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# Synthesis, characterization, crystal structures and electrochemical studies of organotin(IV) carboxylates

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# ABSTRACT

Four new organotin(IV) compounds [Me<sub>3</sub>SnL] (1), {[Me<sub>2</sub>SnL]<sub>2</sub>O}<sub>2</sub> (2), Bu<sub>2</sub>SnL<sub>2</sub> (3) and [Bu<sub>3</sub>SnL] (4), where  $L = O_2C(C_2H_5)CCHC_6H_4F$  have been synthesized by refluxing the corresponding organotin(IV) chlorides with sodium (E)-2-(2-fluorobenzylidene) butanoate (NaL) in dry toluene except **2** for which Me<sub>2</sub>SnO was refluxed with (E)-2-(2-fluorobenzylidene) butanoic acid (LH) in the same solvent. NaL and all the compounds were characterized by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. NaL and compounds 1 and **2** were also characterized by X-ray single crystal analysis which confirmed a linear polymeric structure for compound **1** and a stannoxane for **2**. The structural analyses have shown a bridging behavior of the ligand in trimethyl- and tributyl-, chelating as well as bridging behavior in dimethyl- and a chelating bidentate mode of coordination in dibutyltin(IV) compound which is also confirmed from the crystal analysis for compounds 1 and 2. Cyclic voltammetry was used to evaluate the electrochemical, kinetic and thermodynamic parameters for the electron transfer processes of compounds 1-4. Predominantly adsorption controlled redox processes were exhibited by the slope of  $\log i_p vs. -\log v$  plots. The values of the diffusion coefficient  $(D_0)$  indicated the role of solvent in the mobility of the electro-active species to some extent but the overall rate of the redox process was typical of the adsorption controlled process and could not be explained on the basis of solvation effects. The values of formal potential and charge transfer coefficient were also calculated.

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# 1. Introduction

Owing to the ability of tin to form stable complexes with carbon and hetero atoms, organotin derivatives are becoming the focal point of many research areas such as organic synthesis, synthesis of polyesters, polyurethanes and in the crosslinking of silicon and catalysis such as esterification and *trans*-esterification reactions [1]. Organotin(IV) carboxylates constitute a class of organoitn(IV) compounds and are extensively being studied nowadays due to their potential biocidal activity, cytotoxicity, industrial and agricultural applications. Organotin(IV) compounds containing carboxylate ligand with additional donor atoms such as N, O or S have been shown to exhibit new structural geometries and hence new potential activities [1,2,7]. The most common geometries are monomeric (tetrahedral, octahedral [3], skew trapezoidal [4], trigonal bipyramidal [5,6]), dimeric, tetrameric [7], oligomeric, ladder shaped, hexameric [8] and polymeric (linear [9], zigzag [10] and stannoxanes such as 1D, 2D, and 3D [8]) structures. Apart from these, some cyclic species have also been reported [8]. The monoalkyltin(IV) tricarboxylates exhibit relatively less structural diversity and are not as widespread as the di- and triorganotin(IV) carboxylates [11].

Although a number of new synthetic techniques such as solvothermal synthesis and other are commonly employed for the synthesis of organotin(IV) carboxylates, the conventional synthetic techniques such as standard schlenk technique [8,12] and reflux methods are still in common use [10]. In this research work the complexes are synthesized using the reflux method. The ligand is used to react with the organotin(IV) chlorides under reflux conditions. The synthesized organotin(IV) compounds consist of linear polymeric carboxyl bridged  $[Me_3SnL]_n$  (1) and  $[Bu_3SnL]_n$  (4), tetrameric tetraorganodistannoxane { $[Me_2Sn(OOC(C_2H_5)CCHC_6H_4F)]_2O_2$ (2) and monomeric skew trapezoidal  $Bu_2SnL_2$  (3); each self assembled from the respective organotin(IV) derivative and the ligand under reflux conditions.

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Regarding the biological activities of metal complexes, the oxidation state and redox behavior of the central metal atom are of prime importance among several other parameters [13]. The labilization of the attached ligands, resulting in the biologically active species as well as the inherent activity of the complex without ligand dissociation is critically affected by the former of the two mentioned properties. Hence the *in vivo* interconversion of different oxidation states of the metal complexes has been reported to alter their properties drastically [14,15]. The redox potential of an organometallic compound is a function of several factors. Besides synthesis, the role of the electronic properties of the attached ligands, geometry of the complex and the nature of organic moiety attached to metal in determining the redox potential of the synthesized organotin(IV) carboxylates has been studied and discussed in the present work.

