TRIS(2,4,6-TRIMETHYLPHENYL)ANTIMONY DIHYDROXIDE; SYNTHESIS AND REACTION WITH SULFONIC ACIDS RSO_3H ($R = C_6H_5$, CF_3). CRYSTAL STRUCTURE OF $[2,4,6-(CH_3)_3C_6H_2]_3SbO \cdot HO_3SC_6H_5$

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Summary

Tris(2,4,6-trimethylphenyl)antimony dihydroxide, $Mes_3Sb(OH)_2$, which was prepared by oxidation of Mes_3Sb with H_2O_2, has been shown to react with RSO_3H ($R = C_6H_5$, CF_3) to give the adducts $Mes_3SbO \cdot HO_3SR$, the first examples of solid hydrogen-bonded adducts of a triorganoantimony oxide and an acid. The crystal structure of $Mes_3SbO \cdot HO_3SC_6H_5$ has been determined. The three C(mesityl) atoms and the O atom form a distorted tetrahedron around Sb, the distortion by the bulky mesityl groups being reflected in the C–Sb–C angles (mean: 114.7(3)°) and the C–Sb–O angles: (mean: 103.5(2)°). $C_6H_5SO_3H$ is linked via a short hydrogen bond to O on Sb, with $O(1) \cdots O(2) = 256(1)$ pm. The bond length $Sb–O(1)$ 189.4(5) pm represents the shortest Sb–O distance ever reported.

Introduction

Ph_3MO (M = P, As; Ph = C_6H_5) was found to form adducts such as $Ph_3PO \cdot HF$ [1], $Ph_3PO \cdot HCl$ [2], $Ph_3AsO \cdot HCl$ [3], or $2Ph_3PO \cdot (COOH)_2$ [4], in which HX is bonded via a short hydrogen bond, but also adducts, such as $2Ph_3PO \cdot H_2O_2$ [5] having a normal length hydrogen bond. Analogous hydrogen-bonded Sb and Bi compounds were unknown, and R_3SbO and R_3BiO were reported to react with HX apparently to give compounds of the types $R_3M(OH)X$ or R_3MX_2 or the condensation products $(R_3MX)_2O$ [6,7]. Recent studies of reactions of R_3SbO with sulfonic acids (HX = $R'SO_3H$) showed that the character of the organic group R at Sb and of R' largely determines the type of product formed. These products again may have different structural features, such as the linear [8] or bent Sb–O–Sb bridges [9] in distiboxanes. To clarify the influence of R on the behaviour of R_3SbO, especially the relevance of sterical hindrance, we attempted to make tris(2,4,6-trimethylphenyl)antimony oxide with the intention of investigating its reactions with $C_6H_5SO_3H$ and CF_3SO_3H. During the studies we obtained the first examples of hydrogen-bonded adducts of the type $R_3SbO \cdot HX$.

Experimental

Tris(2,4,6-trimethylphenyl)antimony, Mes$_3$Sb, was prepared in 73% yield from MesMgBr and SbCl$_3$ in THF [10]. Other reagents were used as supplied (Fluka), solvents were purified and dried by standard methods.

IR spectra were recorded with a Perkin–Elmer PE 580B spectrophotometer fitted with KBr windows. C and H were determined microanalytically, Sb was estimated iodometrically [11] after digestion with concentrated H$_2$SO$_4$ and (NH$_4$)$_2$S$_2$O$_8$ followed by reduction of Sb^V [12].

Tris(2,4,6-trimethylphenyl)antimony dihydroxide

A mixture of 1.07 g H$_2$O$_2$ solution (35%, 11 mmol H$_2$O$_2$) and 5 ml acetone was added slowly to a solution of 2.39 g (5 mmol) Mes$_3$Sb in 80 ml acetone cooled in ice, the temperature being kept at 5°C. The mixture was then stirred for 1 h at room temperature, and the solvent volume subsequently reduced in vacuo by about half. Yield 2.03 g (79%). White microcrystalline powder, m.p. 202°C (DTA). Analysis Found: C, 62.7; H, 6.2; calc: C, 63.18; H, 6.87%. Molecular weight: 509 (513) in CHCl$_3$.

