

# Antimony(V) 1,1,1,3,3,3-hexafluoroisopropoxides

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## Abstract

New antimony(V) 1,1,1,3,3,3-hexafluoroisopropoxides have been prepared and characterized by elemental analyses, IR, NMR spectra and mass spectrometric data. The compounds characterized are formulated as  $\text{Sb}[\text{OCH}(\text{CF}_3)_2]_5$ ,  $\text{SbCl}[\text{OCH}(\text{CF}_3)_2]_4$ ,  $\text{SbCl}_2[\text{OCH}(\text{CF}_3)_2]_3 \cdot \text{OEt}_2$ ,  $\text{SbCl}_3[\text{OCH}(\text{CF}_3)_2]_2 \cdot \text{OEt}_2$  and  $\text{SbCl}_4[\text{OCH}(\text{CF}_3)_2] \cdot \text{OEt}_2$ . The IR and mass spectral data are consistent with monomeric species. These compounds react with pyridine to yield adducts of the composition  $\text{SbCl}_{5-n}[\text{OCH}(\text{CF}_3)_2]_n \cdot \text{py}$  (where  $n = 1-5$ ) and these adducts have also been characterized.

## Introduction

Metal alkoxides are a class of compounds involving coordination of the alkoxo oxygen atom to the metal and are susceptible to easy hydrolysis; this restricts the range of alkoxides which may be prepared and studied [1]. Metal alkoxides have aroused interest recently as a result of their applications as ceramic and electronic materials for the chemical vapour deposition of metals and metal oxides [2]. In normal metal alkoxides, the alkoxide group shows a great propensity to bridge two or more metal atoms [3] leading to the formation of polymeric materials. Metal derivatives of fluorinated alkoxides are expected to have properties which may differ from those of normal alkoxides as fluorinated alkoxide anions usually act as unidentate ligands [4].

Metal 1,1,1,3,3,3-hexafluoroisopropoxides have been obtained [5] by two main methods involving the reaction of metal hydrides with hexafluoroacetone or 1,1,1,3,3,3-hexafluoroisopropanol or reaction of alkali metal/thallium 1,1,1,3,3,3-hexafluoroisopropoxide with metal halides. Antimony(V) 1,1,1,3,3,3-hexafluoroisopropoxides have not been synthesized and we report here their synthesis, characterization and reactions with pyridine.

## Experimental

### Instrumentation

The infrared spectra of the compounds were recorded as Nujol/HCB oil mulls between NaCl and CsI plates on a Perkin-Elmer 1430 ratio recording spectropho-

tometer. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Varian EM-390 spectrometer at 90 MHz using  $\text{Me}_4\text{Si}$  and  $\text{CFCl}_3$  as internal standards. Mass spectra were recorded on a VG Micromass-7075 instrument (highest mass measured = 700) and a Varian VG Analytical 11-2505-705 mass spectrometer at 70 eV (highest mass measured = 1000). Molecular weights were measured cryoscopically as  $10^{-2}$  M solutions in nitrobenzene. All manipulations, i.e. synthetic reactions and sample preparation for spectroscopic investigations, were carried out under a dry  $\text{O}_2$ -free nitrogen atmosphere.

### Materials and methods

Anhydrous  $\text{SbCl}_5$  (Fluka) was distilled before use and the fraction distilling at 78 °C collected. 1,1,1,3,3,3-hexafluoroisopropanol (Fluka) was distilled over sodium and the mid-fraction distilling at 57.5 °C was collected and stored in the dark. Chloroform (BDH, AR) and carbon tetrachloride (BDH, AR) were stored separately over fused  $\text{CaCl}_2$  and then distilled over  $\text{P}_2\text{O}_5$ . The fractions distilling at 60 °C ( $\text{CHCl}_3$ ) and 76 °C ( $\text{CCl}_4$ ) were collected. Diethyl ether was stored overnight over fused  $\text{CaCl}_2$  and then distilled over  $\text{P}_2\text{O}_5$ , the fraction distilling at 34.5 °C being collected over sodium wire. Pyridine (BDH, AR) was refluxed over fresh KOH pellets and subsequently distilled over fresh KOH pellets. The fraction distilling at 115.5 °C was collected for use.

The antimony and chlorine contents of the compounds were estimated by known methods [6], while their fluorine contents were estimated by a method outlined earlier [7].

