SYNTHESIS AND CHARACTERIZATION OF TRIBUTYLTIN(IV) COMPLEXES DERIVED FROM PYRIDINE MONOCARBOXYLIC ACIDS

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The complexes of tributyltin(IV) with 2-pyridinecarboxylic acid, 2PycH; 3-pyridinecarboxylic acid, 3PycH; 4-pyridinecarboxylic acid, 4PycH and 5-bromo-3-pyridinecarboxylic acid, 5B3PycH (containing –COOH group and aromatic {N} donor atom) were successfully synthesized. The complexes were prepared by condensation of bis{tributyltin(IV)} oxide, $(Bu_3Sn)_2O$ with the respective free acids utilising the Dean and Stark apparatus to remove water. The free ligands and complexes obtained were characterized quantitatively using C, H, N and Sn elemental analysis as well as spectroscopic methods such as infrared (FTIR) and nuclear magnetic resonance (^{1}H, ^{13}C & ^{119}Sn NMR). Analysis of the free ligands and the complexes showed that the coordination took place via oxygen atoms of the carboxylate group. The carboxylate anions acted as monodentate or bidentate ligands. In some of these complexes, the carboxylate groups form bridges between two central tin atoms leading to the formation of polymeric structure. An X-ray investigation on the tributyltin(IV)- 2PycH complex provides further evidence of the polymeric structure of the complex with trigonal bipyrimidal geometry of the tin atom as predicted by the solid state ^{119}Sn NMR .

Keywords: Tributyltin(IV) carboxylate; Polymer, X-ray, prridine

Abstrak

Kompleks tributilstanum(IV) dengan 2-piridina karboksilik asid, 2PyCH; 3-piridina karboksilik asid, 3-PyCH;4-piridina karboksilik asid,4-PyCH dan 5-bromo-3-piridina karboksilik asid, 5B3PyCH (mengandungi kumpulan COOH dan atom penderma {N}) telah berjaya disintesis. Penyediaan kompleks tersebut telah dilakukan dengan menindak balas bis{tributilstannum(IV)}oksida dengan asid tersebut menggunakan peralatan Dean dan Stark untuk pemisahan air. Ligan bebas dan kompleks telah diciri secara kuantitatif dengan spektroskopi inframerah dan RMN. Data spektroskopi menunjukkan berlaku pengkoordinatan antara atom Sn dengan oksigen kumpulan karboksilik secara monodentat atau bidentat. Terdapat juga kompleks di mana berlaku jejambat antara dua atom Sn yang membawa kepada struktur polimer. Kajian sinar-X ke atas kompleks tributilstanum(IV)- 2PyCH menunjukkan struktur polimer dengan geometri stanum trigonal bipiramid seperti yang dijangka daripada ^{119}Sn NMR dalam keaadaan pepejal.

INTRODUCTION

The synthesis and study of organotin(IV) carboxylate complexes have received considerable attention in recent years due to the large array of applications in industries as well as in biocidal fields [1-13]. However, the discovery of their environmental impact from the late 1980s has led to the decrease in their application and usage [14]. In addition, some reports stated that the used of tributyltin (TBT) in antifouling paints has caused contamination in coastal waters and marine sediments [15-17]. Besides, TBT chemicals cause dramatic effects on shell fishes, inhibit the growth of the marine microalga, *Nannochloropsis oculata*, cause imposex in intertidal dogwhelk *Nucella lapillus* and inhibits human cytochrome P450 aromatase activity [18-20]. Hence, lots of regulation had been implemented to restrict the usage of organotin(IV) compound in the shipping area [14]. On the other hand, in recent years many different types of organotin(IV) carboxylate

compound have been tested for their *in-vitro* activity against a large array of tumor cell lines and have been found to be as effective as traditional heavy metal anticancer drugs, such as "*cis*-platin" and "paraplatin" [5-7]. Moreover, triorganotin(IV) complexes display a higher biological activity compared to di- and mono-organotin analoques [2]. On the basis of spectroscopic measurement as well as previous literature reviews, the coordination number of tributyltin(IV) carboxylates is commonly four or five [21-27].

Based on the literature reviews, two structures of tributyltin(IV) carboxylates derived from 2,6-pyridinecarboxylic acid were reported [27,28]. Both crystal structures are polymeric with the general repeating unit, $[(C_4H_9)_3SnOCOC_5H_3NOCO]_n$ and distinguished by the presence of dicyclohexylammonium [27] and methylphenylammonium [28] as counter-ions of crystallization. The tin atom is five-coordinate and exists in trigonal bipyramid geometry with the O atoms in the axial positions. In addition, the N atom of the pyridine ring does not take part in coordination to tin atom [27,28]. In this study, four tributyltin(IV) carboxylate complexes were obtained by condensation of bis{tributyltin(IV)} oxide, $(Bu_3Sn)_2O$ with 2-pyridinecarboxylic acid, 2PycH; 3-pyridinecarboxylic acid, 3PycH; 4-pyridinecarboxylic acid, 4PycH and 5-bromo-3-pyridinecarboxylic acid, 5B3PycH utilising the Dean and Stark apparatus to remove water. The acids, salts and complexes obtained were characterized quantitatively by microelemental analysis as well as spectroscopic methods such as infrared (FTIR) and nuclear magnetic resonance (NMR).

