

## Reaction of 2,2,2-Trifluoroethoxytetrachloroantimony(V) with Some Oxygen & Nitrogen Donors

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Reactions of 2,2,2-trifluoroethoxytetrachloroantimony(V)  $[Sb(OC_2H_2F_3)Cl_4]$  with oxygen and nitrogen donors yield adducts having 1:1 or 1:2  $[Sb(OC_2H_2F_3)Cl_4 : \text{ligand}]$  stoichiometry. These compounds have been characterized by their analytical data, molar conductance and infrared spectra.

THE preparation of 2,2,2-trifluoroethoxytetrachloroantimony(V)  $[Sb(OC_2H_2F_3)Cl_4]$  has been recently reported by Paul *et al.*<sup>1</sup> and was found cryoscopically to be a monomer in benzene. This is unlike the other alkoxides,  $Sb(OR)Cl_4$  (where R is  $CH_3$ ,  $C_2H_5$  and  $C_2H_4Cl$ ) which have been confirmed to exist as dimers in solution<sup>2</sup> as well as in solid state<sup>3</sup>. This compound, therefore, is likely to form stable complexes with oxygen and nitrogen donors, unlike other metal alkoxides which have been shown to be poor acceptors<sup>4</sup>. The present study reports the formation and characterization of the complexes of 2,2,2-trifluoroethoxytetrachloroantimony(V) with some oxygen and nitrogen donors.

### Materials and Methods

2,2,2-Trifluoroethoxytetrachloroantimony(V) was prepared by treating bis (2,2,2-trifluoroethyl) sulphite with antimony(V) chloride in an equimolar ratio as described earlier<sup>1</sup>. Its complexes with bidentate ligands such as succinimide, and  $\alpha, \alpha'$ -dipyridyl-N,N'-dioxide were prepared by stirring the benzene solution of  $Sb(OC_2H_2F_3)Cl_4$  with the suspensions of the ligands in benzene for 4 hr. The solid products which separated out were filtered, washed with benzene

and dried *in vacuo*. In the case of  $\alpha, \alpha'$ -dipyridyl, 1,10-phenanthroline, triphenylphosphine oxide, 8-hydroxyquinoline and pyridine-N-oxide, the solids separated out just by mixing the solutions of alkoxide and the ligands. Complexes with hexamethylphosphoramide, 2-, 3-, and 4-picoline oxides and pyridine were prepared by mixing equimolar solutions of the alkoxide and the ligand in benzene. The complexes were precipitated out by adding dry ether. The complex of dimethyl sulphoxide was prepared by mixing benzene solution of alkoxide and the ligand.

Antimony<sup>5</sup> and chlorine<sup>5</sup> contents of the complexes were estimated as described earlier. Infrared spectra of the complexes were recorded on Perkin-Elmer 337 and 621 spectrophotometers.

### Results and Discussion

The elemental analyses (Table 1) of the complexes with hexamethylphosphoramide, triphenylphosphine oxide, dimethyl sulphoxide, pyridine-N-oxide, 2-, 3- and 4-picoline oxides, pyridine, 8-hydroxyquinoline and succinimide show them to have 1:1 stoichiometry  $[\text{ligand} : Sb(OC_2H_2F_3)Cl_4]$  whereas those with  $\alpha, \alpha'$ -dipyridyl and its oxide, and 1,10-phen-

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES

Complex	Colour	m.p. (°C)	Sb (%)		Cl (%)	
			Calc.	Found	Calc.	Found
A. Succinimide	Dirty white	90-92	26.2	26.1	30.8	30.4
A. HMPA <sup>-</sup>	Yellow	55	22.3	22.7	26.3	26.8
A. TPPO	White	165	18.8	19.4	20.0	20.0
A. Py-O	do	68-70	26.6	26.2	31.3	31.1
A. (2Pic-O)	Brown viscous liquid	—	25.8	26.2	31.0	31.1
A. (3Pic-O)	do	—	25.8	26.1	—	—
A. (4Pic-O)	White solid	185	25.8	26.2	30.1	31.2
2A. Dipy-O <sub>2</sub>	White	180-82	26.5	27.0	31.1	32.0
A. DMSO	Brown	—	27.5	26.6	—	—
A. Py	White	117-18	27.4	26.9	32.2	31.9
A. 8HQ	Yellow	125-26	23.8	22.8	28.0	28.0
2A. Dipy	White	260	27.5	28.3	32.2	32.1
2A. 1,10 Phen	Yellow	210-11	26.7	26.1	31.4	30.6

