

PREPARATION AND NMR, MASS AND MÖSSBAUER STUDIES OF DI-AND TRIORGANOTIN (IV) DERIVATIVES OF 3-(2-FURANYL)-2-PROPENOIC ACID

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ABSTRACT : *3- (2- Furanyl)-2- propenoic acid has been used to prepare a new series of organotin complexes of general formula R_3SnL ($R=Me, Et, n-Bu, Ph$ and Cy) and R_2SnL_2 ($R=Me$ and $n-Bu$). These complexes have been characterized by elemental analyses, IR, ^1H-NMR , MASS and Mössbaure spectroscopy.*

KEY WORDS : *spectral studies of organotin derivatives of 3-(2-furanyl)-2- propenoic acid.*

INTRODUCTION :

Since long, heterocyclic carboxylic acids have been considered as attractive starting materials for new organotin (IV) syntheses. Most reports show that these derivatives have either octahedral or trigonal bipyramidal geometries [1-3]. Previously we have synthesized a series of

organotin derivatives of 3- (2- thienyl)-2- propenoic acid [11]. Their geometries, oxidation state and mode of tin- carboxylate interaction have been determined. In the present work organotin derivatives of the type R_3SnL ($R=Me, Et, n-Bu, Ph$ and Cy) and R_2SnL_2 ($R=Me$ and

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n-Bu) whereas L= 3-(2-furanyl)-2-propenoic acid have been synthesized. Elemental analyses carried out in the primary investigations were complemented by various spectroscopic techniques like IR, $^1\text{H-NMR}$, MASS and ^{119}mSn Mössbauer spectrometry for structural elucidations. Shifting of characteristic IR peaks, J values, and ^{119}mSn Mössbauer parameters were used to determine the nature of bonding and coordination numbers.

Tin-carboxylate interaction is quite interesting and consistent with reported literature [4-8]. $\Delta\nu$ and Mössbauer parameters are diagnostic for bidentate behaviour of the ligand and trigonal bipyramidal structure is proposed for R_3SnO_2 whereas octahedral for R_2SnO_4 in the solid state. From J values it is proposed that tri- and diorganotin (IV) derivatives are tetrahedral and weak hexacoordinated in solution respectively.

EXPERIMENTAL :

Syntheses were carried out by using reagents of analytical grade. As organotin halides are highly air and moisture sensitive hence all the reactions were carried out under inert atmosphere and in dried solvents [9].

Preparation of Complexes

3-(2-furanyl)-2-propenoic acid was converted

to silver salt by mixing equimolar sodium bicarbonate and corresponding acid in ethanol. Stoichiometric amounts of silver nitrate in water was added while stirring, white precipitates formed were filtered by suction in dark and dried over P_2O_5 .

The 1:1 and 2:1 complexes were prepared by refluxing 0.001 or 0.002 mole of silver salt of acid with 0.001 mole of tri- and diorganotin chlorides in dry chloroform for 8-10 hrs under inert atmosphere. The reaction mixture was cooled and precipitates of silver chloride were filtered. The filtrate was concentrated and crystallized (yield 80-85%).

Physical Measurements

Elemental analyses, m.p and recrystallization solvents are given in Table 1. Infrared spectra were recorded in KBr pellets by using Hitachi Model 270-50 Infrared spectrometer, and characteristic vibrations are given in Table 2. Mass spectra were carried out by MAT-112S Mass spectrometer and reported in Table 3. ^{119}mSn Mössbauer spectra were obtained according to previous [12] method and results are given in Table 2. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 , using Bruker SF 400 MHz and Jeol JNM-PMX 60 MHz spectrometers.

Table 1 : Physical properties of the complexes $\text{R}_n\text{Sn}(\text{C}_7\text{H}_5\text{O}_2)_{4-n}$

Name of compound	M.W	m.p °C	Recrystallization solvents	Elemental analysis	
				%C Cal./exp.	%H Cal./exp.
Me_3SnFA	302	160-162	CHCl_3 /ether	39.86/40.12	4.65/4.87
$\text{Me}_2\text{Sn}(\text{FA})_2$	424	138	CHCl_3 /ether	45.28/45.62	3.77/3.80
Et_3SnFA	344	100	CHCl_3 /methanol	45.35/45.58	5.81/6.04
n-Bu $_3$ SnFA	428	70	CHCl_3 /ether	53.39/53.70	7.26/7.40
n-Bu $_2$ Sn(FA) $_2$	508	55-57	CHCl_3 /ether	51.97/52.06	5.51/5.83
Ph_3SnFA	488	122-125	CHCl_3	61.69/61.70	4.11/4.11
Cy_3SnFA	506	117-119	CHCl_3	59.44/59.80	7.52/7.81

Me = methyl, Et = ethyl, n-Bu = n-butyl, Ph = phenyl, Cy = cyclohexyl

Table 2 : Assignment of Characteristic IR Vibrations and Mössbauer data of the investigated compounds.

