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Synthesis and Characterization of Antimony Carboxylates

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The antimony tris carboxylate of the type, SbL_3 was prepared by the reaction of antimony trichloride with sodium salt of furoic acid in 1:3 stoichiometry, whereas, antimony trichloride adduct, $(SbCl_3(LH))$ ($LH =$ furoic acid) was prepared by the reaction of antimony trichloride with furoic acid in 1:1 ratio. The complexes obtained were characterized by elemental analysis, IR and multinuclear (1H , $^{13}C\{^1H\}$) NMR spectroscopic techniques. Based on spectroscopic data a ligand coordination through oxygen atoms of the carboxylate group has been suggested.

Keyword: Antimony, Furoic acid, Carboxylates

1. Introduction

The chemistry of arsenic, antimony and bismuth has been an active area of research for more than four decades. Sustained interest in compounds of these group V elements is mainly due to their wide range of applications^[1]. Especially antimony (Sb) plays an important role in both, fundamental research and in applications owing to its unique physical properties. Antimony, a semimetal has an energy overlap of 180 mV between conduction and valence bands at 4.2 K, has low carrier densities, long Fermi wavelength and high carrier mobilities. Therefore, antimony compounds are used in electronics, optoelectronics and thermoelectric materials^[2-3]. Antimony sulfide (Sb_2S_3), due to its good photoconductivity, is an important material for solar energy. Its band gap covers the range of solar energy spectrum^[4, 5]. Recent studies^[6] have reported thin film deposition of Sb_2S_3 using $SbCl_3$ (thiosemicarbazone) complexes as single-source molecular precursors. Numerous applications of Sb_2S_3 have been reported in the literature. For example, it is used in television camera^[7], microwave devices^[8], switching devices^[9] and write once, read many times (WORM) kind of storage devices^[10].

Antimony complexes with variety of ligands viz. xanthates, dithiocarbamates, phosphorous based acids have been studied extensively^[11]. Biological activities such as antibacterial, antimalarial, fungicidal of these complexes have been correlated with their specific structures^[11-14]. It has been reported that metal complexes show enhanced biological activity as compared to free ligands due to reduction in polarity of metal after complexation. Though many structure-activity correlation studies of transition metals have been reported^[15-21], very few reports are available on antimony complexes^[22-26].

Carboxylic acid is another ligand system which has been widely studied and a variety of metal carboxylate complexes have been reported. Among main group elements, carboxylic acid derivatives of organotin precursors have been studied in considerable detail. Structural diversity exhibited by these organotin carboxylates is amazing, which ranges from monomers, dimers to oligomeric ladders. It has been demonstrated and extensively investigated that preference for particular structure depends on type of carboxylic acids and stoichiometry of reactants^[27-30]. Structural variations observed in our earlier studies of diorganotin carboxylates^[31,32]

triggered the curiosity to study reactions of carboxylic acids with next element in the periodic table, i.e. antimony. Studies of diorganotin carboxylates have revealed that carboxylate ligands, in absence of any other donor atom acts in a chelating manner which has also been confirmed from X-ray analysis of dimethyl tin diacetate [33]. However as denticity of ligand increases as in case of 2-pyridine carboxylic acid, carboxylate group is no longer chelating, but acts as a bridging ligand [34]. In view of this, we thought it worthwhile to synthesize and characterize antimony carboxylates, where ligand has additional coordination site along with carboxylate moiety. This can help in understanding the factors controlling the structures of these molecules. Thus, the complexes of antimony with furoic acid ligand were prepared and characterized in the present study. Further, the structures of these complexes were predicted from the spectroscopic data.

