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Synthesis, Antimony-121 Mössbauer and Infrared Spectral Characterization of Antimony Trifluoride and Catecholatoantimony(III) Fluoride Adducts with Tridentate Nitrogen Donors

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Abstract

The synthesis of the adducts $SbF_3(L)$ and $(C_6H_4O_2)SbF(L)$ [L = pyridine-2-carboxaldehyde-2-pyridylhydrazone (paphyH); 2,2′:6′,2″-terpyridine (terpy) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpta)] is reported. Infrared data are consistent with the occurred chelation from the terdentate ligand providing an overall pseudo-seven coordination at Sb. The stereoactivity of the antimony lone pair is inferred from the large value of the Mössbauer quadrupole coupling constant observed for all the compounds.

Introduction

The acceptor properties of antimony(III)- and catecholatoantimony(III) halides towards neutral bidentate ligands such as 1,10-phenanthroline (phen) have been previously investigated [1–4]. The tendence shown by antimony to expand its coordination number as in $[(C_6H_4O_2)Sb(phen)_2]^+$ [4] or in the adducts SbX_3(phen) [3] through the probable formation of halogen bridges, induced us to extend our studies by using potentially tridentate ligands having nitrogen donors. Here we report on the synthesis of the compounds $SbF_3(L)$ and $(C_6H_4O_2)SbF(L)$ [L = pyridine-2-carboxaldehyde-2-pyridylhydrazone (paphyH); 2,2′:6′,2″-terpyridine (terpy) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpta)].

These adducts were purposely sought in view of the considerable covalent nature of the Sb–F and Sb–O bonds of the SbF_3 and $(C_6H_4O_2)SbF$ moieties, as well as in consideration of the well assessed tridentate capability of the above ligands, in order to favour the attainment of a six- (pseudo-seven) coordination about Sb.

PaphyH is the Schiff base shown in Fig. 1 in the sin (*E*) and anti (*Z*) isomers.

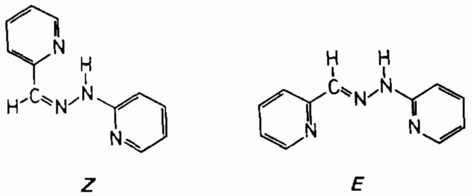

Fig. 1. The (*E*) and (*Z*) isomers of the Schiff base paphyH.

and a number of crystal structures [5–7] substantiate the meridional *NNN* tridentate ability of the (*E*) isomer, both in the neutral and in the monoanionic form.

Tpta has been reported to act primarily as a tridentate ligand, very much resembling terpy, when forming 1:1 adducts with a number of metal centers [8, 9 and refs. therein].

For Group V elements, whereas a number of terpy adducts of the trihalides (MX_3:M = As, Sb, Bi; X = Cl, Br, I; but not all combinations) have been prepared [10] showing various MX_3/terpy ratios, only the 1/1 paphyH adducts with BiX_3 have been so far reported [11].

Experimental

SbF_3 and the ligands were EGA products. The commercial paphyH corresponds to the (*E*) isomer. $(C_6H_4O_2)SbF$ was prepared as previously reported [12]. The complexes were obtained by mixing warm, freshly prepared, methanolic solutions of SbF_3 or $(C_6H_4O_2)SbF$ and the ligand in a 1:1 molar ratio. The products were obtained on cooling and recrystallized from the same solvent.

Conductance measurements were performed on 1 mM methanolic solutions at 25 °C with a LKB 5300

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TABLE I. Analytical and Molar Conductivity Data

Compound	Melting point (°C)	Analyses, found (calc.) (%)			λ_M (ohm^{-1} cm^2 mol^{-1})
		C	H	N	
SbF_3(paphyH)	250 dec.	35.50 (35.29)	2.67 (2.69)	14.86 (14.76)	8.6
$(C_6H_4O_2)SbF$(paphyH)	>350	43.94 (43.55)	2.45 (2.45)	4.27 (4.33)	10.4
SbF_3(terpy)	198–200	43.80 (43.73)	2.67 (2.69)	10.36 (10.20)	7.0
$(C_6H_4O_2)SbF$(terpy)	>350	51.49 (52.32)	3.51 (3.14)	8.60 (8.71)	8.9
SbF_3(tpta)	262–265	43.15 (44.02)	2.63 (2.46)	16.85 (17.11)	6.9
$(C_6H_4O_2)SbF$(tpta)	278–280	50.27 (51.37)	3.02 (2.87)	14.84 (14.97)	8.7

