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Synthesis and Characterization of Organotin(IV) Complexes Derivatives of Methyl- and Nitro-Substituted Monocarboxylic Acid: Preliminary *in vitro* Antibacterial Screening Activity

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Organotin(IV) carboxylate complexes derivatives of 3-methyl-4-nitrobenzoic acid (3-CH_3-4-NO_2-C_6H_3COOH) and 4-methyl-3-nitrobenzoic acid (4-CH_3-3-NO_2-C_6H_3COOH) have been successfully synthesized. Two dibutyltin(IV) complexes with the general formulae {[X-CH_3-Y-NO_2-$C_6H_3COO(C_4H_9)_2Sn]_2O$}$_2$ (X = *meta*, Y = *para* **1**; X = *para*, Y = *meta* **3**) and another two triphenyltin(IV) complexes with the general formulae X-CH_3-Y-NO_2-$C_6H_3COO(C_6H_5)_3Sn{\cdot}CH_3OH$ (X = *meta*, Y = *para* 2; X = *para*, Y = *meta* **4**) were successfully synthesized. The acids and complexes **1-4** obtained were characterized quantitatively and qualitatively. Results of the infrared and NMR spectroscopy on the acids and complexes showed that the coordination took place *via* oxygen atoms from the carboxylate anions. Based on the spectroscopy studies indicated that one methanol molecule also take part in the coordination to tin(IV) atoms moiety in complexes **2** and **4** resulting the tin(IV) atoms exhibited five coordination. From the preliminary *in vitro* antibacterial screening activity, triphenyltin(IV) complexes (**2** and **4**) showed better activity compared to diorganotin(IV) complexes (**1** and **3**).

Key Words: Organotin(IV) complexes, Synthesis, Characterization, *In vitro* antibacterial activity.

INTRODUCTION

Numerous studies on organotin(IV) complexes have been carried out in order to study its biological properties against bacterial, fungal and cancer cells line[1-8]. In fact, organotin(IV) complexes are extensively studied due to its coordination geometries as well as structural diversity (monomer, dimeric, hexameric and oligomeric)[9-13].

In this paper, we report on the synthesis and structural characterization of new organotin(IV) carboxylate complexes derived from 3-methyl-4-nitrobenzoic acid and 4-methyl-3-nitrobenzoic acid. Moreover, the preliminary *in vitro* antibacterial screening activity of the complexes obtained are carried out and the results are reported herein.

EXPERIMENTAL

All the reagents, starting materials as well as the solvents were purchased commercially and used without any further purification. The melting points were determined in an open capillary and were uncorrected. Elemental 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 in the frequency range of 4000-400 cm^{-1}. The spectra for ^1H, ^1H-^{13}C HMQC 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 300MHz FTNMR spectrometer using deuterated $CDCl_3$ and DMSO-d_6 as the solvent and tetramethylsilane, TMS as the internal standard.

Preliminary *in vitro* antibacterial screening activity: The synthesized complexes and parent acids were screened for their *in vitro* antibacterial activity against three Gram-negative (*Escherichia coli*, *Pseudomonas aeruginosa* and *Klebsiella pneumoniae*) and two Gram-positive (*Bacillus subtilis* and *Staphylococcus aureus*) bacterial strains, by inhibition zone method using agar well diffusion method. The seeded agar (nutrient agar medium) was prepared by cooling the molten agar to 40 ºC and then adding bacterial inoculums containing approximately 10^4-10^6 colony forming units (CFU)/mL. The bacterial inoculums were spread on the plate containing agar medium and even coverage was ensured before the agar solidified. The complexes were dissolved in DMSO to

prepare 1 mg/mL concentration. By using a sterile metallic borer, the wells (6 mm in diameter) were dug and the standard drugs and complexes were introduced into the respective wells. The plates were incubated immediately at 37 ºC for 20-24 h. The activity was determined by measuring the diameter of the inhibition zone (in mm).

Preparation of sodium salts: The sodium salts of the acids were obtained by heating under reflux a 1:1 molar mixture of sodium hydroxide, NaOH and respective acid in ethanol (50 mL) for 2 h. After a few days, white precipitates were obtained. Sodium salt of 3-methyl-4-nitrobenzoic acid: FTIR as KBr disc (cm^{-1}) selected data: $\nu(COO)_{as}$ 1635, $\nu(COO)_s$ 1356. Sodium salt of 4-methyl-3-nitrobenzoic acid: FTIR as KBr disc (cm^{-1}) selected data: $\nu(COO)_{as}$ 1650, $\nu(COO)_s$ 1354.

