

Antimony-121 Mössbauer and Infrared Spectral Studies on 1,10-Phenanthroline Adducts of Antimony(III) Halides

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The syntheses of the mono-adducts of 1,10-phenanthroline with SbX_3 ($X = F, Cl, Br$) and $PhSbI_2$ are described. These compounds and the 1:1 adduct between 2,2'-bipyridine and $PhSbI_2$ have been characterized mainly in the solid state by infrared and Mössbauer spectroscopic techniques. The structures of the antimony trihalide complexes appear to be based on halogen bridged polymers in which the stereochemical activity of the lone pair of electrons varies with the halogen, the highest p -character of the lone pair being observed with the trifluoride adduct. Mössbauer results for the $PhSbI_2$ complexes suggest a ψ -octahedral stereochemistry with the lone pair and the Ph group in trans positions.

Introduction

Antimony(III) halides, as well as arsenic(III) and bismuth(III) halides, have been reported to form a wide range of solid adducts with nitrogen containing donors. Even though structural information on such compounds is still rather scarce, the few structures which have been solved together with vibrational

spectroscopic studies indicate that the coordination number, geometry, and the stereochemical behaviour of the lone pair of electrons (1p) are all variable. In this paper we report on the isolation of solid 1:1 adducts between SbX_3 ($X = F, Cl, Br$) and $PhSbI_2$ with 1,10-phenanthroline (Phen), and their characterization by Mössbauer and infrared spectroscopic techniques. Similar 1:1 adducts with 2,2'-bipyridine (Bipy), apart from the SbF_3 complex, have been described [1, 2] and one of these complexes, $PhSbI_2 \cdot Bipy$, has been included in our spectroscopic study.

Experimental and Results

Commercially available reagents and solvents were used. The Phen ligand was used as the commercial monohydrated form. $PhSbI_2$ was synthesized according to a published procedure [3].

Compounds were generally obtained upon mixing freshly prepared CH_2Cl_2 solutions of antimony halide and the ligand in 1:1 molar ratio. $SbF_3 \cdot phen$ was obtained from MeOH solutions. Physical and analytical data are reported in Table I.

TABLE I. Physical, Analytical and Molar Conductivity Data.

Compound (colour)	M.p. (°C)	Analyses, found (calcd.) (%)				λ_M ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
		C	H	N	halogen	
$SbF_3 \cdot Phen$ (white)	190–192	40.11 (40.15)	2.31 (2.25)	7.76 (7.80)		11
$SbCl_3 \cdot Phen$ (p. yellow)	185 (dec.)	35.56 (35.30)	2.06 (1.97)	6.76 (6.86)	25.95 (26.05)	141
$SbBr_3 \cdot Phen$ (b. yellow)	230 (dec.)	26.87 (26.61)	1.59 (1.49)	5.15 (5.17)	42.67 (44.26)	177
$PhSbI_2 \cdot Phen$ (red)	240 (dec.)	37.78 (34.16)	2.06 (2.07)	4.26 (4.43)	39.60 (40.11)	
$PhSbI_2 \cdot Bipy$ (red)	188–190	31.29 (31.56)	2.26 (2.15)	4.38 (4.60)	40.30 (41.69)	

TABLE II. Relevant IR Bands (cm^{-1}).

Compound	Coordinated Phen or Bipy	Other bands (in the skeletal vibration region) and assignment	
$\text{SbF}_3 \cdot \text{Phen}$	1621mw, 1510m, 858ms, 847ms, 728ms, 714ms, 632ms, 425ms	585s, 525s 438ms, 410s 275mw, 260mw	$\nu(\text{Sb-F})$ $\nu(\text{Sb-F})$ $\nu(\text{Sb-N})$ (and $\delta(\text{SbF})?$)
$\text{SbCl}_3 \cdot \text{Phen}$	1624w, 1515m, 855m, 852vs, 734s, 721m 712vs, 644ms, 427m	303mw 270m 232s ca. 210s	$\nu(\text{Sb-Cl})$ and $\nu(\text{Sb-N})$
$\text{SbBr}_3 \cdot \text{Phen}$	1622w, 1515m, 867m, 853s, 734m, 722m, 712s, 645ms, 427mw	302w 280w 248w ca. 205ms?	$\nu(\text{Sb-N})$ $\nu(\text{Sb-Br})?$
$\text{PhSbI}_2 \cdot \text{Phen}$	1620vw, 1512mw, 862mw 845ms, 728(sh), 720s 637m, 415mw	248w 220w ca. 205m?	$\nu(\text{Sb-N})$ and $\nu(\text{Sb-Ph})$
$\text{PhSbI}_2 \cdot \text{Bipy}$	1592m, 1580vw, 1570vw, 761s, 732ms, 725ms, 410m, 346w	242w 232m	$\nu(\text{Sb-N})$ and $\nu(\text{Sb-Ph})$

TABLE III. Mössbauer Data at 4.2 K.