EXPERIMENTAL

Materials and Measurements

Bis{tributyltin(IV)} oxide, $(Bu_3Sn)_2O$ was purchased from Aldrich Chemical Company and all pyridine monocarboxylic acids were obtained from Fluka Chemie AG. All reagents and solvents were purchased commercially and used without any further purification. The melting points were determined in open capillaries and are uncorrected. Microelemental C, H and N analyses were carried out on a Perkin-Elmer 2400 CHN Elemental Analyzer. Tin was determined gravimetrically by igniting a known quantity of each complex to SnO_2. Infrared spectra were recorded using a Perkin-Elmer System 2000 FTIR Spectrophotometer as a KBr disc at 4000-400 cm^{-1} the frequency range. The spectra for ^{1}H and ^{119}Sn NMR were recorded on a Bruker AC-P 400 MHz FTNMR Spectrometer and ^{13}C NMR was recorded on a Bruker AC-P 300 MHz FTNMR Spectrometer using $CDCl_3$ or DMSO as the solvent and tetramethylsilane, TMS as an internal standard.

X-ray crystallography

Room-temperature diffraction data were collected on a Bruker SMART APEX area-detector diffractometer (Mo Kα radiation, λ=0.71073 Å) on a crystal of size 0.34 x 0.28 x 0.21 mm over the range $1.7< \theta <27.0$. The structure was solved and refined by using the SHELXS-97 [29]. The final R (I>2/s(I)) and Rw values were 0.06 and 0.16 respectively. All non-hydrogen atoms were refined anisotropically The perspective view of the molecule was obtained using SHELXTL [30]. The molecule suffered from a severe disordered nature of some of the atoms. Treatment for the disordered atoms showed slight improvement but the thermal parameters are still high. Low temperature experiment is needed for the possibility to improve the the data. The crystal data and refinement parameters are given in Table 6.

Preparation of Tributyltin(IV) Carboxylates

Preparation of *2-pyridinecarboxylatotributyltin(IV), $Bu_3Sn2Pyc$(**1**)*

Complex of 2-pyridinecarboxylatotributyltin(IV), $Bu_3Sn2Pyc$ was obtained by heating at refluxing temperature a 1:1 molar mixture of bis{tributyltin(IV)} oxide, $(Bu_3Sn)_2O$, (2.98 g, 5 mmol) and 2-pyridinecarboxylic acid, 2PycH (1.23 g, 10 mmol) in a mixture of toluene/ethanol (4:1, 50 mL) for 2 hours. A clear colourless solution was obtained by filtration and kept in a bottle and left in the fridge. After three days, some colourless crystals (3.91 g, 95 % yield) were obtained. M.p.: 98.1-98.7 °C. Microelemental: Found for $C_{18}H_{31}N_1O_2Sn_1$: C, 52.94; H, 7.76; N, 3.34; Sn, 28.12 % and calc.: C, 52.46; H, 7.58; N, 3.40; Sn, 28.80 %. FTIR as KBr disc (cm^{-1}): $\nu(COO)_{as}$ 1642, $\nu(COO)_s$ 1395, ν(Sn-O) 408, ν(Sn-C) 545. ^{1}H-NMR: δ: pyridine protons 7.42-7.45 (1H, dt, *J*= 2.8 Hz); 7.80-7.85 (1H, dt, *J*= 7.7 Hz); 8.15-8.17 (1H, d, *J*= 7.8 Hz); 8.73-8.75 (1H, d, *J*= 4.1 Hz); butyl, CH_3 0.91-0.95 (9H, t, *J*= 7.4 Hz); CH_2 1.32-1.42 (12H, hx, *J*= 7.2 Hz); CH_2 1.65-1.73 (6H, qn, *J*= 7.4 Hz) ppm. ^{13}C-NMR: δ: pyridine carbons 125.63, 126.46, 137.27, 149.70, 150.23 ppm; butyl 14.02, 17.49, 27.47, 28.22 ppm; COO 170.12 ppm. ^{119}Sn-NMR: δ: +119.58 ppm.

