

## Synthesis and Characterization of Mixed Catecholate and 1,10-Phenanthroline Complexes of Antimony(III), $C_6H_4O_2SbX \cdot 1,10\text{-phenanthroline}$ ( $X = F, Cl, Br, I$ )

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*The title compounds have been easily synthesized by reacting antimony(III) catecholates,  $C_6H_4O_2SbX$ , with 1,10-phenanthroline. The infrared spectra of the solids are in accordance with a chelating behaviour of the phenanthroline ligand and the molecular monomeric nature of the fluoride derivative. In the case of the chloride, and possibly also for  $X = Br$  and  $I$ , infrared data are better interpreted admitting a consistent ionic  $Sb-X$  bond interaction. The conductance data for their methanolic solutions also indicate a distinctive behaviour of the fluoride derivative, this being weakly ionized, whereas the remaining halides behave as 1:1 electrolytes. The main features of the mass spectra of the fluoro- and chloro-derivatives are reported.*

### Introduction

A research program on antimony(III) and organo-antimony(III) coordination compounds with oligodentate ligands has been recently undertaken in our laboratory. Our observations have been extended to the present 1,10-phenanthroline (Phen) adducts of the already known halogeno phenylene-1,2-diolato-antimonates(III),  $C_6H_4O_2SbX$ . Their synthesis was planned after considering that Phen, as well as other nitrogen donors, easily forms adducts with antimony halides [1] and that Sb(III) in mono-catecholates shows definite acceptor properties as inferred from the halogen-bridged polymeric nature of  $C_6H_4O_2SbX$  themselves [2]. The latter is also supported by the structure of substituted catechol complexes of the type  $[C_6H_5NH][C_6X_4O_2SbX_2]$ , where  $X = Cl$  and  $Br$ , in which the antimony environment consists of two short Sb–O bonds and one short and two longer Sb–X bonds [3, 4].

The interest in these new antimony(III) chelates stems mainly from the different geometries and coordination numbers in principle attainable by Sb. Their structure could in fact be based on four-, five- or six-coordinated antimony and the actual shape

depends on various factors such as the mutual disposition of the chelating ligands, the nature of Sb–X bond, the existence of bridging halogens, and the stereochemical behaviour of the lone pair electrons.

In these respects, the fluoride derivative of the series has been deliberately included in our study since previous work has indicated that fluoro-antimony(III) compounds often show different properties from their analogs with the remaining halides.

Only a few structures of antimony(III) chelates are known and information on the effect of chelating ligands on coordinative geometry of Sb is rather scarce. Therefore, X-ray diffraction studies concerning the present compounds have been also planned. These are currently underway [5] and results will be reported separately.

### Experimental

Commercially available reagents and solvents were used.  $C_6H_4O_2SbF$  and  $C_6H_4O_2SbCl$  were obtained according to reported methods [2, 6].

$C_6H_4O_2SbX \cdot Phen$  ( $X = F, Cl$ ) were prepared by refluxing for half an hour a methanolic suspension of  $C_6H_4O_2SbX$  and Phen in 1:1.5 molar ratio. The bromo- and iodo-derivatives were obtained by refluxing  $C_6H_4O_2SbF \cdot Phen$  with an excess of NaBr or NaI in methanol. In all cases the compounds were collected after cooling as coloured microcrystalline solids and recrystallized from methanol.

Physical and analytical data are reported in Table I. Infrared spectra of solids were examined as Nujol mulls in the  $4000\text{--}180\text{ cm}^{-1}$  range using a Perkin-Elmer 580 spectrophotometer. Infrared bands in the skeletal vibration region are listed in Table II, whereas the remaining spectrum, with the exception of regions covered by nujol bands, is reported in the following.

TABLE I. Physical, Analytical and Molar Conductivity Data for the  $C_6H_4O_2SbX \cdot Phen$  Compounds.

X (colour)	M.P. (°C)	Analyses, found (calcd.) (%)			$\lambda_M$ ( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )
		C	H	N	
F (yellow)	275–277	50.60 (50.39)	2.76 (2.82)	6.57 (6.53)	6.5
Cl (yellow)	280(dec.)	48.80 (48.53)	2.75 (2.71)	6.26 (6.29)	85
Br (dark yellow)	270(dec.)	44.18 (44.12)	2.35 (2.47)	5.67 (5.72)	92
I (red)	315–317	40.09 (40.26)	2.24 (2.25)	5.19 (5.22)	102

TABLE II. Infrared Data ( $\text{cm}^{-1}$ ) for the  $C_6H_4O_2SbX \cdot Phen$  Compounds in the Skeletal Vibration Region.

X = F	X = Cl, Br, I	Assignment
515(sh)		$\nu(\text{Sb}-\text{F})$
502 vs		
470 w	472 w	
452 vw		
435 vw	437 vw	} $\nu(\text{Sb}-\text{N})$ and $\nu(\text{Sb}-\text{O})$
415 m	417 m	
331 vw	331 w	
295 m	288 m	
275 m	265 w	
262 m(sh)		
230 m	225 sh	

$C_6H_4O_2SbF \cdot Phen$ : 1620 w, 1590 w, 1575 w, 1516 m, 1422 ms, 1344 w, 1330 w, 1312 wv, 1250 vs, 1225 w, 1206 w, 1150 w(br), 1104 mw, 1090 w, 1020 mw, 905 vw, 895 vw, 865 m, 853 ms, 795 s, 748 s, 742 s, 725 s, 720 s, 650 m, 638 m, 609 ms, 553 vw, 534 w.