Synthesis of complexes

Preparation of {[3-CH_3-4-NO_2-$C_6H_3COO(C_4H_9)_2$ Sn]$_2$O}$_2$ (1): Complex **1** was prepared by heating under reflux a 1:1 molar mixture of dibutyltin(IV) oxide (0.49 g, 2 mmol) and 3-methyl-4-nitrobenzoic acid (0.36 g, 2 mmol) in acetone (50 mL) as solvent and the mixture was heated under reflux for 2 h. After few days, yellow crystals (0.77 g, 61.0 % yield) were collected. m.p. 216.7-217.1 ºC. Analysis for $C_{64}H_{96}N_4O_{18}Sn_4$: C, 45.55; H, 5.93; N, 3.20; Sn, 16.95 %. Calculated for $C_{64}H_{96}N_4O_{18}Sn_4$: C, 45.64; H, 5.75; N, 3.33; Sn, 17.09 %. FTIR as KBr disc (cm^{-1}): ν(C-H) aromatic 3069, ν(C-H) saturated 2958, 2927, 2861; $\nu(COO)_{as}$ 1635, 1523; $\nu(COO)_s$ 1306, 1339; $\nu(NO_2)$ 1523, ν(Sn-O-Sn) 635, ν(Sn-C) 535, ν(Sn-O) 469. ^{1}H NMR (ppm) ($CDCl_3$): δ: benzene protons 7.99 (s, 12H); methyl, CH_3 2.70 (s, 12H); butyl, CH_3 0.81 (t, 6.7 Hz, 12H), 0.89 (t, 7.1 Hz, 12H); CH_2 1.31-1.45 (m, 16H); CH_2 1.65-1.75 (m, 32H). ^{13}C NMR (ppm) ($CDCl_3$): δ: benzene carbons 124.87, 128.57, 133.61, 134.49, 137.36, 151.94; CH_3 20.47; butyl 13.87, 13.96, 27.08, 27.13, 27.88, 28.12, 29.09, 30.70; COO 171.38. ^{119}Sn NMR (ppm) ($CDCl_3$): δ: -206.97, -208.09.

Preparation of 3-CH_3-4-NO_2-$C_6H_3COO(C_6H_5)_3Sn\cdot CH_3OH$ (2): Complex **2** was obtained by heating under reflux a 1:1 molar mixture of triphenyltin(IV) hydroxide (0.73 g, 2 mmol) and 3-methyl-4-nitrobenzoic acid (0.36 g, 2 mmol) in a mixture of methanol/ethanol (1:1, 60 mL) for 2 h. After few days, yellow solids (0.77 g, 68.8 % yield) were collected. m.p. 95.3-96.1 ºC. Analysis for $C_{27}H_{25}N_1O_5Sn$: C, 57.42; H, 3.92; N, 2.45; Sn, 20.33 %. Calculated for $C_{27}H_{25}N_1O_5Sn$: C, 57.68; H, 4.48; N, 2.49; Sn, 21.11 %. FTIR as KBr disc (cm^{-1}): ν(C-H) aromatic 3068, 3050; ν(C-H) saturated 2991, 2933; $\nu(COO)_{as}$ 1619, $\nu(COO)_s$ 1371, $\nu(NO_2)$ 1510, ν(Sn-O) 449. ^{1}H NMR (ppm) ($CDCl_3$): δ: phenyl protons 7.54-7.58 (m, 9H); 7.86-7.91 (m, 6H); benzene 7.99 (d, 8.4 Hz, 1H); 8.12 (d, 7.9 Hz, 1H); 8.16 (s, 1H); methyl, CH_3 2.65 (s, 3H); CH_3OH 3.49 (s, 3H). ^{13}C NMR (ppm) ($CDCl_3$): δ: phenyl carbons C_{ipso} 138.31 (633.6 Hz), C_{ortho} 137.31 (48.2 Hz), C_{meta} 129.09 (63.7 Hz), C_{para} 130.84 (12.3 Hz); benzene 124.75, 129.39, 133.56, 135.28, 138.05, 152.12; CH_3 20.31; CH_3OH 51.06; COO 170.98. ^{119}Sn NMR (ppm) ($CDCl_3$): δ: -103.30.

