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Synthesis and X-Ray Crystal Structures of Hypervalent Hexacoordinate Antimony Compounds without Halogen Ligands

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ABSTRACT: *Hypervalent hexacoordinate antimony-ate complex {***2-Et$_4$N***: $Rf_3Sb^-Et_4N^+$ (Rf: o-$C_6H_4C(CF_3)_2O$-)} was synthesized by the reaction of Rf_2SbCl with lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide followed by countercation exchange. Reaction of* **2-Et$_4$N** *with triethyloxonium tetrafluoroborate gave the O-ethylated adduct (***3***). X-ray crystallographic analysis of* **2-Et$_4$N** *and* **3** *showed distorted octahedral structures of these compounds.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:33–37, 2001

INTRODUCTION

Hexacoordinate organoantimony-ate complexes (12-Sb-6) [1] have been proposed as intermediates in the reactions of 10-Sb-5 compounds with nucleophiles [2–6]. X-ray structures of some stable organoantimony 12-Sb-6 -ate complexes have been reported but they are limited to compounds having halogen substituents [7,8]. To our knowledge, the only reported X-ray mononuclear structure lacking halogen substituents is $Me_6Sb^-Li^+(THF)_4$, which was recently reported by Seppelt [9], although some dinuclear complexes, such as $[Ph_2Sb(C_2O_4)_2]_2$ [10], have been reported [8]. In this article, we report the synthesis and X-ray crystal structures of $Rf_3Sb^-Et_4N^+$ (Rf: *o*-$C_6H_4C(CF_3)_2O$-: Martin ligand) (**2-Et$_4$N**) and the *O*-ethylated adduct (**3**). The X-ray analysis of **2-Et$_4$N** shows a slightly distorted octahedral structure, and the structure of **3** can be considered to be intermediate between pentacoordinate and hexacoordinate structures but much closer to the hexacoordinate one.

RESULTS AND DISCUSSION

$Rf_3Sb^-Et_4N^+$ (Rf: *o*-$C_6H_4C(CF_3)_2O$-) (**2-Et$_4$N**) was prepared from Rf_2SbCl [11] with lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide [12], followed by countercation exchange as outlined in Scheme 1. The reaction was very sluggish and the main products of the reaction after treatment with water were $Rf_2Sb^-Li^+$ (ca. 30%) and $Rf_2Sb(OH)_2^-Li^+$ (ca. 30%), a hydrolytic product of Rf_2SbCl. However, the crude **2-Et$_4$N** could be isolated from the reaction mixture because of the poor solubility of **2-Et$_4$N** in ethyl acetate although the isolated yield was very low (6%). Pure **2-Et$_4$N** was obtained by recrystallization from acetone/ethyl acetate and was stable to atmospheric moisture. **2-Et$_4$N** was characterized by elemental analysis and X-ray structural analysis.

Although no reaction had taken place between **2-Et$_4$N** and MeI after 5 hours at 50°C in THF, *O*-ethylation was observed by reaction of **2-Et$_4$N** with triethyloxonium tetrafluoroborate at room tempera-

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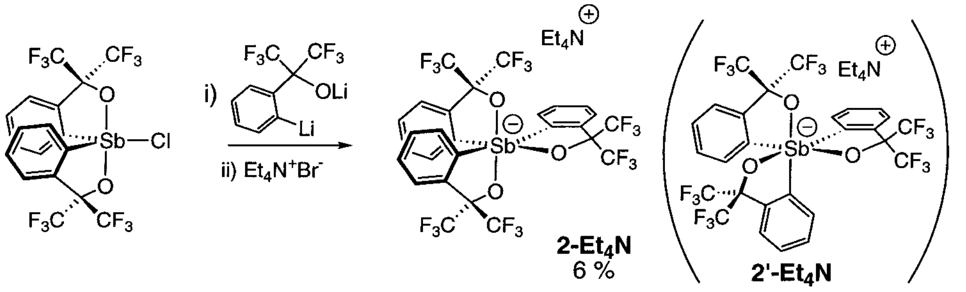
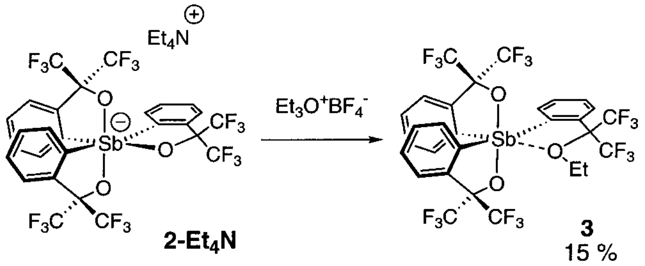


