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Studies on some Antimony(III) Complexes with Tridentate Schiff Base Ligands

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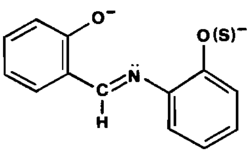
The antimony(III) complexes FSb(Sab), ClSb(Sab) and ClSb(Sat) containing dianonic, potentially tridentate Schiff-base ligands with ONO(Sab^{2-}) and ONS(Sat^{2-}) donor atoms have been prepared and characterized. The mass spectra of these derivatives are reported. The occurrence of chelation by the tridentate ligand is inferred from the infrared data. The antimony-121 Mössbauer parameters at 4.2 K are reported. The magnitudes and the positive sign of eQV$_{zz}$ suggest a consistent p-character of the antimony lone-pair orbital. Observed differencies in the isomer shift and eQV$_{zz}$ values are discussed on the basis of the likely distribution of electron density around antimony.

Introduction

Complexes with the formulae ROSb(Trid) and $Sb_2(Trid)_3$ have been reported recently [1] as the products of the reaction of Sb(III) isopropoxide with tridentate Schiff bases (Trid) having the donor atoms ONO. These are apparently the only examples of compounds of Sb(III) with tridentate dianionic ligands described in the literature. In order to increase our understanding of this type of compound, we have investigated the products obtainable from Sb(III) halides and two Schiff base dianions with a planar tridentate ONO(Sab^{2-}) or ONS(Sat^{2-}) donor system. These represent



Sab$^{=}$ or Sat$^{=}$

typical members of a large class of planar ONO(S) ligands whose coordinating behaviour has been extensively studied in a large number of complexes of main group elements, including Sb(V) (see for example [2–10] and refs. therein).

Experimental and Results

Synthesis

The diprotonated free ligands H_2Sab and H_2Sat (H_2Trid) were obtained from the condensation of

TABLE I. Analytical Data and Relevant IR Absorptions of XSb(Trid) Compounds.

Compound (colour)	M.p. (°C)	Analyses, found (calcd.) (%)				I.R. (cm^{-1})		
		C	H	N	Cl	ν(C–N)	ν(C–O)	ν(Sb–X)
FSb(Sab)	255–258	43.77	2.84	3.64		1610 vs	1535 m	705 s(br)
(red)	(dec.)	(44.36)	(2.58)	(3.98)				
ClSb(Sab)	159–161	42.88	2.70	3.66	9.51	1605 vs	1545 s	300 ms
(orange-red)	(dec.)	(42.38)	(2.46)	(3.80)	(9.62)			
ClSb(Sat)	210–212	41.00	2.56	3.55	9.42	1615 vs	1550 s	315 s
(orange)	(dec.)	(40.61)	(2.36)	(3.64)	(9.22)			

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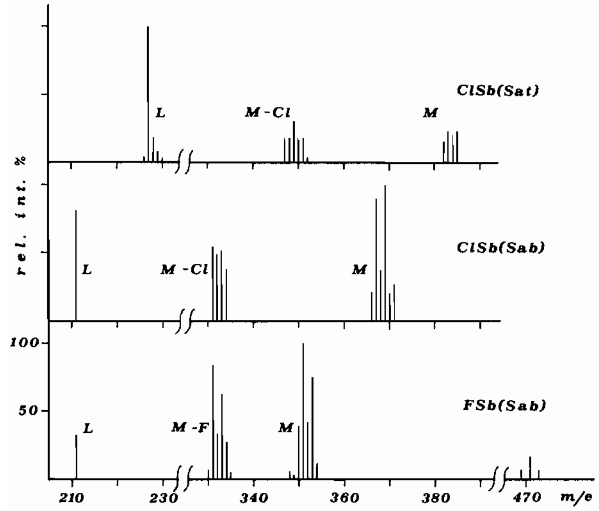

Fig. 1. Mass spectra of XSb(Trid). In the possible formula assignments of the ionic fragments M and L indicate the complex and the tridentate ligand, respectively.

salicylaldehyde with 2-aminophenol and 2-aminothiophenol respectively, as reported elsewhere [2].

Reactions of antimony(III) halides SbX_3 (X = F, Cl, Br) with these ligand systems were carried out using (a) the sodium salt of the ligands and (b) the corresponding $Me_2Sn(Trid)$ complex in the hope of observing a $Trid^{2-}$ metathesis between tin and antimony [6, 9]. All reactions were carried out in an atmosphere of dry nitrogen by mixing methanolic solutions of the appropriate reagents in 1:1 molar ratio. In most cases the reaction resulted in impure or stoichiometrically ill-defined products. Under conditions (a) however, we were able to obtain coloured microcrystalline solid samples of FSb(Sab), ClSb(Sab) and ClSb(Sat). Physical and analytical data are reported in Table I.

Spectroscopic Measurements

IR spectra were run on nujol mulls in the range of 4000–200 cm^{-1} with a Perkin-Elmer 580 spectrophotometer. Relevant absorption bands are also listed in Table I.