2. Experimental

2.1 Materials and Methods

Analytical grade solvents were used which were dried prior to use. Antimony (III) chloride and furoic acid were procured from s. d. fine chemicals. Antimony (III) chloride was used after vacuum distillation (73 °C / 1-2 mm of Hg). It is being sensitive to moisture, all the reactions were carried out in an oxygen free nitrogen atmosphere. Resulting complexes are air stable. The elemental analysis was carried out in the microanalytical laboratory of this department. IR spectra were recorded on Perkin-Elmer spectrum One FT-IR spectrophotometer using KBr pellets from 4000 to 400 cm⁻¹. ¹H and ¹³C{¹H} NMR spectra were recorded in DMSO-d₆ or CDCl₃ on a Bruker Avance II 300 MHz FT-NMR spectrometer. The chemical shifts are relative to internal standard tetramethyl silane. Mass spectra of the compounds were recorded using the laser desorption/ionization-time-of-flight mass spectrometry instrument at BARC, Mumbai.

2.2 Synthesis of Complexes

The reaction of antimony trichloride with sodium salt of furoic acid in 1:3 stoichiometry gave antimony tris carboxylate of the type SbL₃,

whereas its reaction with furoic acid in 1:1 ratio gave adduct, (SbCl₃(LH)) (LH = furoic acid). The syntheses of these compounds are described below.

2.2.1 Synthesis of SbL₃ (LH= furoic acid)

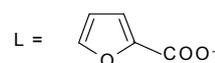
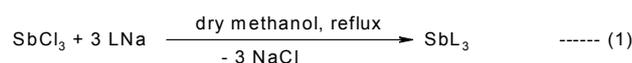
To a weighed quantity of sodium hydride emulsion (0.4747g) dissolved in 30 mL dry methanol, 0.7790 g (6.95 mmol) of furoic acid was added with constant stirring under nitrogen atmosphere and the stirring was continued for thirty minutes. To this sodium furoate salt, antimony (III) chloride (0.5013 g, 2.19 mmol) was added and the reaction mixture was refluxed in an oil bath for 10 h. Then it was cooled and filtered through G-3 crucible under inert atmosphere. The filtrate was evaporated under reduced pressure. The product obtained was recrystallized from dry methanol (yield: 0.705 g, 70.50%).

2.2.2 Synthesis of SbCl₃(LH) (LH = furoic acid)

To a weighed quantity of antimony chloride (0.7628 g, 3.34 mmol) dissolved in 30 ml methanol, 0.3740 g (3.34 mmol) furoic acid was added with continuous stirring under inert atmosphere at room temperature. The stirring was continued for 10 h. Then the solvent was removed under vacuum and the product obtained was recrystallised from dry methanol (yield: 0.625 g, 54.98 %).

3. Results and Discussion

The reaction of antimony trichloride with sodium salt of furoic acid in 1:3 stoichiometry in dry methanol gave antimony tris carboxylate of the type SbL₃ (eqn. 1), whereas its reaction with furoic acid in 1:1 ratio resulted in an adduct of the type, (SbCl₃(LH)) (LH = furoic acid) (eqn. 2).



The resulting compounds are white solids. They were further characterized by elemental analysis, IR and multinuclear (^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopic techniques. Elemental analysis of these compounds is given in Table 1. It is observed that the stoichiometry between metal

and ligand is 1:3 in case of tris derivative, whereas for adduct the elemental analysis matches with 1:1 stoichiometry between metal and ligand.

In order to establish the coordination modes of the furoic acid ligand with antimony metal centre,

Table 1: Physical and analytical data of the complexes

Compound	Molecular formula	Melting point °C	Elemental analysis % found (calculated)			
			Sb	Cl	C	H
SbL ₃	SbC ₁₅ H ₉ O ₉	215	25.90 (26.76)	-----	39.51 (39.56)	2.01 (1.97)
SbCl ₃ (LH)	SbCl ₃ C ₃ H ₄ O ₃	190-193	36.01 (35.78)	30.84 (31.25)	18.01 (17.64)	1.24 (1.18)