IR (cm^{-1}; KBr(disc): 3650(m), 3010(w), 2960(w), 2923(m,b), 2860(sh), 1600(m), 1555(w,b), 1455(m,vb), 1400(w), 1382(w), 1290(m), 1262(vw), 1242(vw), 1030(m,b), 925(w), 845vs,b), 705(m), 585(m), 550(sh), 538(sh), 520(s), 492(m), 360(w,b), 345(w).

^{1}H-NMR (ppm; in CDCl$_3$, at 37°C): 2.63 (s; 4-CH_3), 2.91 (s; 2-CH_3), 7.36 (s; Me$_3$C$_6$$H_2$).

Tris(2,4,6-trimethylphenyl)antimony oxide-phenylsulfonic acid (1 / 1)

A solution of 0.34 g (2 mmol) C$_6$H$_5$SO$_3$H in 5 ml acetone .was added to a suspension of 1.03 g (2 mmol) Mes$_3$Sb(OH)$_2$ in 30 ml acetone. The yellow solution was stirred for 2 h at room temperature and then concentrated to 15 ml. The whitish crystalline product was filtered off, washed with 5 ml petroleum ether (b.p. 50–60°C), was dried in vacuo. Yield 0.53 g (41%), m.p. 247°C. Analysis Found: C, 60.60; H, 6.10; Sb, 18.26. calc: C, 60.65; H, 6.01; Sb, 18.63%.

IR (cm^{-1}; Nujol mull between CsBr plates): 2970(vs,vb), 1600(w), 1560(w), 1295(m), 1235(vs,b), 1175(vs,b), 1125(s), 1075(w), 1035(s), 1020(s), 1000(m), 925(w), 870(w), 855(m), 765(s), 730(s), 700(m), 690(m), 615(vs), 590(w), 570(m), 550(m).

^{1}H NMR (ppm; in CDCl$_3$, at 37°C): 2.31 (s; 4-CH_3), 2.42 (s; 2-CH_3), 6.99 (s; Me$_3$C$_6$$H_2$), 7.16–7.31 (m; 3- and 4-H in C$_6$H$_5$SO$_3$), 7.44–7.69 (m; 2-H in C$_6$H$_5$SO$_3$).

An analogous reaction of 0.65 g (1.26 mmol) Mes$_3$Sb(OH)$_2$ and 0.43 g (2.52 mmol) C$_6$H$_5$SO$_3$H in the presence of 2,2-dimethoxypropane gave the same product. Yield 0.24 g (29%), m.p. 246°C.

Tris(2,4,6-trimethylphenyl)antimony oxide-trifluoromethylsulfonic acid (1 / 1)

CF$_3$SO$_3$H (0.30 g; 2 mmol) was added to a suspension of 1.03 g (2 mmol) Mes$_3$Sb(OH)$_2$ in 30 ml acetone. After 0.5 h stirring at room temperature the solution was concentrated to 15 ml and petroleum ether was added. Colourless crystals separated on standing overnight, and were isolated as described above. Yield 0.47 g (36%), m.p. 230°C (decomp.; DTA). Analysis Found: C, 52.3; H, 5.4; Sb, 18.75. calc: C, 52.11; H, 5.31; Sb, 18.86%.

IR (cm^{-1}; Nujol mull between CsBr plates): 3100(s,vb), 1599(m), 1563(m), 1450(m,b,), 1405(w), 1390(w), 1295/1290(vs,b), 1240(vs,b), 1222(s), 1170(sh), 1160(vs,b), 1029(vs), 930(w), 865(m), 850(vs), 757(m), 700(w), 675(s), 640(vs), 588(w), 571(w), 560(vw), 545(m), 520(s), 500(w), 350(s,b), 315(w), 240(m).

^{1}H NMR (ppm; in CDCl$_3$, at 37°C): 2.30 (s, 4-CH_3), 2.35 (s, 2-CH_3), 7.02 (s; Me$_3$C$_6$$H_2$).