Name of compound	$\nu_{asm}(cm^{-1})$	$\nu_{sm}(cm^{-1})$	$\Delta\nu$	IS _(mm⁻¹)	QS _(mm⁻¹)	Γ	QS/IS
	C-O						
Ag-FA	1647s	1386s	261				
Ph ₃ SnFA	1641s	1381s	260	1.26	3.39	1.61	2.6
Cy ₃ SnFA	1650s	1395m	255	1.46	2.80	0.96	1.9
Bu ₃ SnFA	1644s	1386s	258	1.38	3.50	0.92	2.54
Me ₂ Sn(FA) ₂	1641s	1377s	264	1.16	3.35	0.88	2.89
Et ₃ SnFA	1648s	1382s	266	-	-	-	-
Me ₃ SnFA	1641s	1383s	258	1.24	3.48	0.89	2.80
Bu ₂ Sn(FA) ₂	1646s	1388s	258	1.33	3.21	0.92	2.4

FA = 3-(2-furanyl)-2-propenoic acid, AgFA = Silver salt of 3-(2-furanyl)-2-propenoic acid, asm = asymmetric, sm = symmetric and s = strong, m = medium.

RESULTS AND DISCUSSION :

The infrared spectral data of the compounds reported here are listed in Table 2. Characteristic vibrational frequencies have been identified by comparing spectra of the complexes with their precursors. The silver salt formation by the deprotonation of carboxylic group is evidenced by the absence of broad (OH) band at 2730-2950cm⁻¹ [4]. The ester formation of the ligand with tin(IV) is confirmed by the absence of $\nu_{(Ag-O)}$ and $\nu_{(Sn-Cl)}$ vibrational bands at 535 and 333cm⁻¹ respectively in precursors, whereas peaks in the range 441-477cm⁻¹ indicate the presence of $\nu_{(Sn-O)}$ band of these compounds. The IR data show that position of the $\nu_{(C-O-C)}$ band of the ring remains unchanged in going from free ligand through silver salt to these complexes, thus indicating no involvement of ring oxygen during complexation. Moreover $\nu_{(C=C)}$ and $\nu_{(Sn-C)}$ are in the range 1557 - 1572cm⁻¹ and 549-586cm⁻¹ respectively.

All these compounds show two strong absorptions in the region characteristic for $\nu_{(COO)}$ [4-6], one, in the range 1641-1650cm⁻¹ $\nu_{asm(COO)}$ while the other in the range 1377- 1395cm⁻¹ $\nu_{s(COO)}$. The association of carboxylate group to tin(IV) is proposed on the basis of magnitude of sepa-

ration of the $\nu_{asm(COO)}$ and $\nu_{s(COO)}$ bands ($\Delta\nu_{values}$) and is compared with the silver salt of the acid. As the $\Delta\nu_{values}$ are quite comparable, hence it can be proposed that, the carboxylate group is acting as a bidentate chelate in diorganotin while as bridging in other complexes. These results are further supported by ^{119m}Sn Mössbauer spectroscopy.

MASS Spectra

The 80ev monoisotopic MASS spectral fragmentation of the compounds are described in Table 3. A very weak molecular ion peak was observed only when R=Ph while none of the rest exhibited this behaviour. In both type of complexes primary decomposition is either due to loss of the R group or rarely due to tin-oxygen cleavage. Secondary fragmentation is a consequence of loss of either R group or CO₂ molecule. However, the latter is the more frequent and probable pathway. Peaks for R₃Sn⁺ and R₂Sn⁺ are either absent or very weak, indicating that the fragmentation route through these species is not favourable. Formation of species like C₅H₅⁺ is probably due to ring opening of the ligand followed by elimination of SnO.

Table 3 : 80ev monoisotopic mass spectra of $R_nSn(C_7H_5O_2)_4-n$

Ionic species	R=Me	R=Et	R=n-Bu	R=Ph	R=Cy
$ R_3Sn(COO)C_6H_5O ^+$	-	-	-	11	-
$ R_2Sn(COO)C_6H_5O ^+$	90.82	100	28	58	88
$ Sn(COO)C_6H_5O ^+$	-	-	-	5	35
$ R_2SnC_6H_5O ^+$	100	17	-	37	38
$ RSnC_6H_5O ^+$	-	6	8	-	-
$ SnC_6H_5O ^+$	35	35	32	38	-
$ R_3Sn ^+$	30	30	-	-	-
$ R_2Sn ^+$	-	-	-	-	4
$ RSn ^+$	-	-	-	42	18
$ SnH ^+$	55	12	64	67	67
$ Sn ^+$	18	10	18	8	10
$ C_7H_6O_3 ^+$	7	14	100	100	32
$ C_6H_5O ^+$	14	-	6	22	-
$ C_5H_5 ^+$	75	48	65	-	-
$ C_4H_7 ^+$	-	-	-	-	100

Mössbauer Spectra

The Mössbauer quadrupole splitting parameter (QS) and isomer shift (IS) values at 80K for the organotin(IV) derivative are listed in Table 2.