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*Preparation of pentakis(1,1,1,3,3,3-hexafluoroisopropoxy)antimony(V), Sb[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>5</sub>*

A solution of SbCl<sub>5</sub> (1.2 g, 4.0 mmol) in c. 10 ml of chloroform was added dropwise to a suspension of sodium 1,1,1,3,3,3-hexafluoroisopropoxide [8] (3.9 g, 20.5 mmol) in c. 3 ml of 1,1,1,3,3,3-hexafluoroisopropanol and 10 ml of chloroform. The mixture was stirred vigorously for 1 h and then refluxed over a water bath for 5 h. The suspension containing dissolved alkoxide and insoluble sodium chloride was filtered under anhydrous conditions to remove sodium chloride and the filtrate evacuated to yield a solid, which was washed 2–3 times with dry carbon tetrachloride and finally evacuated to give a white solid. This was recrystallised from 1,1,1,3,3,3-hexafluoroisopropanol yielding 42% of the pure product.

A similar procedure was adopted for the preparation of chlorotetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)antimony(V), SbCl[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> to give 30% yield of the pure product after recrystallisation.

*Dichlorotris(1,1,1,3,3,3-hexafluoroisopropoxy)antimony(V) monodiethyl ether, SbCl<sub>2</sub>[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>·OEt<sub>2</sub>*

A solution of SbCl<sub>5</sub> (1.1 g, 3.7 mmol) in 50 ml of chloroform was added dropwise to a suspension of sodium 1,1,1,3,3,3-hexafluoroisopropoxide (2.1 g, 11.1 mmol) in c. 15 ml of diethyl ether. The contents were worked up in the same way as described for the preparation of the pentakis derivative, yielding 82% of the white solid.

A similar procedure was adopted for the preparation of trichlorobis(1,1,1,3,3,3-hexafluoroisopropoxy)antimony(V) monodiethyl ether, SbCl<sub>3</sub>[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·OEt<sub>2</sub>, and tetrachloro(1,1,1,3,3,3-hexafluoroisopropoxy)antimony(V) monodiethyl ether, SbCl<sub>4</sub>OCH(CF<sub>3</sub>)<sub>2</sub>·OEt<sub>2</sub>.

*Preparation of the pyridine adducts*

These adducts were generally prepared by dissolving the alkoxide in excess pyridine. Separation of the solid adducts was effected by the addition of diethyl ether.

## Results and discussion

The compounds Sb[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>5</sub> and SbCl[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> have been prepared by the metatheses of sodium-1,1,1,3,3,3-hexafluoroisopropoxide and antimony(V) chloride in 5:1 and 4:1 proportions using a 1,1,1,3,3,3-hexafluoroisopropanol/chloroform mixture as the reaction medium. In diethyl ether the reaction of sodium 1,1,1,3,3,3-hexafluoroisopropoxide with antimony(V) chloride (in 3:1, 2:1 and 1:1 proportions) was complete within a short period of time, but the products obtained were found to possess only one diethyl ether molecule coordinated to antimony. These compounds

have been formulated as SbCl<sub>2</sub>[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>·OEt<sub>2</sub>, SbCl<sub>3</sub>[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·OEt<sub>2</sub> and SbCl<sub>4</sub>[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>1</sub>·OEt<sub>2</sub>, respectively. It was also found that the reaction of Sb[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>5</sub> and SbCl[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> with diethyl ether gave 1:1 diethyl ether adducts. All these compounds are hygroscopic, sparingly soluble in 1,1,1,3,3,3-hexafluoroisopropanol, CHCl<sub>3</sub> and diethyl ether, and exothermally soluble in pyridine, dimethylformamide and dimethyl sulphoxide but insoluble in non-polar solvents. Their analytical data are listed in Table 1. Cryoscopic studies in nitrobenzene showed that the compounds Sb[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>5</sub> (Mol.Wt.: Found, 937; Calc. for monomer, 956) and SbCl[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (Mol.Wt.: Found, 807; Calc. for monomer, 824.5) exist as monomers. The cryoscopic data for the other three compounds, however, did not give reproducible results.