Compound	δ (mm s^{-1})	eQV_{zz} (mm s^{-1})	η	2Γ (mm s^{-1})
$\text{SbF}_3 \cdot \text{Phen}$	-13.97(3)	16.8(3)	0.01(4)	2.62(6)
$\text{SbCl}_3 \cdot \text{Phen}$	-15.38(7)	9.2(3)	0.86(7)	3.20(7)
$\text{SbBr}_3 \cdot \text{Phen}$	-15.95(2)	5.7(5)	0.49(25)	2.83(10)
$\text{PhSbI}_2 \cdot \text{Phen}$	-14.29(3)	27.7(4)	0.15(4)	2.55(7)
$\text{PhSbI}_2 \cdot \text{Bipy}$	-14.15(3)	26.3(4)	0.35(3)	2.94(6)

Conductance measurements were performed on 1.0 mM methanolic solutions of the more soluble SbX_3 complexes, and molar conductivities at 25 °C are given in Table I.

Infrared spectra of the solids were run on nujol mulls in the range of 4000–180 cm^{-1} using a Perkin-Elmer 580 spectrophotometer. Relevant infrared absorptions are reported in Table II.

The ^{121}Sb Mössbauer spectra were recorded at 4.2 K using the apparatus and procedures described previously [4]. 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 $\text{Ca}^{121\text{m}}\text{-SnO}_3$ source, the ground-state quadrupole coupling constant eQV_{zz} , the asymmetry parameter η and the linewidth 2Γ , are given in Table III. Typical spectra for $\text{SbF}_3 \cdot \text{Phen}$ and $\text{PhSbI}_2 \cdot \text{Phen}$ are shown in Fig. 1.

Discussion

Conductance measurements show that the trichloride and tribromide adducts are appreciably ionised in methanol, whereas $\text{SbF}_3 \cdot \text{Phen}$ behaves essentially as a molecular species. Thus, our findings for the SbCl_3 and SbBr_3 adducts resemble those reported [1, 5] for $\text{MX}_3 \cdot \text{Bipy}$ ($\text{M} = \text{As}, \text{Sb}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{AsCl}_3 \cdot \text{Phen}$ in nitrobenzene. However, the simple ionization of one halide, leading to $[\text{MX}_2\text{L}]^+ \text{X}^-$, which has been proposed [1, 5] does not apply to the case of our compounds in methanol because observed conductivities are clearly higher than those of typical 1:1 electrolytes in this solvent, which are expected to be in the range 80–115 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ for 1.0 mM solutions [6].

The IR spectra of solid adducts in the 1600–400 cm^{-1} range show the typical shifts and splittings of certain bands of free Phen (1615 m, 1505 ms, 842 vs,

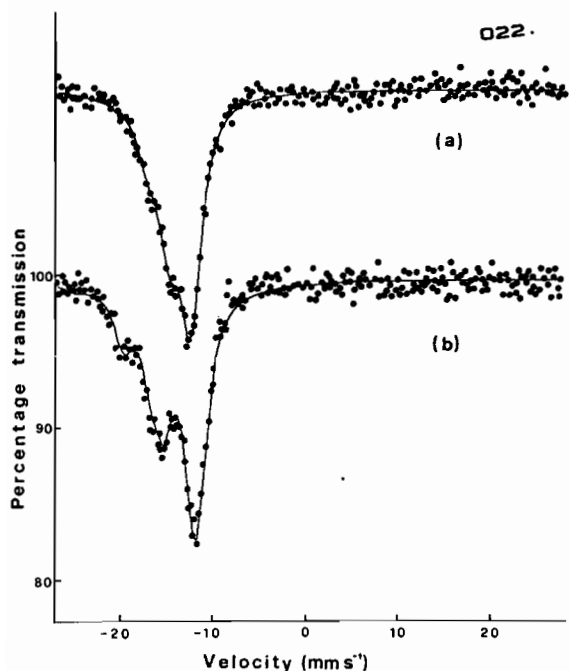


Fig. 1. Antimony-121 Mössbauer Spectra at 4.2 K of (a) $\text{SbF}_3 \cdot \text{Phen}$ and (b) $\text{PhSbI}_2 \cdot \text{Phen}$.