Preparation of *3-pyridinecarboxylatotributyltin(IV), $Bu_3Sn3Pyc$ (**2**)*

Complex ***2*** *was prepared by a* similar method and 3-pyridinecarboxylic acid, 3PycH was used instead of 2PycH in acetonitrile (70 mL). After 2 weeks, some colourless crystal (2.06 g, 50 % yield) were obtained. M.p.: 76.5-77.8 °C. Microelemental: Found for $C_{18}H_{31}N_1O_2Sn_1$: C, 53.25; H, 7.28; N, 3.53; Sn, 28.61 %. And calc.: C, 52.46; H, 7.58; N, 3.40; Sn, 28.80 %. FTIR as KBr disc (cm^{-1}): $\nu(COO)_{as}$ 1644, $\nu(COO)_s$ 1345, ν(Sn-O) 428, ν(Sn-C) 557. ^{1}H-NMR: δ: pyridine protons 7.32-7.36 (1H, dq, *J*= 3.0 Hz); 8.28-8.31 (1H, td, *J*= 8.1 Hz); 8.69-8.71 (1H, d, *J*= 4.9 Hz); 9.22-9.23 (1H, dd, *J*= 2.1 Hz); butyl, CH_3 0.90-0.94 (9H, t, *J*= 7.4 Hz); CH_2 1.32-1.42 (12H, hx, *J*= 6.6 Hz); CH_2 1.62-1.70 (6H, qn, *J*= 7.2 Hz) ppm. ^{13}C-NMR: δ: pyridine carbons 123.48, 128.56, 137.99, 151.86, 152.66 ppm; butyl 14.03, 17.17, 27.39, 28.21 ppm; COO 170.16 ppm. ^{119}Sn-NMR: δ: +117.26 ppm.

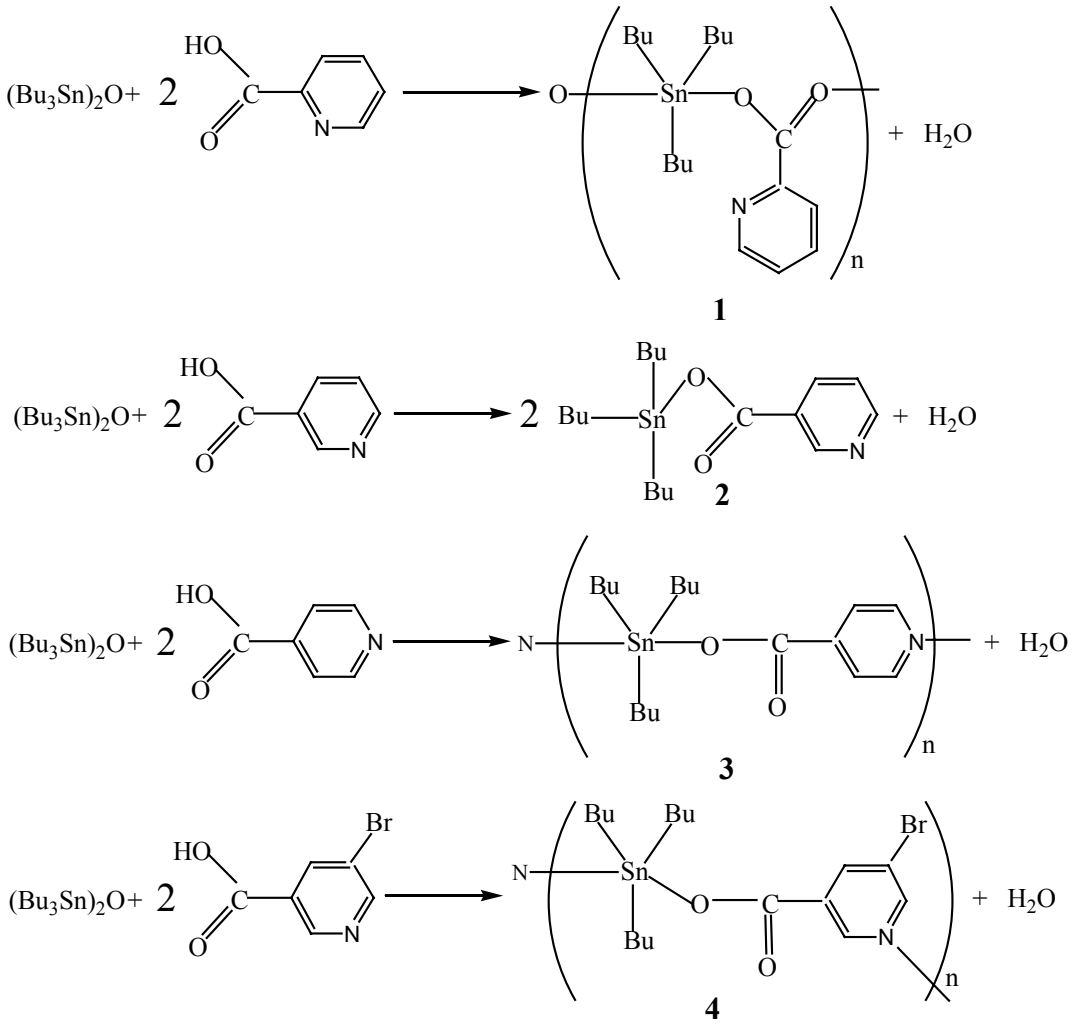

FIGURE 1. Reaction scheme for the synthesis and proposed structure of complexes **1** – **4**