SCHEME 1

ture for three days in dichloromethane (Scheme 2). The adduct **3** was isolated by chromatographic treatment (SiO$_2$: ethyl acetate/*n*-hexane = 1/9) and was characterized by NMR spectroscopy (^{1}H and ^{19}F), elemental analysis, and X-ray structural analysis after recrystallization from dichloromethane/*n*-hexane.



SCHEME 2

X-Ray Crystal Structures of 2-Et$_4$N *and* 3

Figures 1 and 2 show the crystal structures of **2-Et$_4$N** and **3**. Selected bond lengths and bond angles for the structures of **2-Et$_4$N** and **3** are listed in Table 1 together with those for Rf$_2$Sb(*p*-CH$_3$C$_6$H$_4$) (**4**) [13] and Rf$_2$Sb(*p*-CH$_3$C$_6$H$_4$)(F)$^-$Et$_4$N$^+$ (**5-Et$_4$N**) [13] for comparison. The structure of **2-Et$_4$N** is clearly determined to be the mer configuration. Almost all of the bonds in **4** are elongated in **2-Et$_4$N** because of the incoming oxide anion. The three Sb–O bond lengths (a, b, f in Table 1) in **2-Et$_4$N** are similar: 2.087(6), Sb-O1 (a); 2.035(6), Sb-O2 (b); 2.112(6), Sb-O3 (f) Å. However, the Sb–O3 bond (f) trans to the carbon substituent is longer than those [Sb-O1 (a) and Sb-O2 (b)] trans to the oxygen substituents. The trend is also observed in **5-Et$_4$N** where the Sb–O3 bond (f: 2.107(4) Å) trans to the carbon substituent is longer than that [Sb-O1 (a): 2.066(4) Å] trans to the fluorine substituent. These results are consistent with previous reports for hexacoordinate antimony anions such as PhSbX$_5^-$ [8]. For example, in PhSbCl$_5^-$Cs$^+$, the Sb–Cl bond (2.437 Å) trans to the phenyl substituent is longer than those (2.407 and 2.414 Å) trans to the chlorine substituents [14].

The bond angles in **2-Et$_4$N** are compared with those of **4**. Since the equatorial angles (∠C1–Sb–C10 (∠cd), ∠C1–Sb–C19 (∠ce), and ∠C10–Sb–C19 (∠de) in Table 1) in **4** are almost identical and close to 120° [121.5(1)° (∠C1–Sb–C10); 119.8(2)° (∠C1–Sb–C19), and 118.7(2)° (∠C10–Sb–C19)], the geometry about antimony in **4** can be considered to be that of a trigonal bipyramid (TBP), although the apical O1–Sb–O2 bond angle (∠ab in Table 1; 170.6(1)°) deviates significantly from 180°. The angles ∠C1–Sb–C10 and

