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The Far Infrared and Raman Spectra of Orthophenylenedioxyantimony(III) Halides

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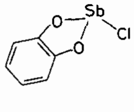
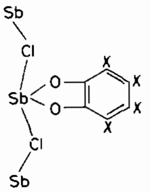
The orthophenylenedioxyantimony(III) halides, $(C_6H_4O_2)SbX$ (X = F, Cl or Br) were prepared by adding methanolic solutions of antimony(III) halides to orthodihydroxybenzene in methanol and recrystallising the products from acetonitrile. The structures of the compounds could be based on a trigonal pyramidal coordination (I) for the antimony,



I



II

similar to that found in $SbCl_3$ [1]. However, the alternative chloro-bridged chain polymer structure (II) has to be considered in view of the chloro-bridged structures of SbOCl [2] and $Sb_4O_5Cl_2$ [3], and the double halide-bridged antimony environments found in the related dihalo–tetrahalo-1,2-diphenoxoantimonate(III) complexes [4], $RH^+[C_6X_4O_2SbX_2]^-$. The complex $(C_5H_5NH)(C_6Cl_4O_2SbCl_2)$, for example, has an antimony environment consisting of two short Sb–O bonds at 2.05 and 2.07 Å, one short Sb–Cl bond at 2.47 Å and two longer Sb–Cl distances (2.88 and 3.00 Å) to bridging Cl atoms [4].

We now show that X-ray diffraction data on $(C_6H_4O_2)SbCl$ and the vibrational spectra of the series of halides $(C_6H_4O_2)SbX$ (X = F, Cl, Br) are consistent with the polymer structure (II) rather than with the monomer (I).

X-ray diffraction single crystal rotation and Weissenberg photographs taken with CuK_α radiation about the *b* and *c* axes of $(C_6H_4O_2)SbCl$ show that the crystals are monoclinic with a = 7.42, b = 7.80, c = 5.86 Å, β = 88°, D_o = 2.59 g cc^{-1}, D_c = 2.62 g cc^{-1} for Z = 2. The only systematic absences are hk0 with k odd and the space group is $P2_1/m$ or $P2_1$. All crystals of $(C_6H_4O_2)SbCl$ gave patterns corresponding to a polycrystalline sample when investigated along the *a*-axis which indicated a degree of disorder in this direction. This disorder prevented the determination of the complete single crystal structure but Weissenberg intensity data collected about the *b* and *c* axes with MoKα leads to a partial structure. The Sb atoms were located by means of a Patterson synthesis and refined to converge in the position x = 0.0197, y = 0.25, z = 0.151. A three-dimensional Fourier map was then used to locate the Cl atoms in bridging positions at z = 0.651 between the Sb atoms. The positions of the lighter atoms could not be located accurately with the data available but the Sb and Cl positions favour the

TABLE I. Far Infrared and Raman Data (cm^{-1}) for the $(C_6H_4O_2)SbX$ Compounds.

X		F		Cl		Br	
		IR	R	IR	R	IR	R
Sb–X	A_1	572vs	564vs	292s	280s	264vs	226s
Stretch	B_2	548s	545ms	348s	326	292s	280ms
Sb–O	A_1	300s	280vs	320s	312	328s	324s
Stretch	B_2	240vs	232s	252vs	240s	240vs	226s
		164s		190m	180mw	160sh	180m
Bending		120w		112m		120ms	
and		104m	108m	96m		92ms	
Lattice		84m		72w		68sh	
		72vw					

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TABLE II. Normal Modes of the Cl–Sb(O_2)–Cl Vibrating Unit of C_{2v} Symmetry.

Modes	Number of Modes of Symmetry			
	A_1	A_2	B_1	B_2
Sb–O stretch	1		1	
Sb–Cl stretch	1			1
Bending	2	1	1	1
Total	4	1	2	2
Activity	IR/R	R	IR/R	IR/R

polymeric structure (II) and Sb–Cl distances of about 2.9 Å.

The far infrared and laser Raman spectra of the compounds ($C_6H_4O_2$)SbX (X = F, Cl or Br) were recorded in the range 40–600 cm^{-1}. The data (Table I) show coincidences between infrared and Raman bands and have been assigned in terms of a Cl–Sb-(O_2)–Cl vibrating unit. The assigned bands for the Sb–X stretching modes show the expected decrease in frequency with increasing mass of halide. The bands may be reasonably assigned on the assumption that the vibrating unit is the Cl–Sb(O_2)–Cl moiety of structure (II) that has C_{2v} symmetry. A normal coordinate analysis reveals the normal modes given in Table II with their infrared or Raman activity. Eight infrared and nine Raman active bands are thus expected. The observed spectra are in good agreement with this analysis in that eight infrared bands are observed in all three compounds. The additional very weak band at 72 cm^{-1} in the infrared spectrum of the fluoride may be associated with a lattice mode. Only four of the nine possible Raman bands are observed which is not surprising in view of the low intensity of the scattered radiation at low energies. There is, moreover, reasonable agreement between the frequencies of the coincident bands found in the infrared and Raman spectra.

In summary, we conclude that, on the basis of far infrared and Raman data the compounds ($C_6H_4O_2$)-SbX (X = F, Cl, or Br) form an isostructural series with a bridging $(ClSbO_2C_6H_4)_n$ chain polymer structure in which the Sb atoms are four coordinated with two Sb–O and two Sb–X bonds to bridging X atoms as suggested by a partial structure determination of ($C_6H_4O_2$)SbCl.

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