Preparation of *4-pyridinecarboxylatotributyltin(IV), $Bu_3Sn4Pyc$ (**3**)*

A similar method to that of **1** was utilized, substituting 4-pyridinecarboxylic acid, 4PycH for 2-pyridinecarboxylic acid, 2PycH in acetone (50 mL). After a few days, some white precipitates (3.77 g, 91 % yield) were obtained. M.p.: 143.6-144.1 °C. Microelemental: Found for $C_{18}H_{31}N_1O_2Sn_1$: C, 52.66; H, 7.51; N, 3.30; Sn, 28.70 % and calc.: C, 52.46; H, 7.58; N, 3.40; Sn, 28.80%. FTIR as KBr disc (cm^{-1}): $\nu(COO)_{as}$ 1649, $\nu(COO)_s$ 1353, ν(Sn-O) 427, ν(Sn-C) 551, ν(Sn-N) 461. ^{1}H-NMR: δ: pyridine protons 7.86-7.88 (2H, dd, *J*= 4.4 Hz); 8.71-8.72 (2H, dd, *J*= 4.4 Hz); butyl, CH_3 0.90-0.94 (9H, t, *J*= 7.3 Hz); CH_2 1.32-1.42 (12H, hp, *J*= 7.2 Hz); CH_2 1.64-1.76 (6H, qn, *J*= 6.9 Hz) ppm. ^{13}C-NMR: δ: pyridine carbons 124.04, 140.38, 150.47 ppm; butyl 14.98, 17.25, 27.36, 28.18 ppm; COO 169.89 ppm. ^{119}Sn-NMR: δ: +115.83 ppm.

Preparation of *5-bromo-3-pyridinecarboxylatotributyltin(IV), $Bu_3Sn5BPyc$ (4)*

A similar method to that of **1** was utilized, substituting 5-bromo-3-pyridinecarboxylic acid, 5B3PycH for 2-pyridinecarboxylic acid, 2PycH in acetonitrile (70 mL). After a few days, some yellow precipitates (3.63 g, 74 % yield) were obtained. M.p.: 68.5-69.1 °C. Microelemental: Found for $C_{18}H_{30}N_1O_2Br_1Sn_1$: C, 43.69; H, 5.93; N, 2.98; Sn, 23.95 % and calc.: C, 44.03; H, 6.17; N, 2.85; Sn, 24.17 %. FTIR as KBr disc (cm^{-1}): $\nu(COO)_{as}$ 1654, $\nu(COO)_s$ 1333, ν(Sn-O) 424, ν(Sn-C) 573, ν(Sn-N) 469. ^{1}H-NMR: δ: pyridine protons 8.44-8.45 (1H, t, *J*= 2.0 Hz); 8.79-8.77 (1H, d, *J*= 2.3 Hz); 9.11-9.12 (1H, d, *J*= 1.7 Hz); butyl, CH_3 0.89-0.92 (9H, t, *J*= 7.3 Hz); CH_2 1.31-1.40 (12H, hx, *J*= 7.3 Hz); CH_2 1.62-1.70 (6H, qn, *J*= 7.5 Hz) ppm. ^{13}C-NMR: δ: pyridine carbons 120.83, 129.97, 140.61, 149.63, 153.62 ppm; butyl 14.01, 17.29, 27.38, 28.16 ppm; COO 168.57 ppm. ^{119}Sn-NMR: δ: +125.92 ppm.

RESULTS AND DISCUSSION

Complexes **1** and **2** were obtained as single crystals however complexes **3** and **4** were obtained as precipitates. Molecular sieves were added during heating at refluxing temperature remove water formed during the reaction [31]. In addition, the water liberated in the reaction was removed by azeotropic dehydration using the Dean and Stark apparatus. Microelemental analysis C, H, N and Sn obtained were in agreement with the predicted formula . Moreover, complexes **1** – **4** gave sharp melting points indicating the of the isolated complexes were fairly pure. The melting points and microelemental analysis results of these complexes are presented in Table 1.