HMPA = hexamethyl phosphoramide; TPPO = triphenylphosphine oxide; Py-O = pyridine-N-oxide; 2-, 3- and 4-Pic-O = 2-, 3- and 4-picoline-N-oxides; Dipy-O<sub>2</sub> =  $\alpha, \alpha'$ -dipyridyl-N,N'-dioxide; DMSO = dimethyl sulphoxide; Py = pyridine; 8HQ = 8-hydroxyquinoline; Dipy = dipyridyl; and 1,10-Phen = phenanthroline.

TABLE 2 — MAJOR INFRARED FREQUENCIES ( $\text{cm}^{-1}$ ) OF COMPLEXES\* OF 2,2,2-TRIFLUOROETHOXYTETRACHLOROANTIMONY(V) AND PURE LIGANDS

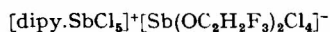
Compound			$\nu(\text{C-O-Sb})$	$\nu(\text{O-Sb})$
Sb(OC <sub>2</sub> H <sub>2</sub> F <sub>3</sub> )Cl <sub>4</sub> (A)	—	—	1170	670
A. Succinimide	1770, 1695w, 1625 (1770, 1695, $\nu\text{C=O}$ )	—	1150	635
A. HMPA†	1050 (1205; $\nu\text{P=O}$ )	990, 757 (980, 740; $\delta\text{P-N}$ )	1160	—
A. TPPO†	1120 (1190; $\nu\text{P=O}$ )	—	1125	—
A. Py-O†	1200 (1240; $\nu\text{N-O}$ )	824 (835; $\delta\text{N-O}$ )	1170	—
A. (2Pic-O)	1200 (1245; $\nu\text{N-O}$ )	810 (857; $\delta\text{N-O}$ )	1149	660
A. (3Pic-O)	1140-50 (1250; $\nu\text{N-O}$ )	808-784 (845; $\delta\text{N-O}$ )	1140-50	660-70
A. (4Pic-O)	1200 (1245; $\nu\text{N-O}$ )	818 (850; $\delta\text{N-O}$ )	1150	—
2A. Dipy-O <sub>2</sub>	1250, 1200 (1262, 1255; $\nu\text{N-O}$ )	841, 804 (852, 840; $\delta\text{N-O}$ )	1120	630
A. DMSO	930 (1050, $\nu\text{S=O}$ )	710 (690; $\nu\text{C-S}$ )	—	—
A. Py‡	1615 sh, 1600	—	1150	670
A. 8HQ	1600, 1550	—	1174	674
2A. Dipy	1608, 1580, 1020	—	1150	670
2A. 1,10 Phen	1600, 1030, 845	—	1170	—

\*Corresponding vibrations along with assignments for the pure ligands are given in parentheses.

† $\nu(\text{O}\rightarrow\text{Sb})$  is present at 450, 425 and 418  $\text{cm}^{-1}$  in these complexes while  $\nu(\text{Sb-Cl})$  is present at 340 (330, 350), 330  $\text{cm}^{-1}$  respectively.

‡ $\nu(\text{Sb-Cl})$  is present at 340  $\text{cm}^{-1}$ .