Preparation of {[4-CH_3-3-NO_2-$C_6H_3COO(C_4H_9)_2$ Sn]$_2$O}$_2$ (3): This complex was prepared by a similar method to those described for complex **1**, except substituting 3-methyl-4-nitrobenzoic acid with 4-methyl-3-nitrobenzoic acid. Acetone (50 mL) was used as solvent and the mixture was heated under reflux for 3 h. A clear yellow transparent solution was isolated by filtration and kept in a bottle. After few days, yellow crystals (0.90 g, 71.3 % yield) were collected. m.p. 209.3-209.9 ºC. Analysis for $C_{64}H_{96}N_4O_{18}Sn_4$: C, 45.46; H, 5.52; N, 3.25; Sn, 16.99 %. Calculated for $C_{64}H_{96}N_4O_{18}Sn_4$: C, 45.64; H, 5.75; N, 3.33; Sn, 17.69 %. FTIR as KBr disc (cm^{-1}): ν(C-H) aromatic 3095, ν(C-H) saturated 2957, 2927, 2870; $\nu(COO)_{as}$ 1620, 1530; $\nu(COO)_s$ 1341, 1407; $\nu(NO_2)$ 1530, ν(Sn-O-Sn) 636, ν(Sn-O) 480. ^{1}H NMR (ppm) ($CDCl_3$): δ: benzene protons 7.52 (d, 6.9 Hz, 4H); 8.21 (d, 7.6 Hz, 4H); 8.61 (s, 4H); methyl, CH_3 2.72 (s, 12H); butyl, CH_3 0.77 (t, 6.9 Hz, 12H), 0.89 (t, 7.2 Hz, 12H); CH_2 1.28-1.45 (m, 16H); CH_2 1.63-1.78 (m, 32H). ^{13}C NMR (ppm) ($CDCl_3$): δ: benzene carbons 126.37, 132.99, 133.37, 134.38, 138.03, 149.54; CH_3 20.95; butyl 13.87, 14.01, 26.34, 27.14, 28.18, 28.43, 29.18, 30.56; COO 170.97. ^{119}Sn NMR (ppm) ($CDCl_3$): δ: -207.39, -211.19.

Preparation of 4-CH_3-3-NO_2-$C_6H_3COO(C_6H_5)_3Sn\cdot CH_3OH$ (4): Complex **4** was prepared by a similar method to those described for complex **2**, except replacing 3-methyl-4-nitrobenzoic acid with 4-methyl-3-nitrobenzoic acid and methanol (50 mL) was utilized in the synthesis. After few days, yellow solids (0.68 g, 60.7 % yield) were collected. m.p. 133.7-134.3 ºC. Analysis for $C_{27}H_{25}N_1O_5Sn$: C, 57.80; H, 4.01; N, 2.43; Sn, 20.82 %. Calculated for $C_{27}H_{25}N_1O_5Sn$: C, 57.68; H, 4.48; N, 2.49; Sn, 21.11 %. FTIR as KBr disc (cm^{-1}): ν(C-H) aromatic 3065, ν(C-H) saturated 2981, 2932, 2864; $\nu(COO)_{as}$ 1641, $\nu(COO)_s$ 1336, $\nu(NO_2)$ 1529, ν(Sn-O) 448. ^{1}H NMR (ppm) ($CDCl_3$): δ: phenyl protons 7.48-7.51 (m, 9H); 7.71-7.88 (m, 6H); benzene 7.38 (d, 7.9 Hz, 1H); 8.20 (d, 7.9 Hz, 1H); 8.68 (s, 1H); methyl CH_3 2.62 (s, 3H); CH_3OH 3.47 (s, 3H). ^{13}C NMR (ppm) ($CDCl_3$): δ: phenyl carbons C_{ipso} 138.22, C_{ortho} 137.32 (49.1 Hz), C_{meta} 129.48 (65.1 Hz), C_{para} 130.82 (13.3 Hz); benzene 127.12, 130.53, 133.13, 134.80, 137.97, 149.58; CH_3 20.91; COO 170.98. ^{119}Sn NMR (ppm) ($CDCl_3$): δ: -100.11.