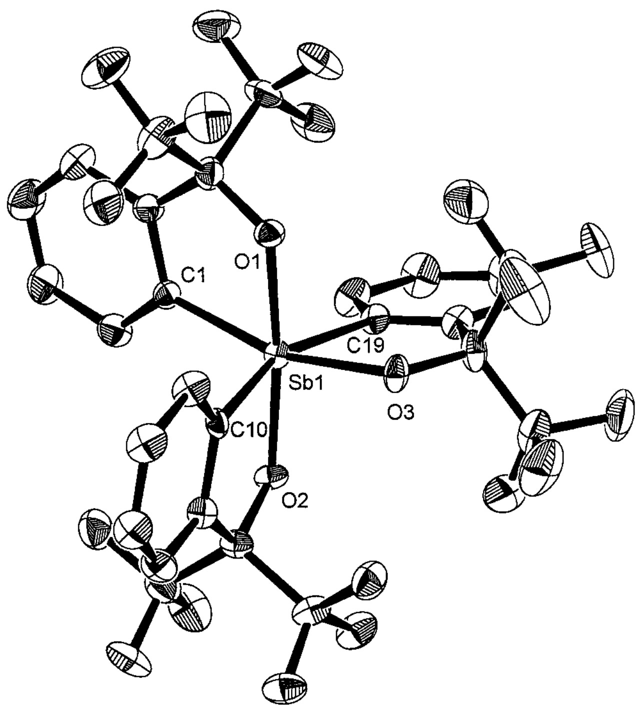


FIGURE 1

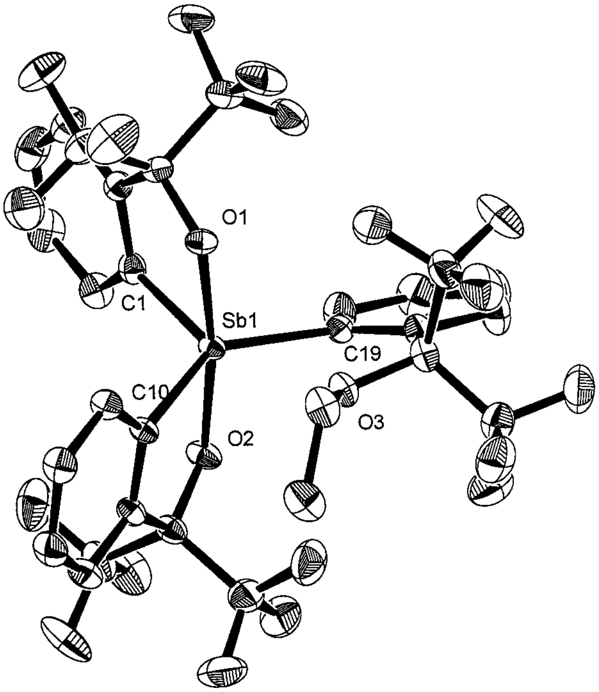


FIGURE 2

$\angle$C1–Sb–C19 in **2-Et$_4$N** are reduced to approach 90° [102.3(3)° ($\angle$C1–Sb–C10), 97.9(3)° ($\angle$C1–Sb–C19)], and the angle $\angle$C10–Sb–C19 is widened to be 158.7(2)°, which are quite different from those of **4**. The angles ($\angle$C1–Sb–C10, $\angle$C1–Sb–C19, and $\angle$C10–Sb–C19) in **2-Et$_4$N** are almost the same as those in **5-Et$_4$N** [100.6(2)° ($\angle$C1–Sb–C10, $\angle$cd), 98.7(2)° ($\angle$C1–Sb–C17, $\angle$ce) and 159.6(2)° $\angle$C10–Sb–C17, $\angle$de]. Therefore, the fundamental structure of **2-Et$_4$N** is essentially the same as that of **5-Et$_4$N** and can be considered as a slightly distorted octahedral structure.

The Sb–OEt (Sb–O3) length [2.816(4) Å] in **3** is much longer than other Sb–O bond lengths [2.039(3) Å (Sb-O1), 2.052(3) Å (Sb-O2)], but it is still much shorter than the sum of van der Waals radii (3.60 Å) [15], indicating the attractive interaction between the central atom and the oxygen atom in the OEt group. The angles $\angle$C1–Sb–C10 [114.6(2)°] and $\angle$C1–Sb–C19 [106.0(2)°] in **3** are wider than those of the corresponding angles in **2-Et$_4$N** and **5-Et$_4$N**, but are narrower than those in **4**. In addition, the angle $\angle$C10–Sb–C19 [138.7(2)°] in **3** shows the intermediate value between the corresponding values in **2-Et$_4$N** (or **5-Et$_4$N**) and **4**. Therefore, the structure of **3** can be considered to be intermediate between pentacoordinate and hexacoordinate structures but more closely resembles a hexacoordinate structure.

