2037(5)	0.3334(5)	0.2860(5)	82
C(21)	−0.1074(3)	0.1115(4)	0.1487(3)	47
C(22)	−0.1379(3)	0.1545(4)	0.0779(4)	51
C(23)	−0.2256(4)	0.1253(5)	0.0286(4)	73
C(24)	−0.2833(4)	0.0575(5)	0.0506(4)	80
C(25)	−0.2519(4)	0.0169(5)	0.1227(4)	76
C(26)	−0.1640(3)	0.0411(5)	0.1736(4)	57
C(27)	−0.0834(4)	0.2311(5)	0.0451(4)	60
C(28)	−0.3806(5)	0.0295(8)	−0.0012(5)	122
C(29)	−0.1377(4)	−0.0141(5)	0.2494(4)	75
C(31)	0.0498(3)	0.1611(4)	0.3449(3)	51
C(32)	−0.0190(4)	0.1974(5)	0.3729(3)	62
C(33)	−0.0024(5)	0.1934(8)	0.4486(4)	92
C(34)	0.0808(5)	0.1591(8)	0.4999(5)	110
C(35)	0.1492(5)	0.1235(6)	0.4698(4)	80
C(36)	0.1362(4)	0.1237(5)	0.3957(4)	60
C(37)	−0.1136(4)	0.2409(6)	0.3220(4)	82
C(38)	0.1003(8)	0.155(1)	0.5835(6)	177
C(39)	0.2177(4)	0.0840(5)	0.3707(4)	67
C(41)	−0.0329(4)	0.5070(5)	0.1922(4)	77
C(42)	0.0198(5)	0.5091(5)	0.1345(4)	76
C(43)	−0.0027(5)	0.6101(6)	0.0887(5)	91
C(44)	0.0197(6)	0.7076(8)	0.1391(6)	130
C(45)	−0.0349(6)	0.7045(6)	0.1959(5)	111
C(46)	−0.0102(6)	0.6032(7)	0.2421(5)	100
C(47)	−0.1313(6)	0.5022(7)	0.1505(6)	113
C(48)	−0.1600(5)	0.6016(8)	0.1050(6)	125
C(49)	−0.1072(7)	0.6132(9)	0.0483(6)	138
C(50)	−0.1361(6)	0.7046(7)	0.1523(7)	141

for non-hydrogen atoms and equivalent isotropic values U_{eq} of the anisotropic temperature factors β_{ij} are given in Table 2, and selected bond lengths and bond angles in Table 3. Tables of hydrogen atom coordinates, structure factors and a full list of bond lengths and angles are available from the authors.

The central atom Sb is in a slightly distorted trigonal bipyramidal environment, with the atoms C(11), C(21) and C(31) forming the equatorial plane and O(1)

Table 3

Bond lengths (pm) and angles (°) in tris(2,4,6-trimethylphenyl)hydroxoantimony 1-adamantylcarboxylate with e.s.d.'s in parentheses [a]

Sb(1)–O(1)	202.6(3)
Sb(1)–O(2)	212.1(3)
Sb(1)–O(3)	362.0(6)
Sb(1)–C(11)	214.4(4)
Sb(1)–C(21)	215.4(4)
Sb(1)–C(31)	213.1(6)
O(1)–Sb(1)–O(2)	175.5(2)
C(11)–Sb(1)–C(21)	119.1(2)
C(11)–Sb(1)–C(31)	119.7(2)
C(21)–Sb(1)–C(31)	121.1(2)
O(1)–Sb(1)–C(11)	91.6(2)
O(1)–Sb(1)–C(21)	90.8(2)
O(1)–Sb(1)–C(31)	90.3(2)
O(2)–Sb(1)–C(11)	86.6(2)
O(2)–Sb(1)–C(21)	86.6(2)
O(2)–Sb(1)–C(31)	94.2(2)

[a] Numbering of atoms as in Fig. 1.

(hydroxyl group) and O(2) (the unidentately bonding oxygen of the carboxylate group) in apical positions. The C–Sb(1)–C angles are ca. 120°. The O(1)–Sb(1)–O(2) angle (175.5(2)°) is smaller than the ideal value of 180° (Table 3).

The Sb(1)–OH bond distance (202.6(3) pm) is in the range for typical covalent Sb–O single bonds, such as those in Ph_4SbOH (204.8 pm) [11] and $Ph_3Sb(OCH_3)_2$ [12] (203.9(8) and 202.7(8) pm, respectively). This is consistent with the fact that there is no evidence for intermolecular hydrogen bonding between carboxyl oxygen and the hydroxyl group, which would be expected to result in a shorter bond length. The absence of a hydrogen bond was also indicated by the IR data (see below).

The Sb(1)–O(2) distance of 212.1(3) pm agrees well with values for triorganoantimony dicarboxylates, e.g. for $Me_3Sb(OOCC_4H_3S)_2$ (213.6(6) and 212.4(6) pm) [13] and $Me_3Sb(OOCCH_2NHCOPh)_2$ (213.0(12) and 210.5(13) pm) [14]. Any additional weak interaction between the second O of the carboxylate group and Sb, which has been observed in the triorganoantimony dicarboxylates mentioned above, cannot be of significance since the distance of 362.0(6) pm is only a little smaller than the sum of the Van der Waals radii for Sb and O (372 pm) [15]. In the triorganoantimony dicarboxylates the corresponding distances are 308.0(7) (mean) and 300.6(14) pm (mean), respectively [13,14]. The bond distances and angles within the aromatic groups bonded to antimony are in the usual range, and are not listed in detail.