# 2. Experimental

## 2.1. Materials and methods

Dimethyltin(IV) oxide, trimethyl-, tributyl- and dibutyltin(IV) chlorides were purchased from Aldrich and used without further purification. All the solvents were dried according to the reported standard procedures [16]. The melting points were obtained in a capillary tube using a Gallenkamp, serial number C040281, UK, electro-thermal melting point apparatus. FT-IR spectra were recorded on a Nicolet-6700 FT-IR spectrophotometer, thermoscientific, USA, in the range from 4000 to 400 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Advance Digital 300 MHz NMR spectrometer, Switzerland, using CDCl<sub>3</sub> as an internal reference [ $\delta^1$ H (CDCl<sub>3</sub>) = 7.25 and  $\delta^{13}$ C (CDCl<sub>3</sub>) = 77.0 ppm]. The spectra were acquired at room temperature (298 K).

# 2.2. X-ray crystallographic studies

A colorless prismatic crystal of **1** and colorless plate crystals of **2** and NaL were used for data collection. The crystals were coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation. Details of crystal data and structure refinement have been provided in Table 1. The data were collected at a temperature of 173(2) K for **1** and 123(2) K for **2** and NaL using  $\omega$  and  $\varphi$  scans, corrected for Lorentz and polarization effects and for absorption using multi-scan method [17,18].

The structures were solved by the direct methods [19] and expanded using Fourier techniques [20]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97 [21a] converged with unweighted and weighted agreement factors, *R* and *wR* = 0.0305 and 0.0918 (all data) for **1**, 0.0302 and 0.0761 (all data) for **2** and 0.0416 and 0.0781 for NaL, and goodness of fit, *S* = 1.076, 1.053 and 1.154, respectively. The absolute structure parameter *x* [21b] indicated the presence of racemic twinning in NaL. ATWIN instruction with the default matrix *R* = (-100, 0 - 10, 00 - 1) in the least-squares refinement cycles lead to a BASF parameter of 0.2147. The Friedel pairs of reflections (865) were merged.

The weighting schemes were based on counting statistics and the final difference Fourier maps were essentially featureless. The figures were plotted with the aid of ORTEP-3 [22].

# 2.3. Electrochemistry

Voltammetric experiments were performed using an SP-300 potentiostate, serial number 0134, BioLogic Scientific Instruments, France. Measurements were carried out in DMSO solution

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Crystal data and structure refinement parameters for NaL and compounds 1 and 2.

Compound	NaL	1	2
Moiety Formula	C <sub>11</sub> H <sub>18</sub> F Na O <sub>5.50</sub>	C <sub>14</sub> H <sub>19</sub> F O <sub>2</sub> Sn	C <sub>26</sub> H <sub>32</sub> F <sub>2</sub> O <sub>5</sub> Sn <sub>2</sub>
Formula mass	280.24	356.98	699.90
(g III01 <sup>-</sup> )	Orthorhombic	Orthorhombic	Monoclinic
space group	r u u Z	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	$P Z_1/n$
Unit cell dimension	S		
a (A)	12.4218(8)	6.6797(3)	10.5396(3)
b (Å)	75.112(5)	10.1047(4)	15.5407(4)
<i>c</i> (Å)	5.6337(3)	21.7370(11)	17.3810(4)
α (°)	90.00	90.00	90.00
β (°)	90.00	90.00	106.7558(15)
γ (°)	90.00	90.00	90.00
$V(Å^3)$	5256.4(6)	1467.17(12)	2726.01(12)
$\theta$ Ranges			
for data			
Collection (°)	2.17 - 25.00	3.58 - 30.02	2.45 - 26.04
Ζ	16	4	4
$\rho_{calc}$ (g cm <sup>-3</sup> )	1.417	1.616	1.705
F(000)	2368	712	1384
Crystal	$0.09 \times 0.08$	$0.16 \times 0.12$	0.16  imes 0.14
size (mm)	× 0.02	× 0.12	× 0.04
T (K)	123(2)	123(2)	173(2)
Index ranges			
h	-14 - 14	-9-9	-13-13
k	-88-87	-14 - 14	-19-18
1	-6-6	-30-30	-21-21
Total data	1268	2447	5272
Unique data	1169	2419	4807
Final R indices	$R_1 = 0.0416$	$R_1 = 0.0305$	$R_1 = 0.0302$
$[I>/2\sigma(I)]$	$wR_2 = 0.0781$	$wR_2 = 0.0918$	$wR_2 = 0.0761$

containing 0.1 M tertiarybutylammonium perchlorate (TBAP) under a N<sub>2</sub> saturated environment in a conventional threeelectrode cell with saturated calomel electrode as reference, a Platinum wire having diameter of 0.6 mm as counter and a bare glassy carbon electrode (GCE) with a surface area of 0.196 cm<sup>2</sup> as the working electrode. Prior to experiment the GCE was polished with alumina (Al<sub>2</sub>O<sub>3</sub>) on a nylon buffing pad followed by washing with acetone and finally with distilled water. Electrochemical measurements were carried out at room temperature ( $25 \pm 0.5$  °C).