the IR spectra of complexes were compared with the IR spectrum of the ligand. IR spectrum of furoic acid showed a strong broad band at 3406 cm^{-1} which was assigned to ν_{OH} of the $-\text{COOH}$ group. This band remained unaltered in the spectrum of $\text{SbCl}_3(\text{LH})$ indicating that this group is not deprotonated after the complexation. However, this band disappeared in the IR spectrum of tris complex. Bands observed at 1691 cm^{-1} and 1585 cm^{-1} are due to $-\text{COO}$ asymmetric and symmetric stretchings, respectively. These bands showed shift to lower frequencies compared to free acid indicating participation of the carboxylate group in the bonding. The asymmetric ν_{COO} and symmetric ν_{COO} for SbL_3 were observed in the region 1580-1610 and 1330-1360 cm^{-1} respectively. The magnitude of $\Delta\nu$ ($\nu_{\text{asym COO}} - \nu_{\text{sym COO}}$) is found to be 217 cm^{-1} . It is comparable to corresponding sodium salt which indicates presence of bidentate carboxylate group [35]. The bands due to $\nu_{\text{Sb-C}}$ and $\nu_{\text{Sb-O}}$ appear between 459- 484 cm^{-1} and 561 – 585 cm^{-1} range, respectively. These values are consistent with the literature values [36-39]. An additional new band at $\sim 522 \text{ cm}^{-1}$ was also observed in the compounds which could be assigned to $\nu_{\text{Sb-O}}$. Similar observations have been reported in the literature [40].

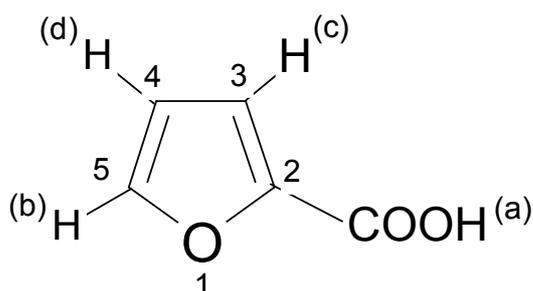
The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data of ligand as well as complexes is summarized in Table 2 and the

spectra are given in Figures 1-6. The ^1H NMR spectrum of 2-furan carboxylic acid showed expected integration and peak multiplicities. The aromatic protons of 2-furan carboxylic acid appeared in the region 6.55- 7.60 ppm. The hydroxyl proton appeared at 11.28 ppm. In the ^1H NMR spectrum of tris derivative, SbL_3 , the deprotonation of ligand is clearly seen from the disappearance of the peak present at 11.28 ppm in the spectrum of the ligand (Fig.1 and 2). This indicates coordination of the ligand through carboxylate group. The presence of ring protons in tris derivative is observed in 6.37-7.48 ppm range, whereas in case of adduct they are observed in 6.65-7.92 ppm range. In case of adduct the presence of $-\text{COOH}$ proton could not be detected, which may be due to proton exchange in the solution (Fig. 3). However, IR spectrum of this complex showed the presence of ν_{OH} frequency due to $-\text{COOH}$ group.

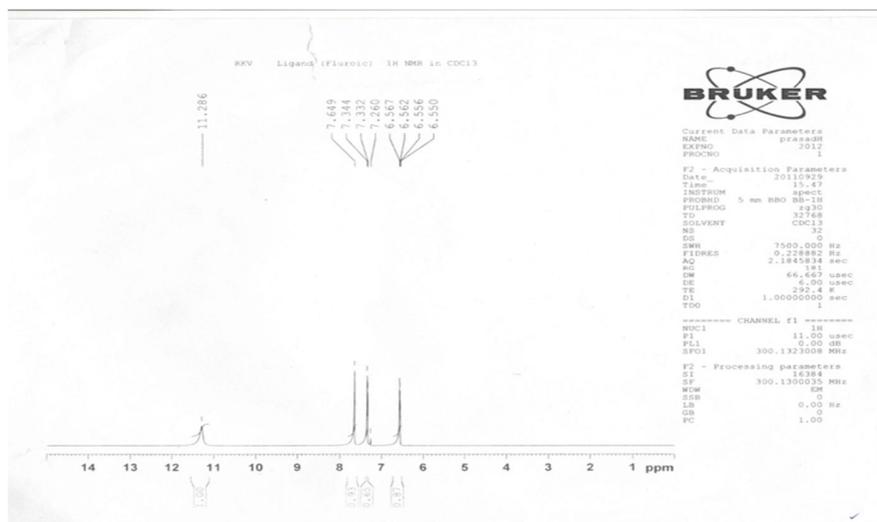
In the ^{13}C NMR of ligand, the presence of all the carbon atoms could be detected (Fig. 4). The signals due to carbons present in the heterocyclic ring of the ligand are observed at 147.45, 143.73, 120.19 and 112.26 ppm. In case of tris derivative these signals are observed at 154.03, 141.88, 110.62 and 110.51 ppm (Fig. 5), whereas in the spectrum of the adduct they are present at 147.46, 143.63, 118.33 and 112.27 ppm (Fig.6).