$C_6H_4O_2SbCl \cdot Phen$ : 1620 w, 1585 w, 1575 w, 1514 m, 1425 m, 1342 mw, 1326 vw, 1318 vw, 1302 vw, 1257 s, 1250 s, 1222 w, 1203 mw, 1142 w, 1100 mw, 1090 w, 1020 w, 910 w, 896 w, 864 m, 854 ms, 795 ms, 742 ms, 735 ms, 722 vs, 642 ms, 617 ms, 545 w.

$C_6H_4O_2SbBr \cdot Phen$  and  $C_6H_4O_2SbI \cdot Phen$  show an infrared spectrum practically identical with that of the chloride.

Conductance measurements were performed on 1.0 mM methanolic solutions at 25 °C, using an LKB 5300 B instrument. Molar conductivity data are reported in Table I.

The mass spectra of the fluoride and the chloride derivatives were obtained using a Jeol JMS-01SG-2 double focusing spectrometer, at 75 eV (100  $\mu\text{A}$ ).

These show a complex dependence on temperature. The molecular peak is always absent. This appears to be ascribed to an easy dissociation of the Phen ligand, whose ionic fragments constitute in fact the most intense signals even at low temperature. Other major fragments were identified as  $C_6H_4O_2SbX$  and  $C_6H_4O_2Sb$ . The relative intensity of peaks due to the latter is strongly increasing with temperature and near the melting (or decomposition) point a bis-catecholate species,  $(C_6H_4O_2)_2Sb$ , appears in the spectra.

## Discussion

The infrared spectra of the adducts can be profitably compared with those of parent species,  $C_6H_4O_2SbX$  and Phen, and with spectra of phenanthroline–metal complexes (see for example 7, 8 and Refs. therein), including  $SbX_3 \cdot Phen$  species [1]. In the 1600–400  $\text{cm}^{-1}$  region the distinction between single contributions from the catecholate and Phen ligand systems is not always possible; nevertheless, most of the typical small shifts of certain bands of free Phen (1615, 1505, 842, 622, 408  $\text{cm}^{-1}$ ) which are characteristic of this ligand upon chelation [7, 8], can be recognized. Among the various absorptions attributable to the catecholate ligand, a distinctive feature appears to be a strong band or a doublet, at about 1250  $\text{cm}^{-1}$ , whose likely assignment is the C–O stretching vibration of coordinated CO groups.

In the skeletal vibrations region  $C_6H_4O_2SbF \cdot Phen$  shows only one band attributable to  $\nu(\text{Sb}-\text{F})$ , which is in accordance with its molecular monomeric structure. The latter is in fact known [5], and the coordination about Sb may be described as a distorted tetragonal pyramid with the two nitrogens (257 and 245 pm), one oxygen (206 pm) and the fluorine (196 pm) atoms forming the basis, the second cate-

cholato oxygen (201 pm) being in the apical position. The measured  $\nu(\text{Sb}-\text{F})$  frequency may appear too low when compared for instance with those of  $\text{C}_6\text{H}_4\text{O}_2\text{SbF}$  itself (572 and 548  $\text{cm}^{-1}$ ) [2], where bridging F atoms are present, but this may well be the consequence of the increased coordination number about antimony and the relatively large Sb-F bond distance which is in the upper range observed for antimony compounds with 'terminal' fluoro ligands. The proposed assignments for  $\nu(\text{Sb}-\text{N})$  and  $\nu(\text{Sb}-\text{O})$ , Table II, were made on the basis of very similar frequencies displayed in the 300–200  $\text{cm}^{-1}$  region by  $\text{SbF}_3\cdot\text{Phen}$  (275, 260  $\text{cm}^{-1}$ ) [1] and  $\text{C}_6\text{H}_4\text{O}_2\text{SbF}$  (300, 240  $\text{cm}^{-1}$ ) [2].

The remaining  $\text{C}_6\text{H}_4\text{O}_2\text{SbX}\cdot\text{Phen}$  (X = Cl, Br, I) compounds show identical spectra (different from that of the fluoride) even at low frequency. For this reason, although in the case of the chloride the band at 288  $\text{cm}^{-1}$  has the expected energy for a Sb-Cl stretching, assignment to this mode cannot be straightforward. Indeed, the features observed below 300  $\text{cm}^{-1}$  seem better attributable to Sb-N and Sb-O stretching and there exists a definite possibility that the  $\nu(\text{Sb}-\text{Cl})$  mode might be absent in the spectrum of  $\text{C}_6\text{H}_4\text{O}_2\text{SbCl}\cdot\text{Phen}$ . In this case this compound (and possibly the bromo- and the iodo-derivatives) would be structurally different from the fluoride. The presence of considerably ionic halide appears at present the most reasonable hypothesis.

The molar conductance data for methanol solutions, Table I, also indicate a distinctive behaviour of the fluoride. This appears to be weakly dissociated, whereas data for X = Cl, Br and I are typical of 1:1 electrolytes, their conductivities for 1.0 mM solutions being expected in the range 80–115  $\text{ohm}^{-1}$

$\text{cm}^2 \text{mol}^{-1}$  [9]. Further studies have been planned in order to clarify the solution ionization scheme of these salts. Possibly, cationic species containing both the catecholato and the Phen ligands are present but equilibria involving dissociation of the Phen ligand as well as the existence of  $\text{C}_6\text{H}_4\text{O}_2\text{Sb}(\text{Phen})_2^+$  species where antimony attains a higher coordination number, cannot be excluded. In order to gain further information on this cationic species the synthesis and the structural characterization of some salts with non-coordinating anions such as  $\text{Ph}_4\text{B}^-$  has been also planned, and the results will be published later.

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