# 2.4. Synthesis

Reactions of the sodium salt of the ligand (NaL) with trimethyl, dibutyl and tributyltin(IV) chlorides in 1:1, 2:1 and 1:1 molar ratios, respectively afforded air stable compounds **1**, **3** and **4** whereas, to affect the synthesis of **2**, the ligand (LH) was refluxed with dimethyltin(IV) oxide in 2:1 molar ratio. The general synthetic procedures and numbering pattern are shown in Scheme 1.

$$R_3 \text{SnCl} + \text{NaL} \rightarrow R_3 \text{SnL} + \text{NaCl}$$
  

$$R = \text{Methyl}(\mathbf{1}), \quad n - \text{Butyl}(\mathbf{4})$$
(1)

$$4(\text{methyl})_2\text{SnO} + 4\text{LH} \rightarrow (\text{methyl})_8\text{Sn}_4\text{L}_4\text{O}_2(2) + 2\text{H}_2\text{O}$$
(2)

$$(n - \text{Butyl})_2 \text{SnCl}_2 + 2\text{NaL} \rightarrow (n - \text{Butyl})_2 \text{SnL}_2(3) + 2\text{NaCl}$$
(3)

# 2.4.1. Synthesis of sodium (E)-2-(2-fluorobenzylidene) butanoate (NaL)

The ligand viz., (*E*)-2-(2-Fluorobenzylidene) butanoic acid (LH) has been synthesized and reported earlier [23]. The sodium salt of the ligand was prepared by drop wise addition of an equimolar amount of sodium hydrogen carbonate dissolved in distilled water



Scheme 1. General synthetic procedure and numbering pattern of LH and compounds 1-4.

to an ethanolic solution of ligand. The solution was stirred for 1 h at 60 °C followed by filtration. The filtrate was allowed to evaporate to get the colorless crystals of the salt. M.p. 88–89 °C. IR (cm<sup>-1</sup>): 1643  $\nu$ (OCO)<sub>asym</sub>, 1388  $\nu$ (OCO)<sub>sym</sub>,  $\Delta \nu = 255$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.2 (s, 1H, H3), 7.25–6.92 (m, 4H, Ar-H), 2.22 (q, H10, 2H), 0.86 (t, H11, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 177.7 (C-1), 130.4 (C-2), 144.5 (C-3), 124.24 {15.0} (C-4), 159.8{243.8} (C-5), 115.2{21.8} (C-6), 129.4{8.2} (C-7), 128.2{3.0} (C-8), 123.91{3.0} (C-9), 21.4 (C-10), 12.5 (C-11).

# 2.4.2. Trimethylstannyl 2-(2-fluorobenzylidene) butanoate (1)

The sodium salt of the ligand (NaL) (0.500 g, 2.33 mmol) was refluxed for 6 h with trimethyltin(IV) chloride (0.465 g, 2.33 mmol) in dry toluene in a two necked round bottom flask. At the end the turbid solution was allowed to cool down to room temperature. The sodium chloride formed was filtered off and the filtrate was rotary evaporated. The resultant solid was recrystallized from ethanolic solution. (Yield: 0.80 g, 83%). M.p. 104–105 °C. FT-IR (cm<sup>-1</sup>): 1641 v(OCO)<sub>asym</sub>, 1453 v(OCO)<sub>sym</sub>,  $\Delta v$  = 188, 543 v(Sn–C), 541 v(Sn–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.7 (s, 1H, H3), 7.19–7.06 (m, Ar-H, 4H), 2.47 (q, H10, 2H), 1.15 (t, H11, 3H), 0.63 [H<sub>α</sub>, 9H, <sup>2</sup>J (<sup>119/117</sup>Sn<sup>-1</sup>H) 58/56 Hz]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 177.7 (C-1), 130.4 (C-2), 144.5 (C-3), 124.2{14.2}(C-4), 159.8{247.5} (C-5), 115.2{21.8} (C-6), 129.4{8.3} (C-7), 128.2{3.8} (C-8), 123.9{3} (C-9), 21.4 (C-10), 12.5 (C-11), -2.2 [C- $\alpha$ , <sup>1</sup>J (<sup>119</sup>Sn<sup>-13</sup>C) = 397 Hz].

# 2.4.3. Bis(-2-(2-fluorobenzylidene)butanoato)tetramethyldistannoxane (**2**)

Compound 2 was prepared by fluxing dimethylstannyl oxide (0.659 g, 4 mmol) with LH (0.776 g, 4 mmol) in dry toluene for 6 h using Dean-stark apparatus. The reaction mixture was then cooled, filtered and subsequently rotary evaporated to get the dry product which was then recrystallized in the same way as **1**. (Yield: 0.95 g, 70%). M.p. 122–123 °C. FT-IR (cm<sup>-1</sup>): 1540 v(OCO)<sub>asym</sub>, 1398 v(OCO)<sub>sym</sub>,  $\Delta v = 142$ , 551 v(Sn–C), 476 v(Sn–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.8 (s, 1H, H3), 7.35 - 7.09 (m, Ar-H, 4H), 2.51 (q, H10, 2H), 1.19 (t, H11, 3H), 0.93 and 0.99 [H<sub>α</sub>, 6H, <sup>2</sup>J (<sup>119/117</sup>Sn<sup>-1</sup>H) 75/71 Hz]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 177.5 (C-1), 130.2 (C-2), 136.5 (C-3), 123.7{14.3} (C-4), 160.4{248.2} (C-5), 115.7{21.8} (C-6), 130.3{8.2} (C-7), 130.02 {3.7} (C-8), 128.6{3.0} (C-9), 21.5 (C-10), 13.8 (C-11), 4.8 (C- $\alpha$ ).