3-Methyl-4-nitrobenzoic acid, 3-CH_3-4-NO_2-C_6H_3COOH: The parent acid, 3-methyl-4-nitrobenzoic acid, 3-CH_3-4-NO_2-C_6H_3COOH was purchased from Acros Organics and used without any further purification. FTIR as KBr disc (cm^{-1}): selected data: ν(OH) 2827-2552, $\nu(COO)_{as}$ 1682, $\nu(COO)_s$ 1311. ^{1}H NMR (ppm) (DMSO-d_6): δ: benzene protons 7.94 (dd, 1.4 Hz, 8.4 Hz, 1H); 8.02 (d, 4.5 Hz, 1H); 8.05 (s, 1H); methyl 2.54 (s, 3H). ^{13}C NMR (ppm) (DMSO-d_6): δ: benzene carbons 125.46, 128.94, 133.70, 134.36, 135.42, 152.32; methyl 19.95; COO 166.72.

4-Methyl-3-nitrobenzoic acid, 4-CH_3-3-NO_2-C_6H_3COOH: The parent acid, 4-methyl-3-nitrobenzoic acid, 4-CH_3-3-NO_2-C_6H_3COOH was also purchased from Acros Organics and used without any further purification. FTIR as KBr disc (cm^{-1}): selected data: ν(OH) 2832-2546, $\nu(COO)_{as}$ 1699, $\nu(COO)_s$ 1319. ^{1}H NMR (ppm) (DMSO-d_6): δ: benzene protons 7.58 (d, 7.8 Hz, 1H); 8.07 (d, 7.9 Hz, 1H); 8.36 (s, 1H); methyl 2.55 (s, 3H). ^{13}C NMR (ppm) (DMSO-d_6): δ: benzene carbons 125.79, 130.87, 134.18, 138.49, 149.57; methyl 20.54; COO 166.32.

RESULTS AND DISCUSSION

In this study, complexes **1-4** have been obtained in solid state. The micro-elemental analysis for C, H, N and Sn data obtained were in agreement with the predicted formula for complexes **1-4**. Complexes **1-4** gave a sharp melting point indicated the isolation of fairly pure complexes. An outline of the proposed structure for complexes **1-4** are depicted in Fig. 1.

The ν(O-H) bands for the acids were absent in the infrared spectra of salts and complexes **1-4** showed the deprotonation and coordination of the carboxylate anion. Complexes **1-4** revealed that the $\nu(COO)_{as}$ was shifted to a lower wavelength number compared to the parent acids which signify that the coordination took place *via* the oxygen atoms of the carboxylate anion. Complexes **1-4** showed that the $\nu(COO)_{as}$ and $\nu(COO)_{s}$ are in the range of 1641-1523 and 1407-1306 cm^{-1}, respectively. 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[14]. From the infrared spectra of complexes **1** and **3**, two Δν values (329 and 183 cm^{-1} for complex **1**; 179 and 123 cm^{-1} for complex **3**) were observed. The Δν values were either comparable or lower than the Δν of the sodium salt of the respective acids, indicating that the carboxylate anions were bonded to the tin(IV) atom in a bidentate mode[14]. As a result, two tin(IV) atoms exhibited a distorted trigonal bipyramidal geometry and while another two tin(IV) atoms exhibited a distorted octahedral geometry in complexes **1** and **3**.

For complexes derived from triphenyltin(IV) carboxylate, Δν below 200 cm^{-1} would be expected for bridging or chelating carboxylates, but greater than 200 cm^{-1} for the monodentate bonding carboxylate anions[15]. Hence, the carboxylate anion in complexes **2** and **4** would be expected to bond to the tin(IV) atom in monodentate manner since the Δν above 200 cm^{-1}. Based on the elemental analysis, a methanol molecule was present in complexes **2** and **4**. It was believed that the methanol molecule have taken part in the coordination to the tin(IV) atom. The absorption bands of the aliphatic and aromatic functional groups centered around 3000 cm^{-1} should be sharp, but they appear as small hump together with the ν(OH) band observed in the region of 3641-3542 cm^{-1} in the spectra of complexes **2** and **4** which might be due to the effect of the methanol molecule. As a result, the tin(IV) atom of complexes **2** and **4** were five-coordinated and exhibited a trigonal bipyramidal geometry. For further information, similar case and structure has been reported by our research group[16].