Mes$_3$SbO · HO$_3$SC$_6$H$_5$ was crystallized from CHCl$_3$ by addition of petroleum ether (b.p. 50–60°C) to give suitable single crystals. Crystal data: C$_{33}$H$_{39}$O$_4$SSb, M = 653.49, orthorhombic, space group *Pbca*, *a* 1688.6(8), *b* 1691.8(9), *c* 2135.2(8) pm, V 6099.8 × 10^6 pm^3, Z = 8, D_c = 1.423 Mg m^{-3}, F(000) = 2688, μ(Ag-K_α) 0.53 mm^{-1}, graphite-monochromated Ag-K_α radiation λ 56.08 pm, crystal size 0.32 × 0.32 × 0.18 mm, temperature 292(1) K, lattice parameters from least-squares fit with 25 reflexions up to 2θ = 30.8°, CAD 4 diffractometer, $\omega/2\theta$ scans, scan speed 1.8–5° min^{-1}, three standard reflexions recorded every 2.5 h, only random deviations; 7426 reflexions measured in the range $1 \le \theta \le 21°$, $0 \le h \le 21$, $0 \le k \le 21$, $0 \le l \le 27$; after averaging 7303 unique reflexions, 2540 with $I > 3\sigma(I)$. The following corrections were applied: Lorentz polarization correction and absorption correction via ψ-scans; max./min. transmission, 1.00/0.95; systematic absences: (0kl) k = 2n + 1, ($h0l$) l = 2n + 1, (hk0) h = 2n + 1. Space group: *Pbca* (No. 61). The structure was solved via Patterson synthesis, ΔF syntheses, and full matrix least squares on F with 2540 observed $I > 3\sigma(I)F_o$ values and 353 refined parameters; all non-H atoms were refined anisotropically and a common isotropic temperature factor was refined for all H-atoms, which were placed in calculated positions (C–H = 95 pm); weighting scheme $w^{-1} = [\sigma^2(I) + (0.06 \cdot F_o^2)^2]^{1/2}$, S = 1.24, R (unweighted) = 0.036, R (weighted) 0.050, max. Δ/σ = 0.03, largest peak in final F map = ±0.6(2) 10^{-6} e pm^{-3}; complex neutral-atom scattering factors from ref. 13; Programs: Enraf–Nonius Structure Determination Package [14], ORTEP [15], POP1 [16].

Results and discussion

Reaction of triarylantimony with 35% hydrogen peroxide in an appropriate solvent provides the usual route to triarylantimony oxides [17]. Oxidation of tris(2,4,6-trimethylphenyl)antimony Mes$_3$Sb by this method, however, gave not the oxide but the dihydroxo derivative (Mes)$_3$Sb(OH)$_2$. Acetone proved to be an appropriate solvent for the preparation of this new compound. It is stable as long as no H$_2$O$_2$ is present during isolation, otherwise the colour of the solid changes from white to orange during drying or in air, and it becomes viscous. An IR absorption at 520 cm^{-1} ($= \nu_{as}$SbO) indicates the presence of an Sb–O (not an Sb=O) bond, and an absorption at 3650(m) cm^{-1} is assigned to ν(OH). Since no band which would have to be attributed to an Sb–O–Sb group was observed, the formation of a dihydroxide during the oxidation reaction is inferred, which, in view of the position and relative sharpness of the ν(OH) band, is presumably monomeric in the solid state (as found for CHCl$_3$ solutions by molecular weight measurements), having a trigonal-bipyramidal environment at Sb, with the two OH groups in apical positions. Attempts to dehydrate this compound were unsuccessful.

The behaviour of Mes$_3$Sb(OH)$_2$ towards sulphonic acids R′SO$_3$H is distinctly different from that of other triorganoantimony hydroxides, e.g. Me$_3$Sb(OH)$_2$, or oxides, e.g. (Ph$_3$SbO)$_2$, which react to give sulphonates R$_3$Sb(O$_3$SR′)$_2$,

$R_3Sb(OH)O_3SR'$, or $(R_3SbO_3SR')_2O$ [6,8,9]. All attempts to make Mes_3Sb-sulphonates from $Mes_3Sb(OH)_2$ and $R'SO_3H$ ($R' = Me$, CH_2CH_2OH, CF_3, Ph, $4\text{-}CH_3C_6H_4$) were unsuccessful. However, using molar ratios $1:1$ and $1:2$ in these reactions, we obtained adducts with the composition $Mes_3SbO \cdot HO_3SR$ ($R = CF_3$, Ph), the first examples of hydrogen-bonded adducts of the type $R_3SbO \cdot HX$, complementing those involving the lighter Group VB elements (see Introduction).