# 2.4.4. Dibutylstannyl bis(-2-(2-fluorobenzylidene)butanoate (3)

Compound **3** was prepared and crystallized in the same way as **1** employing dibutylstannyl chloride (0.608 g, 2 mmol) and NaL

(0.864 g, 4 mmol). (Yield: 1.15 g, 80%). FT-IR (cm<sup>-1</sup>): 1610  $\nu(OCO)_{asym}, 1483\,\nu(OCO)_{sym}, \Delta\nu = 127,523\,\nu(Sn-C),456\,\nu(Sn-O).\,^{1}H$  NMR (CDCl<sub>3</sub>, ppm): 7.75 (s, 1H, H3), 7.34–7.09 (m, Ar–H, 4H), 2.52 (q, H10, 2H), 1.20 (t, H11, 3H), 1.78-1.77 (m, H\_{\alpha}, and H\_{\beta}, 8H), 1.49–1.42 (m, H\_{\gamma}, 4H), 0.95 (t, H\_{\delta}, 6H).\,^{13}C NMR (CDCl<sub>3</sub>, ppm): 177.5 (C-1), 130.1 (C-2), 136.9 (C-3), 124.0{14.2} (C-4), 162.4{248.2} (C-5), 115.7{21.8} (C-6), 132.4{8.1} (C-7), 131.0{3.8} (C-8), 130.1{3.0} (C-9), 21.5 (C-10), 13.8 (C-11), 25.4 [C-\alpha, \,^{1}J\,(^{119}Sn-^{13}C) = 790 Hz], 26.8 [C- $\beta$ ,  $^{2}J\,(^{119}Sn-^{13}C) = 38$  Hz], 26.4 [C- $\gamma$ ,  $^{3}J\,(^{119}Sn-^{13}C) = 82$  Hz], 13.6 (C- $\delta$ ).

# 2.4.5. Tributylstannyl 2-(2-fluorobenzylidene)butanoate (4)

Compound **4** was prepared and crystallized in the same way as **1** using tributylstannyl chloride (0.651 g, 2 mmol) and NaL (0.432 g, 2 mmol). (Yield: 0.70 g, 75%). FT-IR (cm<sup>-1</sup>): 1649  $\nu$ (OCO)<sub>asym</sub>, 1454  $\nu$ (OCO)<sub>sym</sub>,  $\Delta \nu$  = 195, 523  $\nu$ (Sn–C), 455  $\nu$ (Sn–O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.65 (s, 1H, H3), 7.65–7.06 (m, Ar–H, 4H), 2.48 (q, H10, 2H), 1.15 (t, H11, 3H), 1.70-1.62 (m, H<sub> $\alpha$ </sub> and H<sub> $\beta$ </sub>, 12H), 1.44–1.28 (m, H<sub> $\gamma$ </sub>, 6H), 0.94 (t, H<sub> $\delta$ </sub>, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 172.8 (C-1), 130.1 (C-2), 138.9 (C-3), 124.7{14.3} (C-4), 160.3{247.5} (C-5), 115.5{21.8} (C-6), 129.6{8.2} (C-7), 130.0{3.8} (C-8), 123.8{3.8} (C-9), 21.6 (C-10), 13.8 (C-11), 16.6 [C- $\alpha$ , <sup>1</sup>J (<sup>119/117</sup>Sn–<sup>13</sup>C) = 358/343 Hz], 27.9 [C- $\beta$ , <sup>2</sup>J (<sup>119</sup>Sn–<sup>13</sup>C) = 21 Hz], 27.0 [C- $\gamma$ , <sup>3</sup>J (<sup>119</sup>Sn–<sup>13</sup>C) = 64 Hz], 13.7 (C- $\delta$ ).

# 3. Results and discussion

# 3.1. Spectroscopic studies

#### 3.1.1. FT–IR spectra

The frequencies of interest are those associated with COO, Sn–C and Sn–O groups. The absorption band appearing in range 455–476 and 523–551 cm<sup>-1</sup> in the respective FT-IR spectra of the compounds **1–4**, that were absent from the spectrum of the free ligand (NaL), were assigned to the Sn–O [1,6,24,25] and Sn–C stretching modes of vibration, respectively. The asymmetric and symmetric vibrations due to COO moiety were observed at 1649–1610 and 1375–1483 cm<sup>-1</sup>, respectively. The difference between these two modes of vibration ( $\Delta v$ ) indicates the mode of coordination of the ligand to the tin centre [26]. The reduction in  $\Delta v$  values of COO moiety of the ligand is attributed to the reduction of electron density on its oxygen atoms consequent upon coordination to tin(IV) moiety. In the present work, **1**, **2** and **4** showed

Table 2 Selected bond lengths (Å) and bond angles (°) of NaL.