The ^{1}H NMR spectra of complexes **1-4** exhibited similarities to their parent acids. The ^{1}H NMR spectrum of each parent acid exhibited three sets of signals arising from the aromatic protons of the benzene ring. In the upfield regions of the ^{1}H NMR spectra of the complexes **1** and **3** showed the signal of the butyl protons in the range of 0.77-1.87 ppm, respectively. For complexes **2** and **4**, the resonances appeared as two well separated sets of multiplets in the regions centering around δ ≈ 7.51 and 7.85 ppm (downfield) with integration values of 9:6, respectively, ascribed to the aromatic protons of the phenyl group[17].

Evidence of the formation of the complexes is displayed in the ^{13}C NMR spectra. The ^{13}C NMR spectra of complexes **1-4** showed the δ(COO) signal shifted to the downfield region which is lower compared to that of the parent acids indicating the carboxylate anion is bonded to tin(IV) atom. Complexes **1** and **3** were derivatives of organodistannoxane dimer types exhibited two sets of signals corresponding to the butyl groups in the ^{13}C NMR spectra. These two sets of signals were attributed to the butyl groups linked to the exo- and endo-cyclic tin(IV) atom, respectively[18]. Complexes **2** and **4** revealed the chemical shifts of the $\delta(^{13}C)_{ipso}$ at 138.31 and 137.32 ppm, respectively indicative of a four-coordinated tin(IV) atom[19-21]. Generally, the ^{1}H and ^{13}C NMR spectra of the complexes obtain are found to exhibit no additional resonance and thus reflects the purity of the complexes. The ^{1}H-^{13}C HMQC NMR spectra of 4-methyl-3-nitrobenzoic acid and complex **1** are depicted in Figs. 2 and 3 as a representative.