It should be mentioned here that the structure of **2-Et$_4$N**, determined by X-ray analysis, is not **2′-Et$_4$N** (fac configuration) but **2-Et$_4$N** (mer) as shown in Scheme 1. This results from the nucleophilic attack of the aryllithium anti to the Sb-C bond from the least sterically hindered site. The oxide is accepted by the central atom to form octahedral complex due to the strong Lewis acidity of the hypervalent atom, affording a product of kinetic control. However, it is not certain whether **2-Et$_4$N** (mer) is thermodynamically more stable than **2′-Et$_4$N** (fac).

The fact that the alkylation of **2-Et$_4$N** took place at the oxygen anti to the carbon is reasonable, based on the trans influence of the substituent.

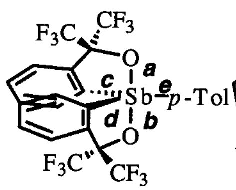
EXPERIMENTAL

Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR (400-MHz) and ^{19}F NMR (376-MHz) spectra were recorded on a JEOL EX-400 spectrometer. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^{1}H or from fluorotrichloromethane for ^{19}F. Elemental analysis was performed on a Perkin-Elmer 2400CHN elemental analyzer. Column chromatography was carried out on Merck silica gel 9385. Thin-layer chromatography was performed with Merck silica gel GF-254 plates. All reactions were carried out under N$_2$ or Ar.

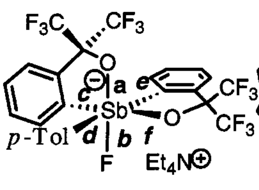
Preparation of **2-Et$_4$N** *{$Rf_3Sb^-Et_4N^+$ (Rf: o-$C_6H_4C(CF_3)_2O$-)}*

Lithium 1,1,1,3,3,3-hexafluoro-2-(2-lithiophenyl)-2-propoxide [12] was prepared from bis(trifluoromethyl)benzyl alcohol (0.427 mL, 2.76 mmol), *n*-BuLi (5.55 mmol in 3.47 mL of n-hexane), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 0.084 mL, 0.555 mmol) in 1 mL of THF and was dissolved in 15 mL of tetrahydrofuran (THF) followed by addition to a cold (−78°C) stirred solution of Rf$_2$SbCl [11] (0.885 g, 1.38 mmol) in 15 mL of THF. The mixture was kept for 1 hour at −78°C and was allowed to warm to room temperature for 5 hours followed by heating under reflux for 1 day. After the reaction mixture had been treated with ice water, the crude product was extracted with THF (50 mL × 3) and washed with aq. NaCl solution (100 mL). After the solvent was evaporated, the crude mixture was dissolved in 20 mL of THF, and tetraethylammonium bromide (2.90 g, 13.8 mmol) was added. The mixture was stirred for 1 day at room temperature and treated with ice water. After extraction with THF, the solvent was evaporated. Ethyl acetate (20 mL) was added to the residue, the insoluble solid was filtered off, and the solid was washed with ethyl acetate, *n*-hexane, and dichloromethane. The solid

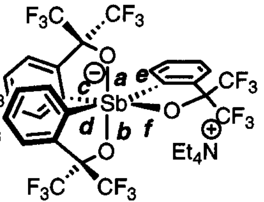
TABLE 1 Bond Lengths and Angles for **4, 5-Et$_4$N, 2-Et$_4$N**, and **3**