Bond lengths (Å)		Bond angles (°)	
01–C1	1.282(4)	C101H10	109.5
O1-H10	0.8400	02-C1-O1	123.2(4)
02–C1	1.246(5)	02-C1-C2	118.8(3)
C1-C2	1.515(5)	01-C1-C2	118.0(4)
Na1–O3W	2.379(3)	03W-Na1-04W	90.37(11)
Na1-O4W	2.388(3)	04W-Na1-05W	108.26(12)
Na1–O5W	2.401(3)	05W-Na1-06W	76.13(10)
Na1-O6W	2.469(4)	03W-Na1-06W	85.65(10)

a bridging structure while **3** showed a chelating mode of coordination for the ligand. These observations were further supported by the crystal structures of the compounds. The stannoxane structure for **2** was supported from its characteristic absorption band of medium intensity observed at 693 cm<sup>-1</sup> assignable to Sn–O–Sn functionality [24,27].

# 3.1.2. <sup>1</sup>H NMR spectra

The methyl protons attached to the tin atom in compounds **1** and **2** exhibited a well defined singlet with  ${}^{2}J$  ( ${}^{119/117}Sn^{-1}H$ ) values 58/56 and 75/71 Hz, respectively. The terminal methyl protons of butyl groups attached to tin atom in compounds **3** and **4** gave a clear triplet each while the rest of the protons exhibited a multifaced pattern. The sharp singlet observed for the single proton attached to C-3 was shifted from 7.8 ppm, to 7.6–7.7 ppm, observed for free ligand and compounds **1–4**, respectively. The methyl and methylene protons of the coordinated ligand gave rise to triplet and quartet at 0.86 and 2.22 ppm, respectively in the spectra of all the compounds.  ${}^{2}J$  [ ${}^{119/117}Sn^{-1}H$ ] in Hz are also calculated and helped to confirm four coordinated geometry around tin atom in compound **1** and the retention of six coordinated geometry around tin centre in **2**, in solution form.

# 3.1.3. <sup>13</sup>C NMR spectra

The <sup>13</sup>C NMR spectra of all the complexes showed a more or less downfield shift of all the carbon resonances compared with those of the free ligand (NaL). The shift is a consequence of the electron

density transfer from the ligand to the acceptor tin atom. The positions of carbon atoms in fluorophenyl group are easily assigned with the help of  ${}^{n}J({}^{19}F-{}^{13}C)$  coupling, where n = 1,2,3,4. The  ${}^{n}J({}^{19}F-{}^{13}C)$  coupling constants calculated, are comparable to those reported in the literature. The reported ranges of the  ${}^{n}J({}^{19}F-{}^{13}C)$  coupling, where n = 1,2,3 and 4 are 230–265, 15–25, 7–12 and 3 Hz, respectively [28–30]. The values observed for  ${}^{n}J({}^{19}F-{}^{13}C)$  coupling are 244–248, 15–21, 8 and 3–4 Hz for n = 1,2,3 and 4, respectively.

The satellites due to  ${}^{n}J$  [<sup>119/117</sup>Sn–<sup>13</sup>C] coupling, shown by the compounds **1**, **3** and **4**, have been calculated which are important indicators for the structural elucidation of organotin(IV) carboxylates. Among the synthesized compounds, **1** exhibited  ${}^{1}J$  [<sup>119</sup>Sn–<sup>13</sup>C] being of the order of 397 Hz, confirming a monomeric tetrahedral geometry in solution [31]. In case of compounds **3** and **4**,  ${}^{n}J$  [<sup>119</sup>Sn–<sup>13</sup>C] values are 790, 38, 82 and 358, 21, 64 Hz respectively. These values suggest a skew trapezoidal geometry around tin for **3** and a monomeric tetrahedral geometry for **4** in solution form. This shows that a reduction of coordination number of tin atom in solution occurs in triorganotin(IV) carboxylates (**1** and **4**). On the other hand, the diorganotin(IV) compounds (**2** and **3**) retain their geometries in solution as well.

# 3.2. Crystal structure

# 3.2.1. Structure of NaL

The structure refinement parameters and selected bond lengths and bond angles of the sodium salt of the ligand (NaL) are given in Tables 1 and 2 while its ORTEP is shown in Fig. 1 which reveals that each of the sodium ions is coordinated by six water molecules. Oxygen atom of each water molecule acts as a bridge between the two sodium ions. This constitutes an infinite 2D sheet of the hexacoordinated sodium ions where the hydrogen atoms of the water molecules are oriented outside. These hydrogen atoms are responsible for hydrogen bonding with the oxygen atoms of the carboxylate moiety of the ligand molecules resulting in their attachment to the ionic layer in a perpendicular manner. Additionally, every sodium ion is in a position suitable enough to establish weaker interaction with a lone pair of an oxygen atom of each the two ligand molecules lying on its two opposite sides.