*Infrared spectra*

The infrared spectra of these compounds show characteristic absorptions at 1090–1100 cm<sup>-1</sup>, 895–880 cm<sup>-1</sup> and 845–830 cm<sup>-1</sup>. The first vibration may be assigned to the C–O stretching mode [9] arising from the hexafluoroisopropoxide group bonded to antimony(V). The other two vibrations are skeletal [10]. The C–F stretching bands appear at 1280–1260 cm<sup>-1</sup> and 1225 cm<sup>-1</sup> [10]. Useful information concerning the bonding situation of the alkoxy ligand can be deduced from the position and number of C–O stretching bands [1, 11]. Normally, in other metal alkoxides associated through alkoxy bridging, the position of ν(C–O) determines whether the OR group is terminal or bridging, i.e. ν(C–O) terminal absorbs at 1150–1050 cm<sup>-1</sup> whereas ν(C–O) bridging is observed at 1050–950 cm<sup>-1</sup>. For the present compounds, no band was present in the latter region and only one band was present in the former region, i.e. 1090–1100 cm<sup>-1</sup>, suggesting the absence of a bridging hexafluoroisopropoxy ligand. The present compounds show Sb–Cl stretching vibrations at 340 cm<sup>-1</sup> [12]. An additional band was observed at 1000–1030 cm<sup>-1</sup> in the spectra of derivatives which contain a coordinated Et<sub>2</sub>O molecule and this has been assigned to ν(C–O) of Et<sub>2</sub>O [13, 14].

*NMR spectra*

The <sup>1</sup>H NMR spectra of these compounds are also listed in Table 1. The band which appears as a low intensity septet is due to the α-hydrogen coupled with six fluorines. The multiplet is situated at δ 4.2–4.4 ppm (*J* = 6.3 Hz). The corresponding signal in pure 1,1,1,3,3,3-hexafluoroisopropanol appeared at δ 4.17 ppm [10]. This shift of the <sup>1</sup>H band to low field in the NMR spectra of antimony(V) 1,1,1,3,3,3-hexafluoroisopropoxides may be due to the higher covalency of the Sb–O bond in these compounds than that of the H–O bond in pure 1,1,1,3,3,3-hexafluoroisopropanol. In the

TABLE 1. Analytical and NMR data for 1,1,1,3,3,3-hexafluoroisopropoxy derivatives of antimony(V) and their adducts with pyridine

Compound <sup>a</sup>	M.p. (°C)	Sb (%)		Cl (%)		F (%)		NMR ( $\delta$ , ppm) <sup>b</sup>	
		Found	Calc.	Found	Calc.	Found	Calc.	<sup>1</sup> H	<sup>19</sup> F
Sb[OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>5</sub>	73	12.24	12.74	–	–	59.25	59.56	4.26(s)	–78(d)
SbCl[OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub>	64	13.98	14.77	4.28	4.30	54.97	55.23	4.30(s)	–77(d)
SbCl <sub>2</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> ·OEt <sub>2</sub>	> 200	15.89	15.94	9.13	9.28	44.25	44.70	4.32(s)	–76.5(d)
SbCl <sub>3</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ·OEt <sub>2</sub>	> 200	18.95	19.22	16.57	16.78	35.87	35.93	4.20(s)	–76.8(d)
SbCl <sub>4</sub> OCH(CF <sub>3</sub> ) <sub>2</sub> ·OEt <sub>2</sub>	> 200	24.10	24.20	28.08	28.17	22.32	22.62	4.40(s)	–78(d)
Sb[OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>5</sub> ·py	> 200	11.29	11.77	–	–	54.99	55.01	4.50(s)	–77(d)
SbCl[OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub> ·py	> 200	13.00	13.05	3.76	3.92	50.26	50.41	4.42(s)	–76(d)
SbCl <sub>2</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> ·py	> 200	15.78	15.84	9.19	9.22	44.31	44.41	4.50(s)	–76.5(d)
SbCl <sub>3</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ·py	> 200	18.79	19.07	16.62	16.65	35.58	35.65	4.45(s)	–77(d)
SbCl <sub>4</sub> OCH(CF <sub>3</sub> ) <sub>2</sub> ·py	> 200	23.23	23.96	27.85	27.89	22.21	22.31	4.40(s)	–78(d)

<sup>a</sup>These compounds were all white solids.<sup>b</sup>s = septet; d = doublet.