The new compounds are soluble in $CHCl_3$ and MeOH. The molecular weight of $Mes_3SbO \cdot HO_3SPh$ measured in $CHCl_3$ (677) corresponds to the calculated value (653) for the undissociated compound, whereas the value in methanol (346) indicates dissociation in this solvent. This conclusion is confirmed by conductivity measurements, the values obtained from 8×10^{-3} molar solutions being appreciably higher for methanol (44.20 S cm^2 mol^{-1}) than for $CHCl_3$ (0.20 S cm^2 mol^{-1}). Since conductivities of solutions of $1:1$ electrolytes in methanol are typically in a range 80 to 115 S cm^2 mol^{-1} [18], it can be inferred that $Mes_3SbO \cdot HO_3SPh$ also behaves like a $1:1$ electrolyte but is not fully dissociated. The absorptions in the IR spectra of $Mes_3SbO \cdot HO_3SPh$ ($Mes_3SbO \cdot HO_3SCF_3$) at 1235 (1240) and 1175 (1160) cm^{-1} are assigned to $\nu_{as}(SO_3)$ and the absorption at 1035 (1029) cm^{-1} to $\nu_s(SO_3)$ [6]. The splitting of the $\nu_{as}(SO_3)$ band is an indication of a rather strong ionic bond character [6], which can be related to a partial transfer of H from the sulphonic acid to Sb-bonded oxygen by formation of a strong hydrogen bridge. The hydrogen bonding is also evident from a broad and very strong band at 2970 (3100) cm^{-1}, which falls within the range of 1800–3100 cm^{-1} which is associated with short (250 to 270 pm) hydrogen bridges [19]. The strong band at 690 cm^{-1}, which upon deuteration is shifted by 5 cm^{-1} to lower wave numbers, is assigned to $\nu(SbO)$. These structural conclusions were confirmed by the results of an X-ray structure
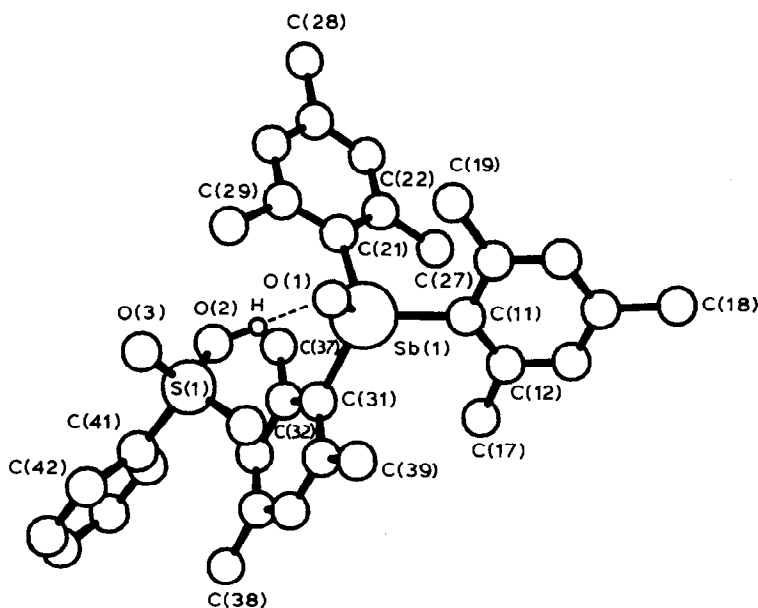

Fig. 1. General view of the molecule, showing atom numbering.

determination on $Mes_3SbO \cdot HO_3SC_6H_5$. The structure of this compound with the numbering scheme is shown in Fig. 1. Atomic parameters and equivalent isotropic values B_{eq} of the anisotropic temperature factors β_{ij} are given in Table 1 and selected bond lengths and bond angles in Table 2. The atoms directly bound to Sb form a distorted tetrahedron. Probably because of repulsion between the bulky mesityl groups, the angles C–Sb–C are all wider and the O–Sb–C angles smaller than the tetrahedral angle of 109.47° (Table 2).

The Sb(1)–O(1) distance of 189.4(5) pm, the shortest Sb–O distance reported to date, indicates appreciable double-bond character. The distance $O(1) \cdots O(2)$ of