TABLE 1. Melting points and elemental analysis data.[+]

Complexes	Melting point (°C)	%C	%H	%N	%Sn	Physical Appearance
1	98.1-98.7	52.94 (52.46)	7.76 (7.58)	3.34 (3.40)	28.12 (28.80)	Colourless crystal
2	76.5-77.8	53.25 (52.46)	7.28 (7.58)	3.53 (3.40)	28.61 (28.80)	Colourless crystal
3	143.6-144.1	52.66 (52.46)	7.51 (7.58)	3.30 (3.40)	28.70 (28.80)	White precipitate
4	68.5-69.1	43.69 (44.03)	5.93 (6.17)	2.98 (2.85)	23.95 (24.17)	Yellow precipitate

[+]Calculated values are given in parentheses.

The infrared spectra of the complexes showed distinct differences from those of the free ligands. The ν(O-H) bands which appeared in the range 2402-2878 cm^{-1} for the free ligands, were absent in the infrared spectra of complexes **1** – **4**. The $\nu(COO)_{as}$ band of the complexes are shifted to lower wave number compared to that of the free ligands, similar observation also reported by others [22, 27, 32]. Complexes **1** – **4** showed $\nu(COO)_{as}$ and $\nu(COO)_s$ in the range of 1642-1654 and 1333-1395 cm^{-1}, respectively. The assignment of important infrared bands for the free ligands, sodium salts and complexes are presented in Table 2.

TABLE 2. Important infrared data for the free ligands and complexes **1** – **4** (cm^{-1}).

Complexes	ν(OH)	$\nu(COO)_{as}$	$\nu(COO)_s$	$\Delta\nu$	ν(Sn-O)	ν(Sn-C)	ν(Sn-N)
PcH	2597	1723	1295	428	-	-	-
PcNa	-	1606	1412	194	-	-	-
NcH	2439	1707	1325	382	-	-	-
NcNa	-	1614	1410	204	-	-	-
4NcH	2402	1715	1334	381	-	-	-
4NcNa	-	1586	1412	174	-	-	-
5BNcH	2878	1675	1290	385	-	-	-
5BNcNa	-	1619	1384	235	-	-	-
1	-	1642	1395	247	408	545	-
2	-	1644	1345	299	428	557	-
3	-	1649	1353	296	427	551	461
4	-	1654	1333	321	424	573	469

Generally, the $\Delta\nu = [\nu(COO)_{as} - \nu(COO)_s]$ value is used to determine the bonding properties of carboxylate anion to tin atom in organotin(IV) carboxylate complexes [22, 33]. Sandhu and Verma in their studies and reports have shown that the $\Delta\nu$ value of complexes greater by 65-90 cm^{-1} than in their sodium salts indicates either asymmetric or monodentate bonding of the carboxylate group to tin(IV) atom [22]. Complex **2** showed has a $\Delta\nu$ 92 cm^{-1} higher than in the sodium salt indicating either an asymmetric or monodentate bonding of the carboxylate group to tin(IV) atom. In addition, complexes **3** and **4** also showed the carboxylate group behaves similarly to the since the $\Delta\nu$ value of complexes **2** and **3** are higher compared to the sodium salt of the acids by 122 cm^{-1} and 86 cm^{-1}, respectively [22]. However, complex **1** behaves as a bidentate bridging ligand since the $\Delta\nu$ value of complexes **1** is comparable to the sodium salt of the acids. It is believed that complex **1** exhibits the same behaviour as that of 2,6-pyridinedicarboxylatotributyltin(IV) - the carboxylate anion acts as a bridge between the tin atoms to form a polymeric chain structure [27,28]. Complexes **3** and **4** showed an additional weak band in the range of 461- 469 cm^{-1} indicating the occurrence of ν(Sn-N) band [34]. This indicates that the pyridine N atom is coordinated to the neighboring tin atom to form a polymeric chain since both complexes show that the carboxylate anions are coordinated to tin in monodentate manner and is unable to bridge to the neighbring tin atom. A band was observed in the region 408-428 cm^{-1} and may be assigned to vibrations associated to the Sn-O stretching frequency [22]. The presence of this band indicates that the Sn atom is bonded to the oxygen atom of the acidic group of the ligands. Moreover, in the infrared spectra of complexes **1** – **4** showed ν(Sn-C) in the range of 545-573 cm^{-1}, respectively [22]. The disappearance of the ν(O-H), shifting of ν(COO) and occurrence of ν(Sn-O) bands in complexes **1** – **4** indicates that the carboxylate groups are coordinated to the Sn atom. An outline of the reaction scheme and proposed structure for complexes **1** – **4** are depicted in Figure 1.