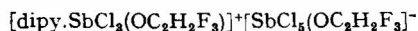
anthroline have 1:2 stoichiometry. All the complexes are either insoluble or have limited solubility in the common organic solvents which precludes their cryoscopic measurements. The complexes with  $\alpha, \alpha'$ -dipyridyl and 1,10-phenanthroline have a good solubility in nitrobenzene and the molar conductance of  $0.37 \times 10^{-3} M$  solution of the former is 27.05  $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$  and of  $0.521 \times 10^{-3} M$  solution of the latter, the value is slightly more than 35  $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$ , indicating these complexes to be 1:1 electrolytes. [Pure Sb(OC<sub>2</sub>H<sub>2</sub>F<sub>3</sub>)Cl<sub>4</sub> has a molar conductance of 8.9  $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$  for its  $1.04 \times 10^{-3} M$  solution in nitrobenzene<sup>1</sup>.] These complexes, therefore, may be considered to have either of the following three structures (I-III), e.g. for dipyrldyl complex:



I



II



III

The formulations are analogous to the salt like structure for the complex 2SbCl<sub>5</sub>. Phenanthroline<sup>6</sup> and a 2:1 complex of antimony(V) chloride with bidentate phosphoryl ligand, R<sub>2</sub>PO-CH<sub>2</sub>-OP-R<sub>2</sub> (ref. 7).

The infrared spectrum (CS<sub>2</sub> or benzene solution) of 2,2,2-trifluoroethoxytetrachloroantimony(V) when compared with the pure 2,2,2-trifluoroethanol shows an additional strong intensity band at 1170  $\text{cm}^{-1}$ , which may be assigned to  $\nu(\text{C-O})$  of the Sb-O-C(R) group. Another band present at 670  $\text{cm}^{-1}$  in this compound may be assigned to the  $\nu(\text{O-Sb})$  stretch.

The doublet bands arising from  $\nu\text{N-O}$  and bending bands arising from pure  $\alpha, \alpha'$ -dipyridyl N,N'-dioxide shift to the lower spectral region (Table 2) in the

spectrum of the complex of this ligand. This may be correlated to the coordination of this ligand<sup>1,8</sup> through both of its oxygen atoms to antimony. It has been reported that these bands shift to the lower frequencies in the complexes of this ligand with metal halides<sup>2,8</sup> and from these findings, the bidentate nature of this ligand has been suggested. In the spectrum of succinimide complex, only one of the vibrations out of the two assigned<sup>9</sup> for  $\nu\text{C=O}$  shifts to the lower spectral region (Table 2) and this can be attributed to the monodentate donor nature of succinimide. In the IR spectra of the complexes of  $\alpha, \alpha'$ -dipyridyl and 1,10-phenanthroline the shift in the characteristic bands of the ligands (Table 2) shows<sup>11</sup> coordination through both the nitrogen atoms. In the spectra of the pyridine-N-oxide, 2-, 3- and 4-picoline-N-oxides, the  $\nu(\text{N-O})$  and  $\delta(\text{N-O})$  shift to the lower spectral region (Table 2). Similarly,  $\nu(\text{P=O})$  of hexamethylphosphoramide and triphenylphosphine oxide shift to the lower spectral region, whereas in dimethyl sulphoxide, the  $\nu(\text{S=O})$  shifts to the lower wavenumber in its complex. These observations are in keeping with coordination of these ligands<sup>2</sup> through oxygen atom to antimony.

The  $\nu(\text{C-O})$  arising from the (R) C-O-Sb vibration has been found to be present at nearly the same position and this reveals that the coordinated alkoxy group is intact in these complexes. Like the pure Sb(OC<sub>2</sub>H<sub>2</sub>F<sub>3</sub>)Cl<sub>4</sub>, the complexes show a strong intensity band at 670  $\text{cm}^{-1}$ , assigned to  $\nu(\text{O}\rightarrow\text{Sb})$  which compares well with the  $\nu(\text{Ti-O})$  stretch in the complexes of Ti(OR)Cl<sub>3</sub><sup>11,12</sup>. Far infrared spectra of the complexes with oxygen donors show the presence of a medium or strong intensity band at 418-450  $\text{cm}^{-1}$ , which may be assigned to the  $\nu(\text{O}\rightarrow\text{Sb})$  in these complexes by comparison with the IR spectra of SbCl<sub>5</sub>. L complexes<sup>13,14</sup> and of Sb(OR)Cl<sub>4</sub>.L (ref. 2) (where R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and L = oxygen donor ligand). Another strong intensity band at 340  $\text{cm}^{-1}$  in the spectra of these complexes (Table 2) is assigned to  $\nu(\text{Sb-Cl})$ <sup>13,15,16</sup>.

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