TABLE 1

ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

	x	y	z	B_{eq} [a]
Sb(1)	0.17615(3)	0.05075(3)	0.14178(2)	2.670(8)
S(1)	0.0457(1)	0.3102(1)	0.0822(1)	4.34(5)
O(1)	0.0982(3)	0.1262(3)	0.1639(2)	3.6(1)
O(2)	0.1064(4)	0.2646(3)	0.1157(3)	5.4(2)
O(3)	0.0181(5)	0.3784(4)	0.1157(3)	7.1(2)
O(4)	−0.0170(4)	0.2599(4)	0.0587(4)	6.5(2)
C(11)	0.1095(4)	−0.0550(5)	0.1533(3)	3.1(2)
C(12)	0.1082(5)	−0.1147(5)	0.1085(4)	3.9(2)
C(13)	0.0640(5)	−0.1815(5)	0.1198(5)	4.7(2)
C(14)	0.0237(6)	−0.1911(6)	0.1758(5)	5.4(2)
C(15)	0.0276(5)	−0.1331(5)	0.2206(4)	4.4(2)
C(16)	0.0698(5)	−0.0645(5)	0.2115(3)	3.4(2)
C(17)	0.1559(6)	−0.1128(5)	0.0492(4)	5.4(2)
C(18)	−0.0245(8)	−0.2667(7)	0.1885(7)	9.1(4)
C(19)	0.0707(6)	−0.0034(6)	0.2627(4)	4.8(2)
C(21)	0.2628(4)	0.0592(5)	0.2123(3)	2.9(2)
C(22)	0.3002(5)	−0.0098(5)	0.2341(4)	3.6(2)
C(23)	0.3494(5)	−0.0037(5)	0.2858(4)	3.8(2)
C(24)	0.3625(5)	0.0670(5)	0.3157(4)	4.1(2)
C(25)	0.3303(5)	0.1346(5)	0.2906(4)	3.9(2)
C(26)	0.2799(5)	0.1316(4)	0.2393(4)	3.2(2)
C(27)	0.2927(6)	−0.0875(5)	0.2012(5)	5.9(3)
C(28)	0.4124(6)	0.0701(7)	0.3733(4)	5.5(3)
C(29)	0.2507(6)	0.2086(5)	0.2134(5)	5 7(2)
C(31)	0.2152(4)	0.0829(4)	0.0510(3)	2.8(2)
C(32)	0.2964(5)	0.0958(5)	0.0393(4)	3.9(2)
C(33)	0.3184(5)	0.1205(5)	−0.0194(4)	4.5(2)
C(34)	0.2625(5)	0.1299(5)	−0.0666(4)	3.9(2)
C(35)	0.1843(5)	0.1167(5)	−0.0536(4)	3.7(2)
C(36)	0.1587(4)	0.0933(5)	0.0043(4)	3.2(2)
C(37)	0.3619(6)	0.0858(8)	0.0861(5)	6.4(3)
C(38)	0.2902(7)	0.1542(6)	−0.1311(4)	6.2(3)
C(39)	0.0711(5)	0.0839(6)	0.0159(4)	3.9(2)
C(41)	0.0945(5)	0.3474(5)	0.0153(4)	3.4(2)
C(42)	0.0638(5)	0.4134(6)	−0.0143(4)	4.6(2)
C(43)	0.0991(6)	0.4437(6)	−0.0668(4)	5.5(2)
C(44)	0.1656(6)	0.4070(6)	−0.0903(4)	5.3(2)
C(45)	0.1965(6)	0.3423(6)	−0.0620(5)	5.4(2)
C(46)	0.1622(5)	0.3122(5)	−0.0088(5)	4.8(2)

TABLE 1 (continued)

	x	y	z	B [b]
H(13)	0.061	−0.222	0.089	9.4(5)*
H(15)	0.000	−0.141	0.259	9.4*
H(171)	0.146	−0.159	0.026	9.4*
H(172)	0.141	−0.068	0.025	9.4*
H(173)	0.211	−0.110	0.059	9.4*
H(181)	−0.048	−0.264	0.229	9.4*
H(182)	−0.065	−0.272	0.158	9.4*
H(183)	0.010	−0.311	0.187	9.4*
H(191)	0.102	0.040	0.250	9.4*
H(192)	0.018	0.014	0.271	9.4*
H(193)	0.093	−0.026	0.300	9.4*
H(23)	0.375	−0.050	0.301	9.4*
H(25)	0.343	0.184	0.309	9.4*
H(271)	0.322	−0.126	0.223	9.4*
H(272)	0.239	−0.103	0.200	9.4*
H(273)	0.313	−0.083	0.160	9.4*
H(281)	0.415	0.123	0.388	9.4*
H(282)	0.389	0.038	0.405	9.4*
H(283)	0.464	0.052	0.364	9.4*
H(291)	0.217	0.199	0.179	9.4*
H(292)	0.222	0.236	0.245	9.4*
H(293)	0.295	0.240	0.200	9.4*
H(33)	0.373	0.131	−0.028	9.4*
H(35)	0.146	0.124	−0.086	9.4*
H(371)	0.411	0.098	0.067	9.4*
H(372)	0.353	0.120	0.120	9.4*
H(373)	0.363	0.033	0.100	9.4*
H(381)	0.246	0.158	−0.158	9.4*
H(382)	0.316	0.204	−0.129	9.4*
H(383)	0.326	0.116	−0.147	9.4*
H(391)	0.063	0.068	0.058	9.4*
H(392)	0.045	0.133	0.009	9.4*
H(393)	0.050	0.045	−0.012	9.4*
H(42)	0.017	0.438	0.002	9.4*
H(43)	0.078	0.489	−0.087	9.4*
H(44)	0.190	0.427	−0.127	9.4*
H(45)	0.242	0.318	−0.079	9.4*
H(46)	0.185	0.267	0.011	9.4*