The relevant data obtained from the ^{1}H NMR spectra for the complexes **1** – **4** are presented in Table 3, and that of ^{13}C and ^{119}Sn NMR data are presented in Table 4 and 5 respectively. Chemical shift values are relative to an internal standard, tetramethylsilane (TMS). The ^{1}H NMR spectra for the complexes **1** – **4** only showed two sets of peaks. These peaks are located in the upfield and downfield region of the ^{1}H NMR spectra. The upfield regions of the ^{1}H NMR spectra showed the signal of the butyl protons in the range of 0.89-1.76 ppm [23-25]. In addition, pyridine protons appear in the downfield region in the range 7.32-9.23 ppm in the spectra of complexes and ligands. These complexes were found to exhibit no additional resonances and thus, reflects the purity of the complexes. The integration of peaks concurs with the number of protons postulated from the structures proposed for the complexes.

TABLE 3. ^{1}H NMR data for ligands and complexes **1** – **4**.[+]

Complexes / Ligands	Chemical Shift (ppm)	
	δH(pyridine)	δH(butyl)
PcH	7.63-7.66 (1H, dt, 5.6 Hz), 7.99-8.03 (1H, dt, 7.7 Hz) 8.29-8.31 (1H, td, 7.8 Hz), 8.87-8.89 (1H, d, 3.6 Hz)	-
NcH	7.52-7.55 (1H, tt, 6.2 Hz), 8.25-8.28 (1H, td, 7.9 Hz) 8.77-8.79 (1H, td, 4.8 Hz), 9.07-9.08 (1H, ts, 0.9 Hz)	-
4NcH	7.80-7.82 (2H, qd, 5.2 Hz), 8.77-8.79 (2H, qd, 5.1 Hz)	-
5BNcH	8.36 (1H, s), 8.89 (1H, s), 9.00 (1H, s)	-
1	7.42-7.45 (1H, dt, 2.8 Hz), 7.80-7.85 (1H, dt, 7.7 Hz) 8.15-8.17 (1H, d, 7.8 Hz), 8.73-8.75 (1H, d, 4.1 Hz)	CH_3; 0.91-0.95 (9H, t, 7.4 Hz) CH_2; 1.32-1.42 (12H, hx, 7.2 Hz) CH_2; 1.65-1.73 (6H, qn, 7.4 Hz)
2	7.32-7.36 (1H, dq, 3.0 Hz), 8.28-8.31 (1H, td, 8.1 Hz) 8.69-8.71 (1H, dd, 4.9 Hz), 9.22-9.23 (1H, dd, 2.1 Hz)	CH_3; 0.90-0.94 (9H, t, 7.4 Hz) CH_2; 1.32-1.42 (12H, hx, 6.6 Hz) CH_2; 1.62-1.71 (6H, qn, 7.2 Hz)
3	7.86-7.88 (2H, dd, 4.4 Hz), 8.71-8.72 (2H, dd, 4.4 Hz)	CH_3; 0.90-0.94 (9H, t, 7.3 Hz) CH_2; 1.32-1.42 (12H, hp, 7.2 Hz) CH_2; 1.64-1.76 (6H, qn, 6.9 Hz)
4	8.44-8.45 (1H, t, 2.0 Hz), 8.76-8.77 (1H, d, 2.3 Hz) 9.11-9.12 (1H, d, 1.7 Hz)	CH_3; 0.89-0.92 (9H, t, 7.3 Hz) CH_2; 1.31-1.40 (12H, hx, 7.3 Hz) CH_2; 1.62-1.70 (6H, qn, 7.5 Hz)

[+] s = singlet; d = doublet t = triplet; q = quartet; qn =quintet; hx = hextet; hp = heptet; m = multiplet.

Evidence for the formation of the complexes is clearly exhibited in the ^{13}C NMR spectra. The ^{13}C NMR spectra show a sharp peak in the downfield region of complexes **1** – **4**, in the range 165.55-170.16 ppm. This signal is assigned to the δ(COO) chemical shifts. Moreover, the ^{13}C NMR spectra of complexes **1** – **4** show the chemical shift δ(COO) are shifted downfield compared to that of the free ligands indicating the carboxylate anions are bonded to tin atom upon complexation. The occurrence of five resonances in the range 120.83-154.78 ppm in the ^{13}C NMR spectra of these complexes and the free ligands are due to the presence of pyridine carbons. Moreover, in the upfield region of ^{13}C NMR spectra, complexes **1** – **4** show the occurrence of CH_3 and and CH_2 in the range 14.01-14.98 and 17.17-28.22 ppm, respectively [23-25]. Generally, the ^{13}C NMR spectra of the complexes were found to exhibit no additional resonances and thus, reflect the high purity of the complexes.