A guide to the coordination states of tin in di- and tri- organotin compounds is provided by QS/IS ratio, which has a value >2.1 for higher than four coordination at tin [13]. Such ratios are observed for all the triorganotin derivatives except the cyclohexyltin derivative for which the ratio is 1.9. On the basis of these ratios the trimethyl, triphenyl and tri-n-buthyltin derivatives are assigned a five-coordinate trans R_3SnO_2 trigonal bipyramidal geometry [14]. The tricyclohexyltin derivative has probably cis five-coordinated trigonal bipyramidal geometry as their QS value is 2.80mmS^{-1} . The diorganotin derivatives have trans R_2SnO_4 octahedral geometries which are predicted on the basis of their QS values.

$^1\text{H-NMR Spectra}^*$

Compound I (Me_3SnFA)

$^1\text{H-NMR}$ (300MHz, in CDCl_3):

$\delta^1\text{H} | ^2\text{J} (^{119}\text{Sn}^1\text{H}) | = 0.58\text{ppm} | 58.3, ^2\text{J} | \text{s}, 9\text{H}, \text{Sn-CH}_3$; 6.33ppm | 20.9 | d, (broad), 1H; 7.73ppm | 21.7 | d, (broad), 1H; 6.45ppm | 2.42, 4.52 | dd, 1H, 4-H; 6.55ppm | 4.5 | d, 1H, 3-H; 7.5ppm | 2.4 | d, 1H, 5-H.

Compound IIa (Et_3SnFA)

$^1\text{H-NMR}$ (300MHz, in CDCl_3):

$\delta^1\text{H} | ^2\text{J} (^{119}\text{Sn}^1\text{H}) | = 1.25\text{ppm} | 87 \pm 5^2\text{J} | \text{m}, 15\text{H}, \text{Sn-C}_2\text{H}_5$; 6.32ppm | 15.7 | d, (broad), 1H; 7.53ppm | 15.72 | d, (broad), 1H; 7.05ppm | 8.6, 3.5 | dd, 1H, 4-H; 7.2ppm | 3.5 | d, 1H, 3-H; 7.33ppm | 5.08 | d, 1H, 5-H.

Compound IIIa (Bu_3SnFA)

$^1\text{H-NMR}$ (60MHz, in CDCl_3):

$\delta^1\text{H} = 0.66\text{-}1.82\text{ppm}, \text{m}, 27\text{H} (\text{Sn-C}_4\text{H}_9)$; 6.09-

* Coupling constants $J(^{119}\text{Sn}^1\text{H})$ in Hz are given in | |

s= singlet, d=doublet, t=triplet, dd= doublet of doublet, 3-H,4-H and 5-H represent positions of the ring protons.

7.57ppm, m, 5H.

Compound IVa (Ph_3SnFA)

$^1\text{H-NMR}$ (90MHz, in CDCl_3):

$\delta^1\text{H}=6.32\text{-}7.90\text{ppm}$, m, 20H(Sn- C_6H_5 and furan ring proton).

Compound Va (Cy_3SnFA)

$^1\text{H-NMR}$ (90MHz, in CDCl_3):

$\delta^1\text{H}=0.19\text{-}2.00\text{ppm}$, m, 33H (Sn- C_6H_{11}); 6.28-7.60, m, 5H.

Compound Vb ($|\text{Me}_2\text{Sn}(\text{FA})_2|$)

$^1\text{H-NMR}$ (400MHz, in CDCl_3):

$\delta^1\text{H} |^n\text{J}(^{119}\text{Sn}^1\text{H})| = 1.12\text{ppm} |73, ^2\text{J}|$, s, 6H, Sn- CH_3 ; 6.35ppm |15.6|d, (broad), 1H; 7.52ppm |15.6|d, (broad) 1H; 6.48ppm |1.8, 1.8|dd, 1H, 4-H; 6.65ppm |3.4|d, 1H, 3-H; 7.5ppm |1.7|d, 1H, 5-H.

Compound VIb ($|\text{Bu}_2\text{Sn}(\text{FA})_2|$)

$^1\text{H-NMR}$ (60MHz, in CDCl_3):

$\delta^1\text{H}=0.66\text{-}1.82\text{ppm}$, m, 18H (Sn- C_4H_9); 6.09-7.57ppm, m, 10-H.