734 vs, 622 ms, 402 m) [7] and free Bipy (1580 ms, 1558 m, 751 s, 735 sh, 402 s) [8] which are characteristic of these ligands upon chelation (see for example [7–10]).

The corresponding Sb–N stretching vibrations can be assigned to one or two medium to weak bands near 250 cm^{-1} according to similar assignments made for the spectra of $\text{SbX}_3 \cdot \text{Bipy}$ complexes [2].

In the skeletal vibration region $\text{SbF}_3 \cdot \text{Phen}$ shows two bands at 585 and 525 cm^{-1} , attributable to Sb–F stretchings. In addition, this compound shows three absorptions in the $440\text{--}410 \text{ cm}^{-1}$ interval, one of which derives from the 402 cm^{-1} band of the Phen ligand, whereas the remaining two must be attributed to modes involving Sb–F motions. These are assigned to $\nu(\text{Sb–F})$ modes by virtue of their energy and, although they appear in a range regarded as borderline between terminal and bridging Sb–F stretching frequencies [11], the total number of $\nu(\text{Sb–F})$ frequencies observed would only be consistent with the presence of bridging fluoro ligands.

With $\text{SbCl}_3 \cdot \text{Phen}$ the intensity of bands appearing between 300 and 200 cm^{-1} suggests that, in addition to $\nu(\text{Sb–N})$, the strong $\nu(\text{Sb–Cl})$ vibrations are also contributing in this region. This would extend the range of these modes to considerably lower frequencies and indicates the presence of bridging chlorine atoms. Analogous results have been found with $\text{SbCl}_3 \cdot \text{Bipy}$ [2].

Further structural information on these complexes, as well as on the remaining adducts whose

$\nu(\text{Sb–X})$ frequencies lie below the lower limit of the instrument, is obtained from their ^{121}Sb Mössbauer spectra.

In the $\text{SbX}_3 \cdot \text{Phen}$ series definite trends for both δ and eQV_{zz} can be recognised. In fact, as the halogen changes from F to Br, δ becomes more negative, implying an increase of the electron density at Sb, while at the same time eQV_{zz} decreases drastically.

Spectral parameters of $\text{SbF}_3 \cdot \text{Phen}$ are very close to those reported for other antimony(III) fluoro-species [12–14], and the value of eQV_{zz} is consistent with the presence of a stereochemically active 1p (as invariably found in this type of compound [13, 14 and Refs. therein]), and through its p-character provides the dominant contribution to the electric field gradient principal component, V_{zz} . Pertinent to this conclusion is the fact that this compound does not show a significant value of η , which would be expected to be the case if V_{zz} and the 1p directions are nearly collinear. Considering that with antimony(III) compounds the s-electron density at the nucleus is mainly dictated by the s-character of the 1p, the concomitant decrease of δ and eQV_{zz} observed with the chloride and the bromide appear attributable to a decrease of the p-character of the 1p along the series. Clearly, as the contribution of the 1p to eQV_{zz} decreases, the p-imbalance created by the ligands may become a substantial part of the observed eQV_{zz} .

Thus, taking into account previous infrared results, it appears reasonable to conclude that the solid state structures of these adducts are based on halogen bridged dimers or chain polymers in which the actual geometry about Sb depend on the changing steric requirements of the 1p. In particular, the directional character of the latter already appears considerably reduced in $\text{SbCl}_3 \cdot \text{Phen}$.

The Phen and Bipy adducts of PhSbI_2 show similar Mössbauer data, suggesting a related structure. In addition, their spectroscopic parameters are close to those observed for PhSbX_3 species [15], and we believe that in this case also the large and positive eQV_{zz} is originating mainly from contributions to V_{zz} from the 1p and the Sb–Ph bond electron densities, which are effectively additive by virtue of a large angle between their directions. This suggests a ψ -octahedral stereochemistry about Sb, with the 1p and Ph groups in *trans*-positions. This hypothesis can be supported by point-charge model calculations of the electric field gradient [16], assuming negative partial field gradient contributions from the ligands in the order $[1p] \sim [\text{Ph}] > [\text{I}] > [\text{N}]$.

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