TABLE II. Relevant IR Adsorptions

L = paphyH		L = terpy		L = tpta		Assignments
SbF_3(L)	$(C_6H_4O_2)SbF$(L)	SbF_3(L)	$(C_6H_4O_2)SbF$(L)	SbF_3(L)	$(C_6H_4O_2)SbF$(L)	
3240m	3200w					ν(N–H)
3190(sh)						
1608s	1605s	1595mw	1592ms	1545(sh)	1545(sh)	
1560ms	1555m	1580(sh)	1580ms	1532vs(br)	1533vs	ν(ring)
		1575mw	1575(sh)	1510(sh)	1525(sh)	
					1510(sh)	
1540ms	1538ms					ν(C–N)[a]
	1255vs		1250vs		1250vs	ν(C–O)
1008mw	1008w	1005ms	1005ms	1003ms	1004mw	ring breath
995m	1002w	998(sh)	996mw	995mw	995(sh)	
580vs	470s	578s	450vs	573s(br)	486s	
478vs		492vs		520s(br)		ν(Sb–F)
430ms		465ms		490m[b]		
	340w		340w			
325mw	305m	265m	295m	268mw	290m	ν(Sb–N)
282m	275(sh)	250(sh)	265m		275m	and
258s[b]	250ms[b]		245(sh)			ν(Sb–O)

[a] Aldiminic. [b] Contribution also from L.

B instrument. Analytical and conductivity data are reported in Table I.

Infrared spectra on nujol and HCBD mulls between CsJ disks were obtained in the 4000–180 cm^{-1} range using a Perkin-Elmer 580 spectrophotometer. Relevant bands are reported in Table II.

^{121}Sb Mössbauer spectra were recorded using the apparatus and procedures described elsewhere [13]. Both source ($Ca^{121m}SnO_3$, nominally 0.5 mCi) and absorber (containing 12 mg Sb per cm^2) were cooled at liquid nitrogen temperature. About 2.10^5 counts per folded channel (128) were accumulated and the spectra were computer fitted by a least-squares procedure to the sum of twelve lorentzians (halfwidths in the range 2.4–2.9 mm s^{-1}). The final parameters are given in Table III together with literature data [2–4, 13, 14] for related compounds. Figure 2 shows a representative spectrum.

Discussion

The new adducts are yellow or pale yellow microcrystalline solids, stable in air for only a few weaks.

TABLE III. ^{121}Sb Mössbauer Parameters

Compound	δ (mm s^{-1})	eQV_{zz} (mm s^{-1})	η	Reference
SbF_3	−14.6	19.6	0	14
SbF_3(phen)	−13.9	16.8	<0.1	3
SbF_3(paphyH)	−13.8	16.2	<0.1	
SbF_3(terpy)	−13.8	13.5	<0.1	
SbF_3(tpta)	−14.0	13.8	<0.1	
$(C_6H_4O_2)SbF$	−13.8	18.4	0.42	13
$(C_6H_4O_2)SbF$(phen)	−14.3	15.4	<0.1	2
$(C_6H_4O_2)Sb(phen)_2^+$	−14.0	16.1	<0.1	4[a]
$(C_6H_4O_2)SbF$(paphyH)	−13.3	19.1	<0.1	
$(C_6H_4O_2)SbF$(terpy)	−13.5	16.7	<0.1	
$(C_6H_4O_2)SbF$(tpta)	−13.8	17.2	<0.1	

[a] BPh_4^- salt.

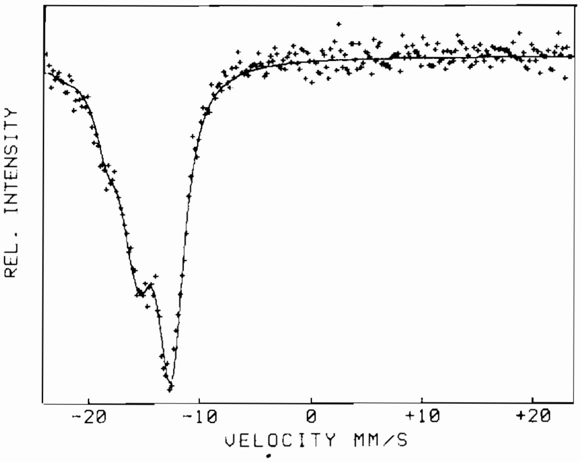

Fig. 2. Mössbauer spectrum of $(C_6H_4O_2)SbF$(paphyH).