TABLE 2. Mass ion peaks of antimony(V) 1,1,1,3,3,3-hexafluoroisopropoxides

Sb[OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>5</sub>		SbCl[OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>4</sub>		SbCl <sub>2</sub> [OCH(CF <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> ·OEt <sub>2</sub>		SbCl <sub>4</sub> OCH(CF <sub>3</sub> ) <sub>2</sub> ·OEt <sub>2</sub>	
<i>m/z</i>	Assignment <sup>a</sup>	<i>m/z</i>	Assignment <sup>a</sup>	<i>m/z</i>	Assignment <sup>a</sup>	<i>m/z</i>	Assignment <sup>a</sup>
503	Sb(OR) <sub>2</sub> (OCHF) <sup>+</sup>	490	Sb(OR) <sub>2</sub> Cl <sup>+</sup>	525	M <sup>+</sup> – OR	428	M <sup>+</sup>
430	Sb(OR – CHF)(OR – CF)F <sub>2</sub>	471	Sb(OR)(OR – F)Cl <sup>+</sup>	521	M <sup>+</sup> – (CF <sub>3</sub> ) <sub>2</sub> ·Cl	269	SbOR <sup>+</sup> – F
429	Sb(OR – CHF) <sub>2</sub> F <sub>2</sub>	342	Sb(OR)ClF <sup>+</sup>	490	M <sup>+</sup> – (OR, Cl)	261	M <sup>+</sup> – OR
355	Sb(OR)F(OCHF) <sup>+</sup>	191	SbOCIF <sup>+</sup>	455	M <sup>+</sup> – (OR, Cl)	226	M <sup>+</sup> – (OR, Cl)
341	Sb(OR)OF <sub>2</sub> <sup>+</sup>	177	SbF <sub>3</sub> <sup>+</sup>	424	M <sup>+</sup> – (OR, Cl <sub>2</sub> CF)	192	SbCl <sub>2</sub> <sup>+</sup>
293	Sb(OR – CF)F <sub>2</sub> <sup>+</sup>	175	SbFCl <sup>+</sup>	358	M <sup>+</sup> – (OR) <sub>2</sub>	191	M <sup>+</sup> – (OR, Cl <sub>2</sub> )
279	Sb(OCHCF <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	167	OR	327	M <sup>+</sup> – [(OR) <sub>2</sub> , CF]	175	SbOF <sub>2</sub> <sup>+</sup>
221	Sb(OCHCF <sub>3</sub> ) <sup>+</sup>	149	(OR – F)	289	M <sup>+</sup> – (OR, CF <sub>3</sub> )	159	SbF <sub>2</sub> <sup>+</sup>
191	Sb – CF <sub>3</sub> <sup>+</sup>	123	SbH <sub>2</sub> <sup>+</sup>	191	M <sup>+</sup> – (OR) <sub>3</sub>	156	SbCl <sup>+</sup>
177	SbF <sub>3</sub> <sup>+</sup>			171	M <sup>+</sup> – [(OR) <sub>3</sub> , HF]		
167	OR			156	M <sup>+</sup> – [(OR) <sub>3</sub> , Cl]		
149	(OR – F)						
137	SbO <sup>+</sup>						
123	SbH <sub>2</sub> <sup>+</sup>						

<sup>a</sup>OR = –OCH(CF<sub>3</sub>)<sub>2</sub>.

spectra of compounds containing a coordinated diethyl ether molecule, two additional peaks appear at  $\delta$  1.1 ppm (quartet) and 3.3 ppm (triplet). The <sup>19</sup>F NMR spectra of all compounds show doublets ( $J = 6$  Hz) and their positions are given in Table 1.

### Mass spectra

The mass spectrometric data for Sb[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>5</sub> (1), SbCl[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (2), SbCl<sub>2</sub>[OCH(CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>·OEt<sub>2</sub> (3) and SbCl<sub>4</sub>OCH(CF<sub>3</sub>)<sub>2</sub>·OEt<sub>2</sub> (4) are listed in Table 2. The mass spectrum of compounds 1, 2 and 3 exhibit no peak attributable to a molecular ion nor any peak at regions higher than those of the parent molecular ions, thus indicating that these compounds exist as monomers in the vapour phase. This observation is similar to that for the hexafluoroisopropoxides of silicon(IV), germanium(IV), titanium(IV), zirconium(IV) and hafnium(IV) [10].

### Reaction with pyridine

Reaction of these compounds with pyridine yielded 1:1 solid adducts whose analytical and NMR details are also listed in Table 1. The trend in shifts in the infrared spectral bands of pyridine in these complexes was the same as observed for the adducts of pyridine with other acceptors [15, 16].

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