The mass spectra were measured with a Jeol JMS-01SG-2 double focusing spectrometer at 75 eV (100 μA). The samples were directly introduced and heated at about 150 °C. Figure 1 shows the mass spectral data in the region ranging from the m/e value corresponding to the ligand ionic fragment to the highest one observed.

The ^{121}Sb Mössbauer spectra were recorded at 4.2 K using the apparatus and procedures described previously [10]. The spectra were curve-fitted using a conventional summation of twelve Lorentzian lines. The final values of the spectroscopic parameters: the chemical isomer shift δ relative to the Ca $^{121m}SnO_3$ source, the ground-state quadrupole coupling constant eQV_{zz}, the asymmetry parameter η and the linewidth 2Γ, are given in Table II.

TABLE II. Mössbauer Data at 4.2 K.

Compound	δ (mm/s)	eQV_{zz} (mm/s)	η	2Γ (mm/s)
FSb(Sab)	−12.43(3)	18.3(3)	0.49(4)	3.60(7)
ClSb(Sab)	−13.67(2)	14.6(3)	0.57(5)	3.52(7)
ClSb(Sat)	−13.49(2)	17.0(2)	0.69(4)	3.64(7)

Discussion

The proposed formulae are supported by the analytical data as well as by the mass spectra. Although no fragmentation pattern is available in the literature for compounds of this general type, the one observed here appears reasonable. We note in all cases clusters of fragments corresponding to the formula weight M and to the loss of X and SbX. M is apparently the molecular ion peak in the cases of ClSb(Trid), and it is the base peak in the spectra of XSb(Sab). In the case of FSb(Sab) peaks are present at m/e values higher than M by about 120 units. In the absence of high resolution measurements their identification poses some problems, and it is difficult to decide whether or not they arise directly from associated species existing in the solid.

Comparison of the infrared spectra with those of the diprotonated ligands [2] reveals band shifts very similar to those observed in a large variety of metal Sab^{2-} or Sat^{2-} complexes, as well as the disappearance of the OH stretch. According to previous studies [2, 6–9] the present data can be interpreted in terms of chelation of Sb(III) by $(Trid)^{2-}$ (the frequencies in the ν(C–N) and ν(C–O) region are diagnostic). A vibrational band which appears in a spectral region free from absorptions due to the ligand can be identified as ν(Sb–X). The high energy of ν(Sb–F) possibly indicates a terminal rather than a bridging Sb–F stretching [11].

The Mössbauer chemical isomer shifts are typical of Sb(III) species. The value and sign of the quadrupole coupling constants are though to be consistent with a major contribution to the principal component of the electric field gradient V_{zz} by a p-electron excess in the antimony lone-pair orbital. However, the large η values reflect a distribution of electron density about the Sb atom of very low symmetry, so that the direction of V_{zz} is not necessarily coincident with that of the stereochemically active lone-pair. This consideration, together with the lack of structural data, renders almost impossible a detailed rationalization of the Mössbauer parameters. Qualitatively, however, it seems reasonable to ascribe the less negative chemical isomer shift and the more positive eQV_{zz} of FSb(Sab) to a low s-character and therefore a high p-character for the non-bonding electrons. Since electronegativity arguments predict a larger electron-withdrawing effect for the fluoride ligand, this would imply utilisation of Sb 5s-electrons in the Sb–F bond at the expense of the s-character of the lone-pair. ClSb(Sab) and ClSb(Sat) show a significant difference in the values for eQV_{zz}, whereas the chemical isomer shift values are very similar. Since Mössbauer data for Sn(IV) [6, 7] and Sb(V) [10] complexes with the same ligands indicate that the S-donor atom of the ONS chelate should be assigned a lower electron-withdrawing ability, as well as a large (more negative) partial field gradient contribution, the present data can be interpreted in terms of a substantial p-electron character in the Sb–O(S) bond. Thus, changes along this bond affect the s-density at Sb mainly *via* a p-shielding effect, while the increased partial electric field contribution of sulphur and its likely geometric relationship to the lone-pair result in an augmentation of eQV_{zz} as observed.

The 'planar' nature of chelating $(Trid)^{2-}$ as demonstrated by the X-ray structures of $R_2Sn(Trid)$ and $R_3Sb(Trid)$ species [3–5, 8], leaves only a few possible stereochemistries for our XSb(Trid) species. These arise from the possibility in the solid state of either monomeric species, or dimeric units with bridges *via* the halogen or a donor atom of the tridentate ligand. An example of the latter possibility is perhaps given by the 'quasi-dimeric' nature of $Me_2Sn(Sab)$ [4]. The resulting pseudo-five or pseudo-six coordinations about antimony(III) are essentially the same as those proposed for tin in X_2-Sn(Trid) species [6] with replacement of a halide by an electron lone-pair. Although the present work does not differentiate between the various possible structures, it is worth noting that in all cases the lone-pair is at approximately 90° to the Sb–O(S) bond, whereas a larger angle would exist between the lone-pair and the Sb–X bond.

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