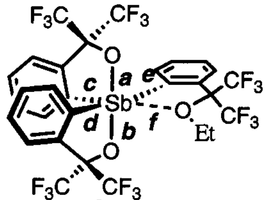
4



5-Et$_4$N



2-Et$_4$N



3

	4	5-Et$_4$N	2-Et$_4$N	3
		Bond Lengths (Å)		
Sb-O1 (a)	2.035(2)	2.066(4)	2.087(6)	2.039(3)
Sb-O2 (b)	2.042(3)	1.999(4)[b]	2.035(6)	2.052(3)
Sb-C1 (c)	2.089(4)	2.148(7)	2.125(8)	2.089(6)
Sb-C10 (d)	2.094(4)	2.124(6)	2.144(6)	2.092(5)
Sb-C19[a] (e)	2.094(4)	2.116(7)	2.144(6)	2.106(5)
Sb-O3 (f)		2.107(4)	2.112(6)	2.816(4)
		Bond Angles (deg)		
∠O1-Sb-O2 (∠ab)	170.6(1)	172.0(2)	172.9(3)	172.1(2)
∠C1-Sb-C10 (∠cd)	121.5(1)	100.6(2)	102.3(3)	114.6(2)
∠O1-Sb-C1 (∠ac)	81.5(1)	79.2(2)	78.6(3)	81.7(2)
∠O2-Sb-C10 (∠bd)	81.2(1)	87.5(2)	80.7(4)	80.8(2)
∠O1-Sb-C10 (∠ad)	94.0(1)	93.7(2)	92.8(4)	94.1(2)
∠O2-Sb-C1 (∠bc)	94.0(1)	92.6(2)	99.7(3)	94.9(2)
∠C1-Sb-C19[a] (∠ce)	119.8(2)	98.7(2)	97.9(3)	106.0(2)
∠C10-Sb-C19[a] (∠de)	118.7(2)	159.6(2)	158.7(2)	138.7(2)
∠O1-Sb-C19[a] (∠ae)	95.7(1)	96.3(2)	97.7(4)	99.5(2)
∠O2-Sb-C19[a] (∠be)	93.7(1)	85.0(2)	89.4(4)	88.3(2)
∠O1-Sb-O3 (∠af)		86.5(2)	85.6(3)	80.3(1)
∠O2-Sb-O3 (∠bf)		101.5(2)	96.8(3)	104.5(1)
∠C1-Sb-O3 (∠cf)		164.8(2)	162.7(3)	158.0(2)
∠C10-Sb-O3 (∠df)		85.5(2)	85.5(3)	79.3(2)
∠C19[a]-Sb-O3 (∠ef)		77.5(2)	76.9(4)	65.1(2)

[a] C17 in **5-Et$_4$**N.
[b] F1 in **5-Et$_4$N**.

was dissolved in acetone, and the insoluble solid was filtered off. After evaporation of the solvent from the filtrate, crude **2-Et$_4$N** was obtained. Pure **2-Et$_4$N** (87.4 mg, 6.4% yield) was obtained after recrystallization from acetone/ethyl acetate. m.p. >300°C (dec). ^{1}H NMR (acetone-d$_6$) 1.34 (tt, 12 H, J = 7, 2 Hz), 3.44 (q, 8 H, J = 7 Hz), 7.3–7.45 (m, 6 H), 7.55–7.65 (m, 5 H), 8.15 (bd, 1 H, J = 7 Hz). ^{19}F NMR (acetone-d$_6$) −73.0 (bs, 6 F), −73.0 (bq, 6 F, J = 7 Hz), −74.0 (bq, 6 F, J = 7 Hz). Anal. Calcd for $C_{35}H_{32}F_{18}NO_3Sb$: C, 42.97; H, 3.30; N, 1.43. Found: C, 42.97; H, 3.11; N, 1.33.

Preparation of 3

To a suspension of **2-Et$_4$N** (29.4 mg, 0.030 mmol) in 0.75 mL of dry dichloromethane was added triethyloxonium tetrafluoroborate (0.050 mmol in 0.050 mL of dichloromethane). The mixture was stirred at room temperature for 3 days. After the solvent had been evaporated in vacuo the crude products were subjected to TLC (ethyl acetate:*n*-hexane = 1:9) to give **3** (Rf = 0.46): 4.0 mg, 15%. m.p. 174–175°C (dec). ^{1}H NMR (acetone-d$_6$) 0.42 (t, 3 H, J = 7 Hz), 4.37 (dq, 1 H, J = 7, 14 Hz), 4.48 (dq, 1 H, J = 7, 14 Hz), 7.3–8.4 (m, 12 H). ^{19}F NMR ($CDCl_3$) −65.7 (bq, 3 F, J = 8 Hz), −68.5 (bq, 3 F, J = 8 Hz), −73.5 (bq, 3 F, J = 8 Hz), −73.7 (bq, 3 F, J = 8 Hz), −75.3 (bq, 3 F, J = 8 Hz), −75.5 (bq, 3 F, J = 8 Hz). Anal. Calcd for $C_{29}H_{17}F_{18}O_3Sb$: C, 39.71; H, 1.95. Found: C, 40.03; H, 1.98.