It is known that the δ values of ^{119}Sn NMR are markedly dependent on the coordination properties around the tin atom in the organotin(IV) complexes. For complexes **1** and **2,** sharp peaks are observed at +119.58 and +117.26 ppm, respectively. This indicates that complexes **1** and **2** are four-coordinate [21]. Moreover, complexes **3** and **4** also showed a sharp peak at +115.83 and +125.92 ppm, respectively indicating that the Sn atom in both complexes are also four-coordinate [21]. Nádvorník and his coworkers in their studies reported that the tin atom moiety of tributyltin(IV) carboxylate complexes, with $^1J(^{119}Sn\text{-}^{13}C)$ in the range 326.70-386.70 Hz, are typically quasitetrahedral arrangement of Bu_3SnX with four-coordinate tin atom [21]. It is believed that sp^3 hybrid orbitals are involves in the bonding of tin atom with the three *n*-butyl groups [21].Complexes **1** – **4** showed coupling constants, $^1J(^{119}Sn\text{-}^{13}C)$, in the range of 356.35-361.53 Hz and lie in the range of 326.70-386.70 Hz, hence, this indicates that the tin atom moiety in complex **1** – **4** are four-coordinated and having tetrahedral geometry. The $^nJ(^{119}Sn\text{-}^{13}C)$ data of complexes **1** – **4** obtained from the NMR spectra show the usual sequence of $^3J(^{119}Sn\text{-}^{13}C) \rangle\rangle {}^2J(^{119}Sn\text{-}^{13}C) \rangle {}^4J(^{119}Sn\text{-}^{13}C)$ similar to that of reported by Nádvorník and his coworkers [21].

Generally tributyltin(IV) carboxylate complexes exist in trigonal bipyramid geometry and the tin atom is five-coordinate in solid phase. Based on the infrared data, complexes **1**, **3** and **4** are believed to exist in trigonal bipyramid geometry and the tin atom is five-coordinate. However, complexes **1**, **3** and **4** show one-coordination less in solution NMR. This observation may be due to depolymerization of the complexes upon dissolution of the solid sample. Hence, complexes **1**, **3** and **4** exhibit five-coordinate in solid phase and exhibit four coordinate in solution phase. However, the tin moiety of complex **2** exhibits four-coordinate as expected in solid or solution phase.

Basically, complexes **2** and **4** are derived from 3-pyridinecarboxylic acid and the carboxylate anion in both complexes are coordinated to Sn atom in monodentate manner. Based on the infrared spectrum, complex **2** does not occur in polymeric chains because the nitrogen atom did not participate in any coordination to the neighboring tin moiety. This may due to the nitrogen atom in complex **2** being less electronegative compared to the oxygen atom from the carboxylate anion and hence, the electron density from the pyridine ring was drawn by the carboxylate anion towards the tin atom for complexation. As a result, the electron donor (nitrogen atom) in complex **2** is too weak to coordinate to the nearby tin moiety to form polymeric chains. However, complex **4** is obtained in polymeric chain when the *meta* position is substituted with bromine atom and the nitrogen atom showed coordination with the neighboring tin moiety. This may due to the high electron density in bromine atom hence causing back-donation of electron to the pyridine ring. As a result, the electron donor (nitrogen atom) in complex **4** is able to coordinate with the neighboring tin moiety to form polymeric chains.

TABLE 4. ^{13}C NMR data for complexes **1** – **4**.

Complexes	Chemical Shift (ppm)		
	Pyridine	Butyl	COO
PcH	125.14, 128.06, 139.18, 147.64, 148.34	-	165.55
NcH	124.63, 127.42, 137.80, 151.06, 154.11	-	167.12
4NcH	123.60, 138.93, 151.47	-	167.04
5BNcH	121.04, 129.19, 139.93, 149.46, 154.78	-	165.84
1	125.63, 126.46, 137.27, 149.70, 150.23	17.49 (1), 28.22 (2)	170.12
2	123.48, 128.56, 137.99, 151.56, 152.66	17.17 (1), 28.12 (2)	170.16
3	124.04, 140.38, 150.47	17.25 (1), 28.18 (2)	169.89
4	120.83, 129.97, 140.61, 149.68, 153.62	17.29 (1), 28.16 (2)	168.57

Ref : $^4CH_3\text{-}^3CH_2\text{-}^2CH_2\text{-}^1CH_2\text{-Sn}$

TABLE 5. ^{119}Sn NMR and $^{n}J(^{119}Sn-^{13}C)$ data for complexes **1 – 4.**

Complexes	$\delta(^{119}Sn)$, ppm	$^{n}J(^{119}Sn-^{13}C)$, Hz			
		n = 1	n = 2	n = 3	n = 4
1	+119.58	356.91	18.93	66.94	nd
2	+117.26	359.39	20.99	64.66	nd
3	+115.83	361.53	21.35	64.89	nd
4	+125.92	356.35	21.20	64.44	nd

nd = not-detected, (low-solubility)