The IR data for the carboxylate and hydroxyl groups and OH are listed in Table 4 together with ^1H NMR data. The NMR spectra are consistent with data expected from the formula of the products **1** to **6**, and need not be discussed. The IR data are of interest for two reasons: (i) for comparison of the structure of **6** as determined by X-ray diffraction with those of **1** to **5**; and (ii) only a few spectra of triorganohydroxoantimony compounds have been reported previously. Table 4 shows that the $\Delta\nu$ values [16] are greater than 300 cm^{-1}, and so for **1** to **5** the previously unidentate carboxylate groups can be inferred as in the case of **6**. A marked difference between the structure of **6** and the structures of **1** to **5** involves the role of

Table 4

Characteristic IR vibrations, and ^1H NMR chemical shifts (in $CDCl_3$) for tris(2,4,6-trimethylphenyl)hydroxoantimony carboxylates

Compound	vs very strong; s strong; b broad IR (cm^{-1})					s singlet; d duplet; br broad ^1H NMR (ppm)					
	$\nu_{as}(CO)$	$\nu_s(COO)$	$\Delta\nu$	$\nu(OH)$	$\nu(SbO(H))$	4-CH_3	2-CH_3	C_6H_2	OH	Carboxylate	H_2O
1	1618vs,b	1300vs,b	318	3380s,b	[a]	2.31s	2.53s	6.95s	2.24s	8.00br CH	2.01br
2	1612vs,b	1311s	301	3400s,vb	544m	2.24s	2.49s	6.86s	3.26br	2.12s CH_3	–
3	1655vs,b	1330vs,b	325	3490vs,b	580s	2.31s	2.54s	7.00s	4.81br	5.58s $CHCl_2$	–
4	1630vs,vb	1315vs	315	3640m[a] 3480s,b	545m	2.25s	2.44s	6.87s	2.71s	4.16br CH_2F 4.69br CH_2F	2.10s
5	1710vs,b	1390vs,b	320	3400s,b	550s	2.29s	2.48s	7.02s	1.49s	–	–
6	1658vs,b	1270vs,b	390	3650m	517s	2.30s	2.57s	6.92s	3.42s	1.60d $C_{10}H_{15}$ 1.82br $C_{10}H_{15}$	–

[a] See text.

the hydroxyl group. The breadth of the ν(OH) bonds and its shift to lower wave numbers (3380 to 3490 cm^{-1}) in the spectra of the latter compounds compared with that (3650 cm^{-1}) for **6** indicates the presence of hydrogen bonds. (The rather sharp absorption in the spectrum of **4** at 3640 cm^{-1} cannot be unequivocally assigned.) The presence of hydrogen bonds has been ruled out for **6** (see above), and this is in agreement with the IR data. Probably the bulk of the mesityl groups together with that of the adamantyl group prevents the formation of a hydrogen bond between OH and the second oxygen of the carboxylate group of a neighbouring molecule. The bulk of the groups R on Sb is apparently not sufficient to prevent the formation of hydrogen bonds in triorganohydroxoantimony carboxylates. This is also presumably the case of other triorganohydroxoantimony compounds, since in (cyclo-$C_6H_{11})_3Sb(OH)X$, with $X = NO_3$ and CH_3COO [17], the presence of hydrogen bonds was inferred from IR data. Further proof for the different behaviour of the hydroxyl group in **1** to **5** and in **6** comes from a comparison of the ν(SbO) values (Table 4). The value is lowest for **6** (517 cm^{-1}), and higher in **2** to **5** (safe assignment of ν(SbO) for **1** was not possible owing to the presence of various other absorptions and possibly overlap in the appropriate region). This shift must be associated with an increase in the bond order of SbO as a consequence of the formation of intermolecular hydrogen bonds. In conclusion, we conclude that compounds **1** to **5** have a trigonal bipyramidal molecular structure analogous to **6**, but that in contrast to **6**, **1** to **5** form one-dimensional chains via intermolecular hydrogen bonds.

Acknowledgement

Financial assistance by Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 R. Rüther, F. Huber and H. Preut, Z. Anorg. Allg. Chem., 539 (1986) 110.
2 H. Preut, R. Rüther and F. Huber, Acta Cryst. C, 42 (1986) 1154.
3 R. Rüther, F. Huber and H. Preut, J. Organomet. Chem., 342 (1988) 185.
4 R. Rüther, F. Huber and H. Preut, Angew. Chem., 99 (1987) 948.
5 F. Huber, T. Westhoff and H. Preut, J. Organomet. Chem., 323 (1987) 173.
6 International Tables for X-ray Crystallography Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press, 1974 (Present distributor D. Reidel, Dordrecht).
7 B.A. Frenz, Enraf–Nonius Structure Determination Package, 4th ed. Version 18, 1981.
8 P. Main, S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.P. Declerq and M.M. Woolfson, A. System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, Univ. of York, England and Louvain, Belgium, 1980.
9 M. Nardelli, PARST. A System of Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis. Univ. of Parma, Italy, 1982.
10 G.M. Sheldrick, SHELXTL PLUS (Release 2) for Nicolet R3m/V Crystallographic Systems for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Univ. of Göttingen, FRG, 1987.
11 A.L. Beauchamp, M.J. Bennett and F.A. Cotton, J. Am. Chem. Soc., 91 (1969) 297.
12 K.-W. Shen, W.E. McEwen, S.J. La Placa, W.C. Hamilton and A.P. Wolf, J. Am. Chem. Soc., 90 (1968) 1718.
13 H. Preut, M. Domagala and F. Huber, Acta Cryst. C, 43 (1987) 416.
14 F. Huber, T. Westhoff and H. Preut, unpublished results.
15 A. Bondi, J. Phys. Chem., 68 (1964) 441.
16 G.B. Deacon and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227.
17 Y. Kawasaki, Y. Yamamoto and M. Wada, Bull. Chem. Soc. Jpn., 56 (1983) 145.