Table 2: ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for furoic acid ligand and its antimony complexes

Compound	^1H NMR data, δ in ppm	$^{13}\text{C}\{^1\text{H}\}$ NMR data, δ in ppm
Furoic acid	6.558 (dd, H(d)), 7.338 (dd, H(c)), 7.649 (dd, H(b)), 11.286 (s, H(a))	163.788 (-COO), 147.450 (C-5), 143.733 (C-2), 120.192 (C-3), 112.263 (C-4)
SbL_3	6.372 (m, H(d)), 6.590 (m, H(c)), 7.477 (m, H(b))	162.535 (-COO), 154.031 (C-5), 141.879 (C-2), 110.621 (C-3), 110.511 (C-4)
$\text{SbCl}_3(\text{LH})$	6.659 (m, H(d)), 7.275 (m, H(c)), 7.913 (m, H(b))	158.383 (-COO), 147.464 (C-5), 143.629 (C-2), 118.332 (C-3), 112.268 (C-4)

**Fig:** Atomic numbering of Furoic acid used in NMR data

The mass spectra of complexes were recorded. The molecular ion peak was not observed. This is mainly due to fact that molecule suffers considerable fragmentation. However, peaks of the ions due to fragmentation of the complex were detected. Thus, a peak at m/z of 157 could be assigned to $[\text{Sb-Cl}]^+$ fragment, whereas another peak present at m/z of 138 was assigned to $[\text{Sb-O}]^+$ fragment. Mass spectrometry has been used for structure elucidation and characterization in recent studies on triaryl antimony carboxylates and similar observations have been reported [39, 41, 42].