Crystallographic Studies of 2-Et$_4$N *and* 3

Crystal data and numerical details of the structure determinations are given in Table 2. Crystals suitable for X-ray structure determination were mounted on a Mac Science MXC3 diffractometer and irradiated with graphite-monochromated MoKα radiation (λ = 0.71073 Å) for data collection.

TABLE 2 Crystallographic Data for **2-Et$_4$N** and **3**

Molecule	**2-Et$_4$N**	**3**
Formula	$C_{35}H_{32}O_3NF_{18}Sb$	$C_{29}H_{17}O_3F_{18}Sb$
Mol. wt.	978.4	877.2
Cryst. syst.	Monoclinic	Monoclinic
Space group	$P2_1$	C2/c
Cryst. dimens. (mm)	1.00 × 0.75 × 0.35	0.65 × 0.45 × 0.30
Color	Colorless	Colorless
Habit	Plate	Plate
a, Å	10.905(3)	39.74(3)
b, Å	18.058(5)	9.957(9)
c, Å	10.421(3)	17.43(1)
α, deg	90	90
β, deg	113.06(2)	114.45(5)
γ, deg	90	90
V, Å^3	1888.1(8)	6277(8)
Z	2	8
D_{calc}(g cm^{-3})	1.72	1.86
Abs. coeff. (cm^{-1})	7.65	9.14
F(000)	972	3424
Radiation (λ, Å)	MoKα, 0.71073	MoKα, 0.71073
Temp. (°C)	23 ± 1	23 ± 1
2θ max (deg)	55	50
Scan rate (deg/min)	6.0	5.0
Linear decay (%)	2	–
Data collected	$\pm h, +k, +1$	$\pm h, +k, +1$
Total data collcd, unique,	4770, 4488,	6153, 5885,
Observed	$4173(I > 3\sigma(I))$	$4605(I > 3\sigma(I))$
No. of parametrics refined	523	460
R, R_w[a]	0.047, 0.052,	0.041, 0.046,
Goodness of fit (obs.)	0.28	0.19
Max shift in final cycle	0.027	0.0014
Final diff map, max(e/Å^3)	1.44	1.78

[a] Function mimimized was sum $[w(|F_o|^2 - |F_c|^2)^2]$ which $w = 1.0/\text{sigma}|F_o|^2$. $R = \text{sum}[||F_o| - |F_c||)/\text{sum}|F_o|$. $R_w = [\text{sum}w(|F_o| - |F_c|)^2/\text{sum}|F_o|^2]^{1/2}$

Lattice parameters were determined by least-squares fitting of 29 reflections for **2-Et$_4$N** with 30° $< 2\theta <$ 35°, and of 27 for **3** with 21° $< 2\theta <$ 28°. Data were collected by use of the $2\theta/\omega$ scan mode. The structures were solved using the SIR-92 program in the teXsan (Rigaku) package [16] and refined by full-matrix least-squares treatment. No absorption correction was made for **2-Et$_4$N** and **3**. Refinement on F was carried out by full-matrix least-squares treatment. Hydrogen atoms were included in the refinement on calculated positions (C–H = 1.0 Å) riding on their carrier atoms with isotropic thermal parameters. All computations were carried out on an SGI O_2 computer using the teXsan program [16].

SUPPLEMENTARY MATERIAL AVAILABLE

A complete description of the X-ray crystallographic structure determination on **2-Et$_4$N** and **3** have been deposited at the Cambridge Crystallographic Data Centre (CCDC deposition numbers: 149214 and 149215).

ACKNOWLEDGMENTS

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