TABLE 6. Crystal data and refinement parameters for complex $Bu_3Sn2Pyc$ (1)

Compound	
Empirical Formula	$[Sn(C_{18}H_{31}NO_2]_n$
Formula weight	412.13
Temperature	273 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
a	26.444 (7) Å
b	10.979 (3) Å
c	19.488 (5) Å
α, β, γ	90 ° , 131.65(1), 90°
V	4227.4(19) A^3
Z	8, 1.295 Mg/m^3
D_c/g cm^3	1.295 mm $^{-1}$
F (000)	1696
Crystal size	0.34 x 0.28 x 0.21 mm
Refinement method	Full matrix least-square
θ range (°)	2.06- 25.00°
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0693$, $wR_2 = 0.1693$

X-ray structure of $Bu_3Sn2Pyc$ (1)

The molecular structure of (1) provides a strong evidence for the trigonal bipyrimidal geometry (Fig.2) of the tin atom as predicted from the ^{119}Sn NMR in solid state. Both oxygen atoms of the carboxylate group are coordinated but to two Sn atoms and therefore makes the 2-Pyc ligand acting as a bridge leading to the formation of a polymeric structure. The O1 and O2 atoms occupy the apical positions with an angle about the Sn atom of 168.73(19)°. The basal C7 , C11 and C15 atoms are at the angle about the central Sn atom between 116 and 125°. The Sn1-O1 is slightly shorter than Sn1-O2 indicates that the hydrogen at O1 atom has undergone deprotonation. Other relevant bond parameters are shown in Table 7.

TABLE 7. Selected bond lengths (Å) and bond angles (°) of complex $Bu_3Sn2Pyc$ (1)

Panjang/sudut ikatan	Nilai	Panjang/sudut ikatan	Nilai
Sn1-C7	2.093(11) Å	C7-Sn1-C11	116.4(5)
Sn1-C11	2.130(9)	C7-Sn1-O2	91.7(4)
Sn1-C15	2.097(12)	C15-Sn1-O2	87.9(4)
Sn1-O1	2.333(6)	C11-Sn1-O2	86.0(3)
Sn1-O2	2.274(5)	C7-Sn1-O1	92.9(4)
O1-C6	1.237(8)	C15-Sn1-O1	97.6940
O2-C6	1.255(8)	C11-Sn1-O1	82.8(3)
C7-Sn1-C15	127.2(5)°	O1-Sn1-O2	168.73(19)
C15-Sn1-C11	116.2(5)		

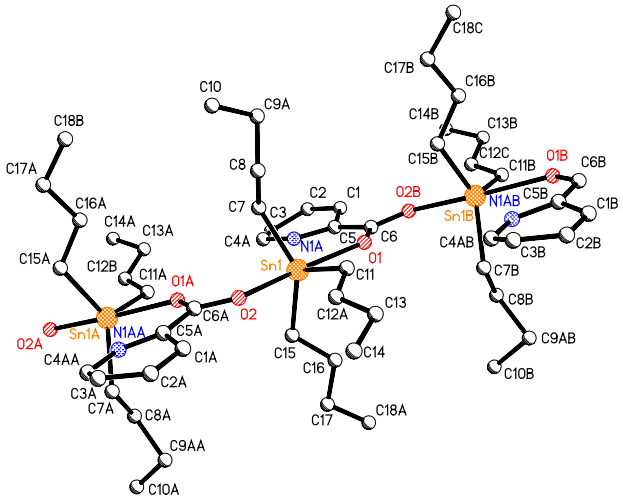

FIGURE 2 . Molecular structure of complex $Bu_3Sn2Pyc$ (1) . Hydrogen atoms are omitted for clarity.

CONCLUSION

Complexes **1** – **4** have been successfully synthesized. Microelemental analysis C, H, N and Sn data are in agreement with the predicted formula. These complexes give sharp melting points indicating the isolated complexes are fairly pure. The infrared spectra of the complexes shows the carbonyl group is shifted to lower wave number compared to that of the free acid. The appearance of ν(Sn-O) bands indicates that the oxygen atom is coordinated to the Sn atom. The ^{1}H NMR spectra show that the calculated number of protons for each functional group in the complexes are equal to the number of protons predicted from the molecular formula of the complexes. Moreover, the ^{13}C NMR spectra of the complexes obtained were found to exhibit no additional resonances and thus suggesting the high purity of these complexes. In solid state, the Sn atom of complexes **1**, **3** and **4** exhibit five coordination as predicted but in NMR solution complexes **1**, **3** and **4** exhibit four coordination. However, the coordination number of Sn atom in complex **2** is unaffected and remains four-coordinate in solid or solution state.

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