Fig. 1. ORTEP diagram of the sodium salt of the ligand (NaL).



Fig. 2. Packing of NaL showing double layers of ligand molecules sandwitched between those of hydrated sodium ions in aoc plane.

Looking at the packing diagram of the ligand, shown in Fig. 2, it is seen that both sides of the ionic layer are occupied by ligand molecules constituting a double layer of the latter, sandwiched between two consecutive layers of the former.

As is evident from the structure, the ligand molecule is lying as such in the crystal lattice and there is no direct  $O^--Na^+$  bond, however, there are some noteworthy variations in the properties of the NaL compared to those of HL reported earlier by our research group [23]. In this regard, apart from the change in physical properties, there is a considerable shortening of the acidic O-H bond length in NaL compared to that in HL. The O1–H10 bond length in NaL is 0.84 (Å) as opposed to 0.97(2) (Å) in HL. This may be attributed to the reduction of electron density on O1 as a consequence of its weak interaction with sodium ions resulting in strengthening and shortening of O–H bond in crystal lattice. This observation is in line with the shortening of C1–O1 bond (1.282(4) (Å)) of NaL compared to that of HL (1.3006(18) (Å)), again attributable to the same reason.

# 3.2.2. Crystal structure of compound 1

The molecular structure of compound **1** is shown in Fig. 3 whereas the crystal data, selected bond lengths and bond angles are listed in Tables 1 and 3.



Fig. 3. ORTEP diagram of compound 1.

The compound exhibits a carboxylate bridged motif in which the Sn center shows trigonal-bipyramidal coordination, the equatorial plane being defined by the three methyl groups while the axial positions are occupied by two oxygen atoms. According to the literature [32], the geometry around Sn atom can be characterized by the value of  $\tau = (\beta - \alpha)/60$ , where  $\beta$  is the largest of the basal angles around the Sn atom. The angle values  $\alpha = \beta = 180^{\circ}$  correspond to a square-pyramidal geometry, and the value of  $\alpha = 120^{\circ}$  corresponds to a perfect trigonal-bipyramidal geometry. Thus the  $\tau$  value is equal to zero for a perfect square-pyramidal and unity for perfect trigonal-bipyramidal geometry around Sn atom. The angle 0-Sn-O is 171.17° while the sum of the equatorial C-Sn-C angles is 358.9°. The overall structure is an infinite zigzag chain of carboxylate bridged trimethyltin(IV) species (Fig. 4).

#### 3.2.3. Crystal structure of compound 2

The molecular structure of compound **2** is shown in Fig. 5 whereas the crystal data, selected bond lengths and bond angles are listed in Tables 1 and 4.

The geometries of all the tin atoms in **2** can be classified into two types: pentacoordinated tin (Sn2), and hexa-coordinated tin (Sn1). The pentacoordinated tin atoms (Sn2) form three short Sn–O bonds with three oxygen atoms: two from the Sn<sub>2</sub>O<sub>2</sub> moiety and the other one from the carboxylate group, together with the two bonds to methyltin groups. The Sn2 atom may be viewed as highly distorted trigonal bipyramid with the axial site occupied by the O(5) and O(3) atoms ( $\angle$ (O5)–Sn(2)–O(3) = 166.69(9)°) having  $\tau$  = 0.418. The five-coordinate geometry about each of the Sn2 is due to the monodentate coordinated tin atoms, Sn1, forms four short Sn–O bonds with four oxygen atoms: one from the Sn<sub>2</sub>O<sub>2</sub> moiety and the other three from two different carboxylate groups. Together with the two bonds to methyltin groups, the Sn1 atom may be viewed as distorted

Table 3				
Selected bond	lengths (Å) and	bond angles	(°) of compound 1	

Bond lengths (Å)			
Sn1-C1	2.123(4)	01-C4	1.251(5)
Sn1-C2	2.129(4)	02–C4	1.285(5)
Sn1-C3	2.131(5)	O2-Sn1	2.173(3)
Sn1-02	2.173(3)	C4-C5	1.508(5)
Sn1-01	2.394(3)		
Bond angles (°)			
C1-Sn1-C2	116.5(2)	C3-Sn1-O2	97.56(17)
C1-Sn1-C3	121.2(2)	C1-Sn1-O1	84.09(14)
C2-Sn1-C3	121.70(19)	C2-Sn1-01	92.75(14)
C1-Sn1-02	87.22(15)	C3-Sn1-01	85.65(16)
C2-Sn1-O2	92.53(15)	02-Sn1-01	171.17(11)



Fig. 4. Linear polymeric structure of compound 1.

octahedral in geometry. The largest angle around tin atom is 170.44° (= $\angle$  (O(1)–Sn(1)–O(4)). In contrast to the common polymeric stannoxanes, this compound is monomeric tetra-nuclear tetraorganodistannoxane. Here two of the carboxylate ligands exhibit a bridging bidentate mode of coordination while the other two ligands show monodentate mode of coordination (Fig. 6).