**Fig 1:** ^1H NMR of furoic acid ligand in CDCl_3

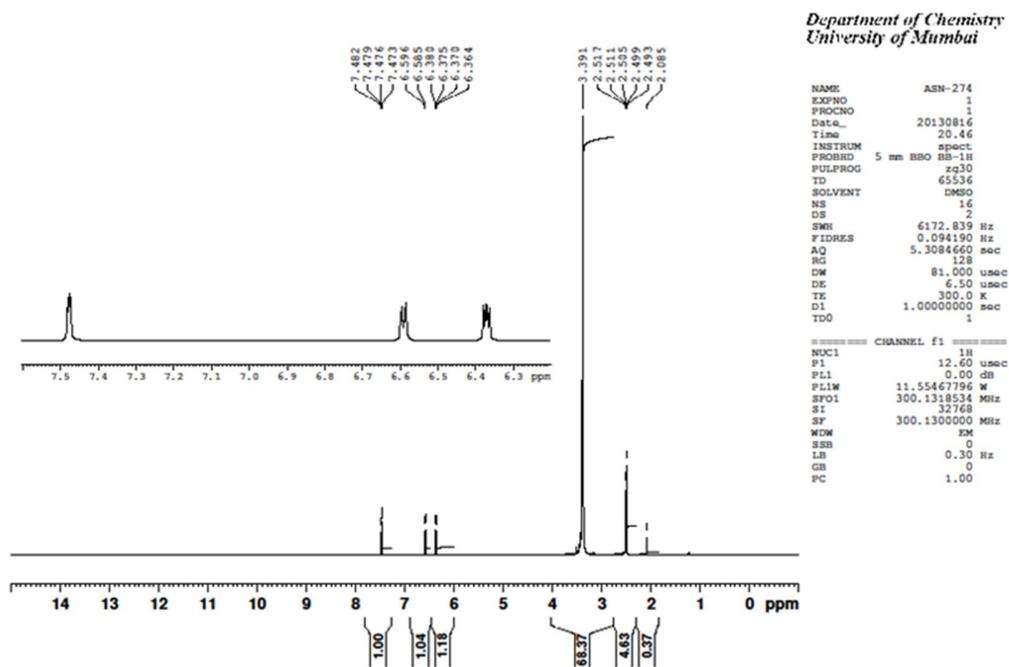


Fig 2: ^1H NMR of SbL_3 complex in dms0-d_6

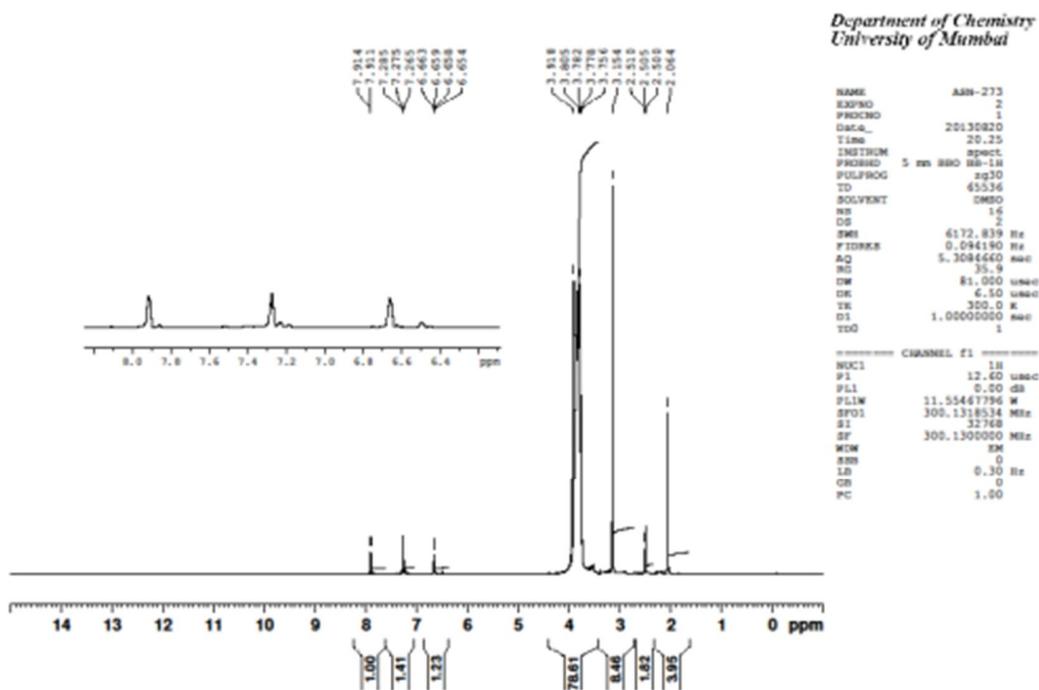


Fig 3: ^1H NMR of $\text{SbCl}_3(\text{LH})$ in dms0-d_6

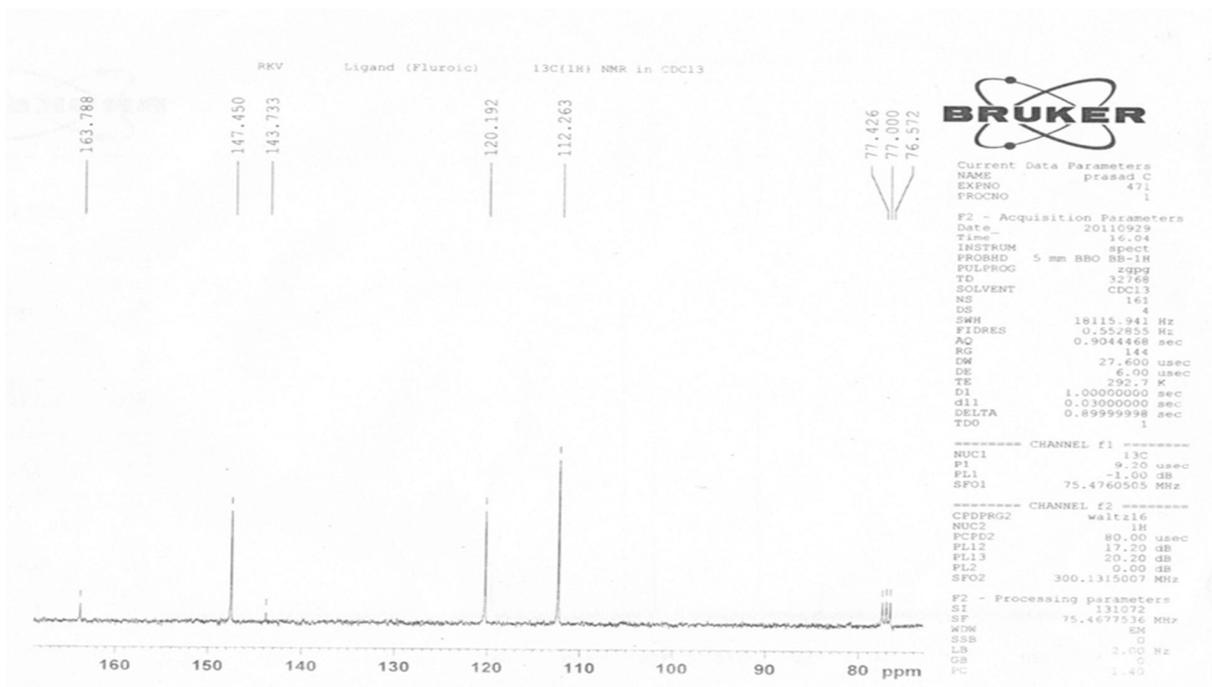


Fig 4: $^{13}\text{C}\{^1\text{H}\}$ NMR of furoic acid ligand in CDCl_3

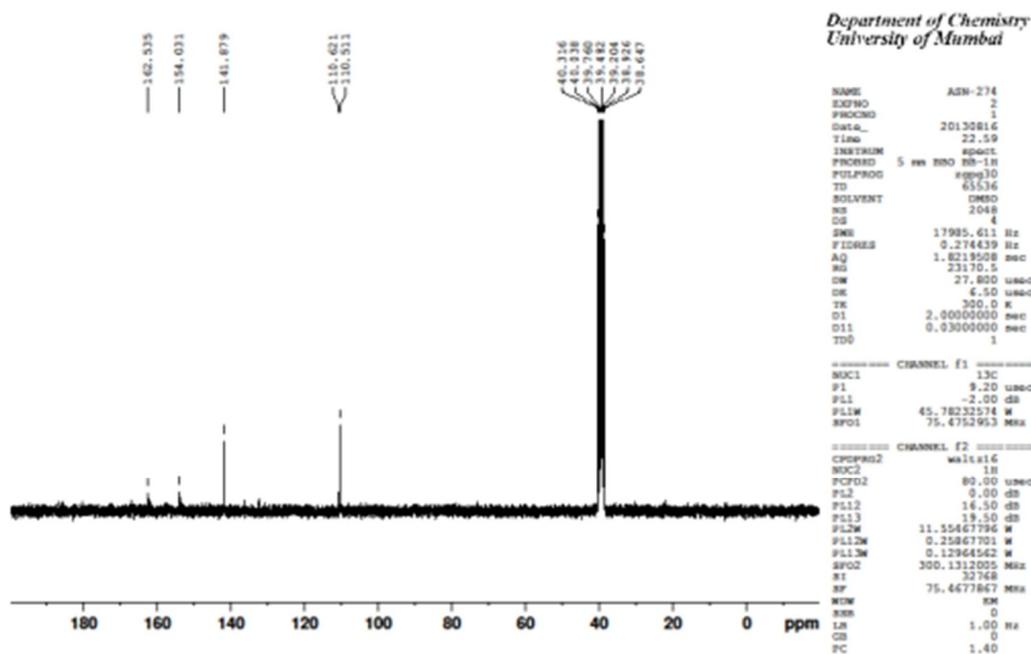


Fig 5: $^{13}\text{C}\{^1\text{H}\}$ NMR of SbL_3 complex in dmsO-d_6

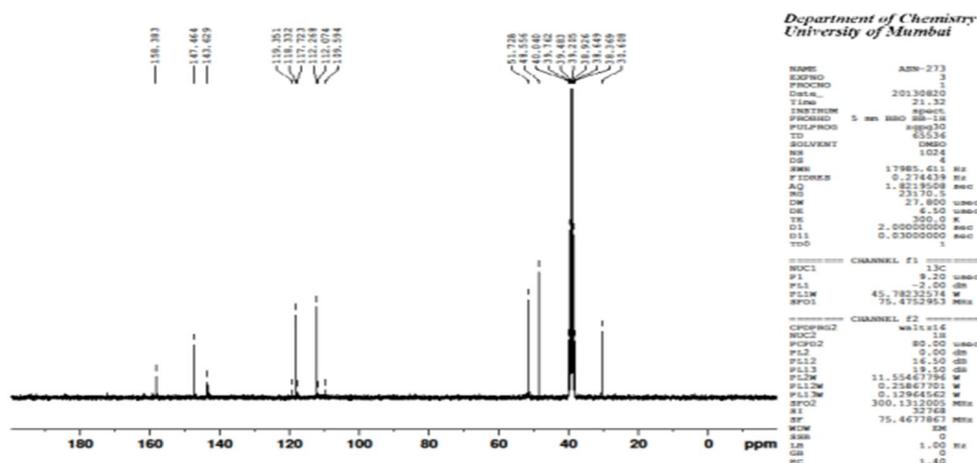


Fig 6: $^{13}\text{C}\{^1\text{H}\}$ NMR of $\text{SbCl}_3(\text{LH})$ in dms0-d_6