[a] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} a_i a_j$. [b] Common isotropic temperature factor.

256(1) pm (in accord with IR data; see above) is in the range expected for rather short O–H $\cdots$ O hydrogen bonds [20], and compares with the value of 255.0(4) pm for $2Ph_3PO \cdot (COOH)_2$ [4].

From a comparison of the S–O bond distances (Table 2) with those in sulphonic acid esters, where bond lengths for the S=O and S–O bonds of about 142.5 pm and 159 pm, respectively, have been found [21,22], it can be concluded (in agreement with the indications from the IR data) that the bonding of the sulphonate group is highly ionic and furthermore the O(3)–S(1)–O(4) angle of 114.0(4)° is comparable with that of 112° in a sulphonate ion [23]. The reason why the adducts $Mes_3SbO \cdot HO_3SR$ are formed instead of sulphonates, e.g. $Me_3Sb(O_3SR)_2$, in the reaction of

TABLE 2

BOND LENGTHS (pm) AND BOND ANGLES (°) WITH e.s.d.'s IN PARENTHESES [a]

Sb(1)–C(11)	212.8(7)	S(1)–O(2)	146.7(7)
Sb(1)–C(21)	210.4(7)	S(1)–O(3)	143.5(7)
Sb(1)–C(31)	211.8(7)	S(1)–O(4)	144.8(7)
Sb(1)–O(1)	189.4(5)	S(1)–C(41)	176.5(8)
C(11)–Sb(1)–C(21)	110.0(3)	O(2)–S(1)–O(3)	113.9(4)
C(11)–Sb(1)–C(31)	119.1(3)	O(2)–S(1)–O(4)	111.8(4)
C(11)–Sb(1)–O(1)	99.8(2)	O(2)–S(1)–C(41)	104.9(4)
C(21)–Sb(1)–C(31)	114.9(3)	O(3)–S(1)–O(4)	114.0(4)
C(21)–Sb(1)–O(1)	105.0(2)	O(3)–S(1)–C(41)	105.5(4)
C(31)–Sb(1)–O(1)	105.7(2)	O(4)–S(1)–C(41)	105.7(4)

The C–C distances and the C–C–C angles in the aromatic groups are in the range 1.36(1) to 1.42(1) Å mean distance: 1.38(1) Å and 117.6(7) to 122.3(7)° (mean angle: 120.0(8)°), and the C–C(methyl) distances and C–C–C(methyl) angles at the 2,3,6-trimethylphenyl groups are in the range 1.49(1) to 1.54(1) Å (mean distance: 1.51(1) Å) and 116.4(8) to 125.4(7)° (mean angle: 120.6(8)°).

[a] Numbering of atoms according to Fig. 1.

$Mes_3Sb(OH)_2$ with sulphonic acids lies to some extent in the bulk of the mesityl groups but primarily in the low nucleophilicity of the sulphonate groups [6]. This suggestion is confirmed by the fact that we recently obtained (i) carboxylates of the type $Mes_3Sb(O_2CR)_2$ and $Mes_3Sb(OH)O_2CR$, the carboxylate and the hydroxo group being appreciably stronger nucleophiles than the sulphonate groups, and (ii) other $Mes_3SbO \cdot HX$ adducts, in which X must be a weak nucleophile, e.g. ClO_4^-.

Acknowledgment

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