# 3.3. Electrochemical studies

Cyclic voltammetry was used to explore the electrochemical redox behavior of compounds 1-4 and the resulting voltammograms at 100 mV s<sup>-1</sup> are given in Fig. 7.

As is evident from the respective voltammograms, one oxidation and one reduction peak was observed for each of the four compounds. The large potential difference between the oxidation and reduction peaks (~2000 mV) provides ample evidence for the independent nature of the irreversible redox processes. The irreversible nature of the redox processes is attributed to the instability of the resulting species in DMSO [33].

The ligand centered relatively weak anodic peaks of the compounds 1-3 occur in the range 0.98–1.13 V. No peak was observed in the oxidation region of the cyclic voltamogram of compound **4** showing its electrochemical stability under the given conditions. The anomalous behavior of butyl derivatives of organotin compounds has been observed by other researchers too [34].

The reduction signals of all the compounds were observed in between -0.95 and -1.06 V as shown in Fig. 7. The cathodic signal of the compounds is attributed to the reduction of tin(IV) to tin(II) species [35,36]. Owing to the similarity of the chemical environment around central metal in these compounds, the individual reduction potential values are lying closer to each other. The more electron donating butyl groups in **3** and **4**, compared to **1** and **2**, render the former pair of compounds less prone to reduction, thus slightly shifting their cathodic potential to more negative values.



Fig. 5. ORTEP diagram of compound 2.

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Selected bond lengths (A	Å) and bond a	ingles (°) of cor	npound <b>2</b> .
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Bond lengths (Å)			
Sn1-05	2.023(2)	Sn2-05	2.032(2)
Sn1-C2	2.103(4)	Sn2-C14	2.112(4)
Sn1-C1	2.120(4)	Sn2-C15	2.113(4)
Sn1-01	2.163(2)	Sn2-05	2.174(2)
Sn1-04	2.265(2)	Sn2-03	2.262(2)
Bond angles (°)			
05-Sn1-C2	107.26(13)	05-Sn2-C14	105.82(13)
05-Sn1-C1	111.36(13)	05-Sn2-C15	112.14(13)
C2-Sn1-C1	140.37(16)	C14-Sn2-C15	141.61(15)
05-Sn1-01	80.88(9)	05-Sn2-05	75.96(9)
C2-Sn1-01	99.98(14)	C14-Sn2-O5	98.20(12)
C1-Sn1-01	94.57(13)	C15-Sn2-O5	96.30(12)
05-Sn1-04	91.12(9)	05-Sn2-03	91.35(9)
C2-Sn1-04	87.34(14)	C14-Sn2-O3	89.00(12)
C1-Sn1-04	83.43(13)	C15-Sn2-O3	84.67(12)
01-Sn1-04	170.44(9)	05-Sn2-03	166.69(9)

The combined plots obtained at different scan rates for each of the compounds are shown in Fig. 8 that clearly indicate that on increasing scan rate, the cathodic peak potential is displaced to more negative potential suggesting irreversibility of the reduction process of the compounds.

For irreversible processes the peak current is given by the Randles–Sevcik model (Eq. (4)) [37]:

$$i_{\rm p} = \left(2.99 \times 10^5\right) n(\alpha n)^{1/2} A C^* D_{\rm o}^{1/2} \nu^{1/2} \tag{4}$$

where  $i_p$  is the peak current in amperes,  $\alpha$  is the charge transfer coefficient, n is the number of electrons involved in the redox process,  $D_0$  is diffusion coefficient in cm<sup>2</sup> s<sup>-1</sup>, C<sup>\*</sup> is the bulk concentration of the compound in mol  $cm^{-3}$ , A is the surface area of the working electrode in  $cm^2$  and v is the potential scan rate in V s<sup>-1</sup>. The values of the diffusion coefficient for the redox processes are calculated employing Eq. (4) by putting various cathodic parameters in it using the slope of  $i_{pc}$  (µA) vs.  $v^{1/2}$  (Vs<sup>-1</sup>) plot (shown in Fig. 9(a)). The values of  $D_0$  thus calculated for compounds 1–4 are listed in Table 4, which show that the mobility of lower coordinated Sn<sup>4+</sup> species is hampered by the facile attachment of relatively more solvent molecules. The slow diffusion of 4 is attributed to its tetracoordinated geometry around tin(IV) center leading to high solvation by solvent molecules and the presence of relatively longer butyl groups. Looking at the coordination number and steric effects of the attached groups to the tin centre, the ease of solvation of the molecules would vary in the order: 1 > 4 > 2 > 3.



Fig. 7. Cyclic voltammograms of 1.40 mM compounds 1–4 at 100 mV s<sup>-1</sup>.

This shows that solvation does play a role in determining the rate of mass transport of these compounds to the electrode surface. However, being adsorption controlled the values of  $D_0$  and their mutual order is not typical of a diffusion controlled process.