Based on the above observations the presence of a six coordinated antimony with three bidentate chelating carboxylate ligands in tris derivative can be suggested. In case of adduct, the antimony centre is five coordinated having three chloride groups and a bidentate carboxylic acid ligand. Therefore, following probable structures (I and II) are proposed for these molecules.

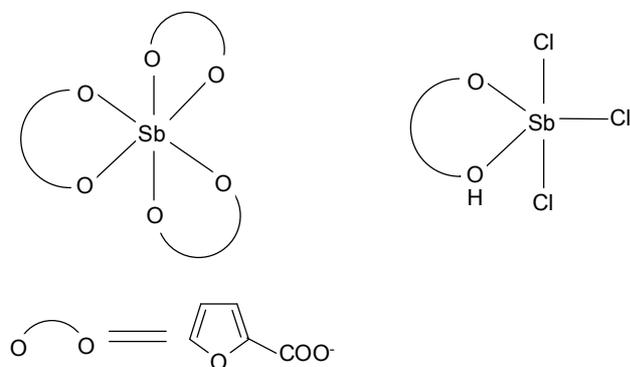


Fig 7: Proposed Structures of (I) SbL_3 (II) $\text{SbCl}_3(\text{LH})$

4. Conclusions

The reactions of antimony (III) chloride with furoic acid in 1:1 stoichiometry at room temperature gave molecular adduct, $\text{SbCl}_3(\text{LH})$, whereas reaction between antimony (III) chloride with sodium salt of furoic acid in 1:3 stoichiometry under refluxing conditions gave tris

derivative of the type SbL_3 (LH = furoic acid). The spectral studies of these complexes suggest that the carboxylate group acts as a bidentate chelating ligand with deprotonation in case of tris derivative. In case of adduct also, the ligand acts in bidentate chelating fashion, however there is no deprotonation. The presence of antimony-oxygen direct bond in these complexes make them potential single-source molecular precursors for the preparation of Sb_2O_3 nanoparticles and thin films.

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