The small measured conductivity values are in accord with the expected low ionizability of the Sb–F bonds as observed for SbF_3 itself [1].

The occurred coordination from the ligands is inferred from infrared spectra particularly from the modification and the shift to higher frequencies of the ring stretching and breathing modes of the pyridine units compared with the free ligands.

For tpta derivatives, the distinction between modes attributable to pyridine rings and to the triazine one, as well as between coordinated and uncoordinated (one residual) pyridine groups, seemed in practice not feasible. We note, however, that infrared shifts observed with the present compounds are similar to those reported for 1/1 metal tpta complexes [9 and refs. therein]. The coordination from paphyH, which is present in the neutral form as indicated by the ν(N–H) band, results also from the bathocromic shift and intensity enhancement of the ν(C–N) (aldiminic) mode.

Previous studies on paphyH derivatives have shown that complexes of the bidentate (*Z*) isomer, Fig. 1, can also exist [15–18], and reported vibrational data [15, 16] do not support the possibility of safely distinguishing between bidentate or tridentate chelates on the basis of infrared bands of the ligand moiety.

Reasonable support for a tridentate chelating behaviour of the ligands comes from the skeletal vibration region where each family of SbF_3 and $(C_6H_4O_2)$-SbF adducts show similar ν(Sb–F) absorptions. The single ν(Sb–F) for the catecholato derivatives is found at a lower frequency than that (502 cm^{-1}) observed for the pentacoordinate species $(C_6H_4O_2)$-SbF(phen) [1], in accord with an increase of the coordination number. The ν(Sb–F) absorptions of the SbF_3 complexes result in a simpler pattern than that observed in the case of SbF_3(phen) (ν(Sb–F): 585, 525, 438, 410 cm^{-1}) [3]. Recorded frequencies for terpy and tpta complexes exclude the presence of bridging fluoro ligands which woul be consistent with a coordination demand from antimony which is now satisfied by a tridentate, rather then bidentate, chelating ligand. The latter consideration does not confidently apply to the case of SbF_3(paphyH) since the lowest lying ν(Sb–F) assignment can be regarded as borderline between terminal and bridging Sb–F stretching frequencies. The number of ν(Sb–F) absorptions observed for the trifluoro derivatives indicates a reduction from the C_{3v} symmetry expected for an isolated SbF_3 unit. The latter, however, is presumably maintaining the pyramidal geometry commonly found (from X-ray studies) for SbF_3 complexes (see for example [19–22]), which is somehow distorted because of the steric and electronic requirements from the chelating ligand and from the antimony nonbonding electron pair.

Mössbauer data, besides showing isomer shift values similar to those measured for related antimony(III) species (Table III), are primarily interpreted, from the positive and relatively large value of eQV_{zz}, as indicating the presence of a stereoactive lone pair in all the complexes. This parallels what was observed for $[(C_6H_4O_2)Sb(phen)_2]^+$ [4] where the attainment of a hexa-coordination does not sensibly reduce the stereoactivity of the antimony lone pair. This behaviour, in turn, seems imputable, also in the case of the present derivatives, to the presence of short, highly s-demanding, Sb–F or Sb–O bonds. Correspondent terpy and tpta derivatives display sensibly similar eQV_{zz} values as expected from the close geometrical similarity of the two chelating ligands. In each series, the paphyH adduct shows a somewhat larger eQV_{zz} value. This could arise from several sources, including a different coordination of the ligand, but a clear rationalization of these data is not feasible in the light of the fairly large variability of the eQV_{zz} parameter for compounds having presumably a close electronic and geometrical structure (Table III).

A possible structure which may be envisaged as the result of the interaction between a 'planar' tridentate *NNN* ligand and a SbF_3 or SbO_2F pyramidal unit seems that derivable from $(C_6H_4O_2)SbF(phen)$ [2] where the chelating ligand is now spanning a larger biting angle. Accordingly, bonds towards donor atoms are expected to be as much as possible crowded in one half of the coordination sphere opposite to the lone pair direction. Following our previous tentative arguments [4], this structural hypothesis could also be in accordance with the low value of the asymmetry parameter, η.

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