Fig. 9(b) shows the linear relation between log  $i_{pc}$  vs. –log v with slope values of 0.19, 0.22, 0.12 and 0.17 for compounds **1–4**, respectively. It reveals predominantly adsorption controlled redox processes [38]. The general linear regression equation for this relation is given as follows:

$$-\log i_{\rm pc}[{\rm mA}] = +{\rm slope} \log v \left[ {\rm Vs}^{-1} \right] + {\rm intercept}$$

For getting further insight into the nature of the electrochemical redox process, the charge transfer coefficients ( $\alpha$ ) of the compounds **1–4** were determined by the application of Bard and Faulkner relation [39]. According to them the value of  $\alpha$  can be calculated as

$$\alpha n = 47.7 / \left[ E_{\text{pa}} - E_{\text{pa}} / 2 \right] \text{mV}$$
(5)

where  $E_{pa}/2$  is the potential where the current is at half the peak value.

The values of charge transfer coefficient ( $\alpha$ ) for the compounds were calculated using Eq. (5) and are listed in Table 5.



Fig. 6. Packing diagram of compound 2.



Fig. 8. Cyclic voltammogramms of compounds 1(A), 2 (B), 3(C) and 4(D) each at scan rates of 40, 60, 80, 100, 120, 140 and 160 mV s<sup>-1</sup>.

For irreversible electrode processes the value of *E* is given by Eq. (6) [40-42]:

$$E = E^{o} + 2.303 RTk^{o} / \alpha nF - 2.303 RT / \alpha nF \log \nu$$
(6)

where  $E^{o}$  is the formal redox potential,  $k^{o}$  is the standard heterogeneous rate constant and F is the Faraday constant. The values of heterogeneous rate constant ( $k^{o}$ ) were determined from the intercept of potential *vs.* negative logarithm of scan rate plot (shown in Fig. 10(a)) by putting various parameters in Eq. (6). The values of

Table 5	
CV parameters for the reduction of the compounds.	

Compound	E (V)	αn	$D \times 10^{7}$ (cm <sup>2</sup> s <sup>-1</sup> )	$k^{\circ}$ (s <sup>-1</sup> )
1	-0.89	0.25	4.80	1.36
2	-0.92	0.28	4.02	0.70
3	-0.96	0.27	4.27	1.66
4	-0.99	0.30	3.13	2.11



Fig. 9. Plots of cathodic peak current vs. square root of the scan rate (a) and log of cathodic peak current vs. -log scan rate (b) for compounds 1-4.



Fig. 10. Plots of cathodic peak potential vs. -log of scan rate (a) and scan rate (b) for compounds 1-4.

formal potential (*E*) were determined from the intercept of reduction peak potential *vs.* scan rate curve (Fig. 10(b)) by extrapolating the curve to the potential axis at v = 0. The values of E<sup>o</sup> are listed in Table 5. According to Eq. (6), there is a linear relation between potential (*E*) and logarithm of scan rate (log *v*) and the generalized linear regression equation thus obtained is given below:

$$E_{\rm pc}(V) = -{\rm slope} \times \log \nu \left[ {\rm Vs}^{-1} \right] + {\rm intercept}$$

The values of  $k^0$  evaluated using Eq. (6) are given in Table 5 which show that the small sized **4** undergoes more facile electron transfer process. Being mononuclear, **3** has higher rate compared to the heavier tetranuclear **2**. Being heaviest, **2** has the smallest rate of electron transfer process among all the four compounds. The order of  $k^0$  supports adsorption controlled process. That is, in case of diffusion controlled redox process, **1** and **4** would have slowest rate, being more prone to coordination by solvent molecules.

# 4. Conclusion

Four new trimethyl-, dimethyl-, dibutyl- and tributyl-organotin compounds (1-4) of sodium (E)-2-(2-fluorobenzylidene) butanoate ligand (NaL) have been successfully synthesized in good yield and characterized using spectroscopic techniques. NaL and compounds **1** and **2** were analyzed by X-ray single crystal analysis as well which revealed the structure of 1 as zigzag polymer and 2 as tetra-nuclear distannoxane. The FT-IR and NMR data were in good agreement with those of single crystal x-ray analysis. The cyclic voltammetric studies in DMSO using TBAP as supporting electrolyte have shown that the compounds exhibit oxidation and reduction processes with the respective peaks centered in the potential ranging from 0.98 to 1.13 and -0.95 to -1.06 V, respectively. The oxidation and reduction processes occur independent of each other and were found predominantly adsorption controlled. In support to this, the values of  $D_0$  were found to vary in the order: 1 > 3 > 2 > 4which is explainable on solvation and steric factors to some extent while the order of  $k^{\circ}$  was found as: 4 > 3 > 1 > 2 which cannot be explained on solvent effect and seems independent of such factors.

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# Appendix A. Supplementary material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 900473, 891369 and 891370 for NaL and compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [Fax +44(1223)336-033], e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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