The $^1\text{H-NMR}$ spectra of compounds I,IIa and Vb are given in Figs. 1,2 and 3 respectively. The number of protons calculated from integration curves are equal to that calculated from the molecular formula of each compounds. From the values of coupling constants (Sn-Me) it was observed that tri- organotin compounds are tetracoordinated, while diorganotin compounds are likely to be weak hexacoordinated [10] in solution. The tetracoordinated trimethyltin (IV) compound has $|^2\text{J}|$ value 58.3Hz having Me-Sn- Me angle 111.16° . The olefinic protons (-CH=CH-) in both types of the compounds are lying trans to each other [8]. The oxygen of the ring does not coordinate to tin(IV).

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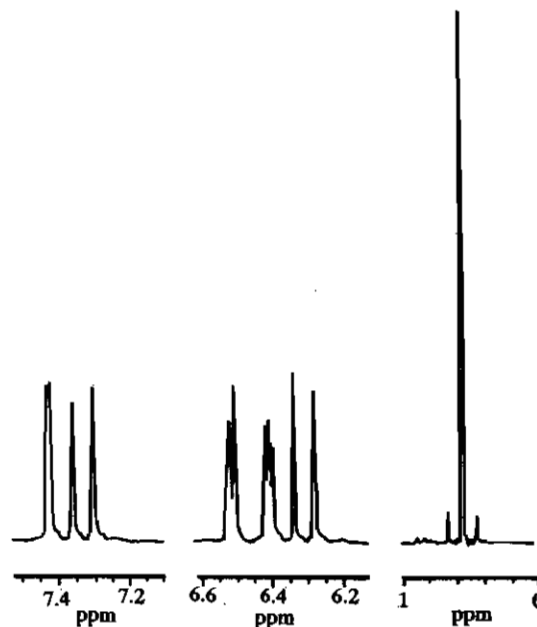


Fig. 1 : $^1\text{H-NMR}$ spectrum of Me_3SnFA

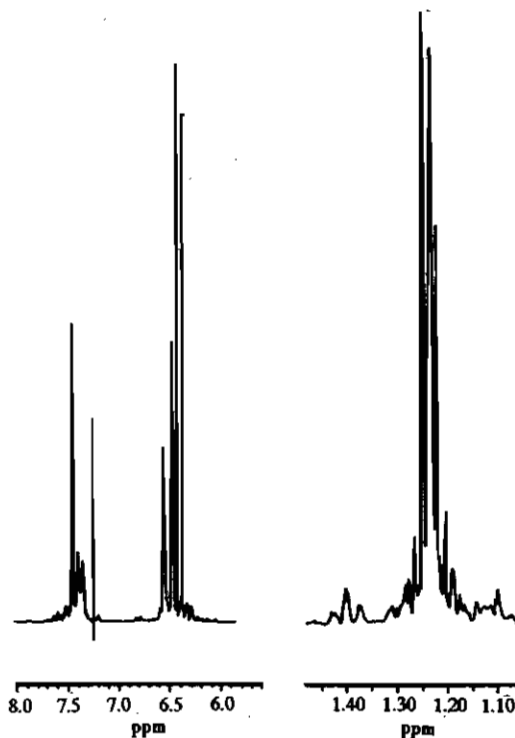


Fig. 2 : $^1\text{H-NMR}$ spectrum of Et_3SnFA

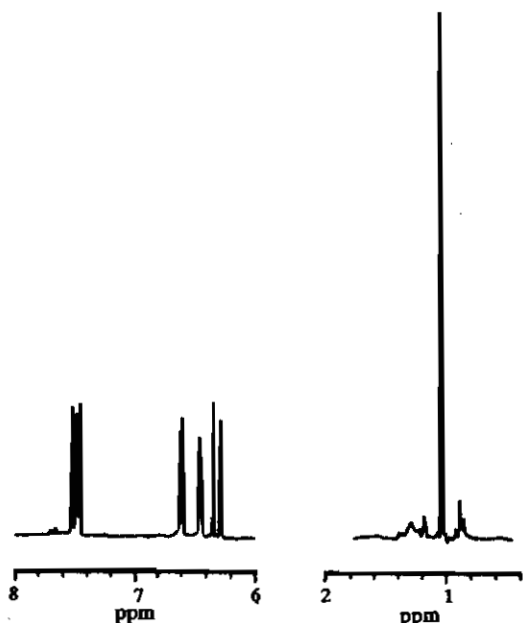


Fig. 3 : $^1\text{H-NMR}$ spectrum of $\text{Me}_2\text{Sn}(\text{FA})_2$

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