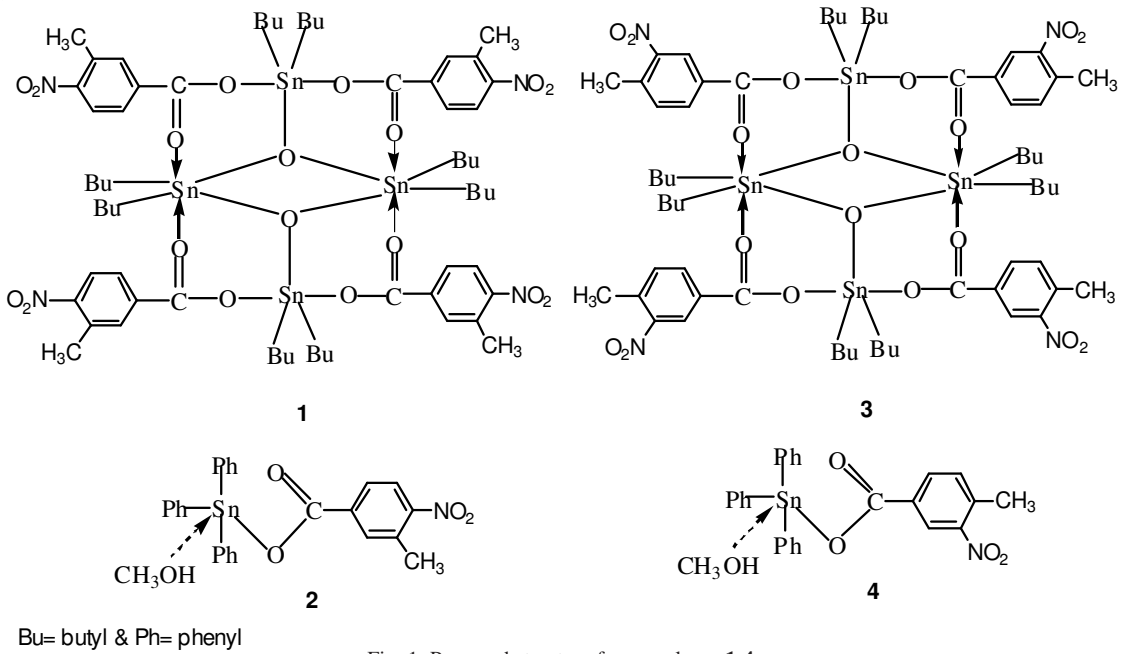

Fig. 1. Proposed structure for complexes **1-4**

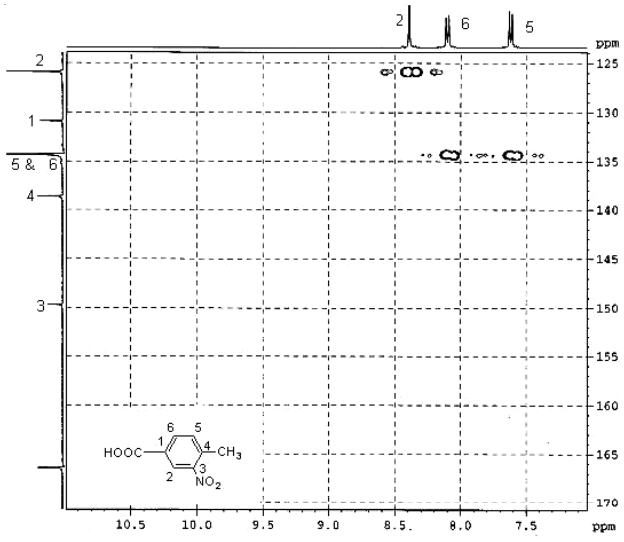

Fig. 2. ^{1}H-^{13}C HMQC NMR spectrum of 4-methyl-3-nitrobenzoic acid

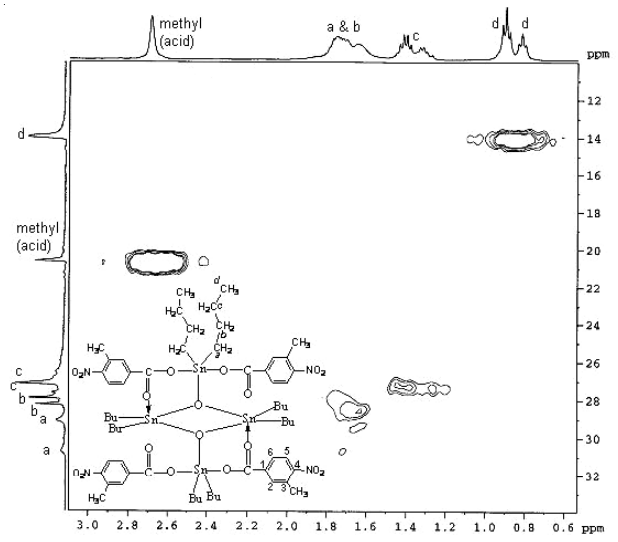

Fig. 3. ^{1}H-^{13}C HMQC NMR spectrum of complex **1**

The $\delta(^{119}Sn)$ value of the four-coordinated complexes fall in the range between +200 to -60 ppm; the five-coordinated complexes between -90 to -190 ppm and the six-coordinated complexes between -210 to -400 ppm[22]. Complex derivatives of organodistannoxane dimer types usually exhibit two well resolved $\delta(^{119}Sn)$ signals (complex **1** = -206.97, 208.09 ppm; complex **3** = -207.39, -211.19 ppm). These two low- and high-field resonances were attributed to the exo- and endo-cyclic tin(IV) atoms[8,18]. Based on the ^{119}Sn NMR spectra, all the tin(IV) atoms in complexes **1** and **3** were five-coordinated and each exhibited a distorted trigonal bipyramidal geometry. Based on the infrared spectral studies, the carboxylate anions were bonded to the tin(IV) atoms of complexes **1** and **3** in a bidentate manner resulting in the tin(IV) atoms exhibiting either a five- or six-coordination geometry but based on the ^{119}Sn NMR spectral studies, all the tin(IV) atoms in complexes **1** and **3** were five-coordinated. This maybe due to the disassociation of the bidentate bonds upon dilution during the preparation of the NMR sample in solution form. Complexes **2** and **4** showed that the $\delta(^{119}Sn)$ values at -103.30 and -100.11 ppm which lie in the range of -40 to -120 ppm [for triphenyltin(IV) complexes], hence, indicating that the tin(IV) atoms in complexes **2** and **4** are four-coordinated with a distorted tetrahedral geometry[19,20]. From the ^{119}Sn NMR spectral studies, it is believed that methanol molecule was disassociated upon dilution during the NMR solution preparation resultant tin(IV) atom in complexes **2** and **4** remained four-coordinated. In another words, this phenomenon may due to the coordinating bond of the methanol is not strong compared to that of the carboxylate anions.

Preliminary *in vitro* antibacterial screening activity: The preliminary *in vitro* antibacterial screening activity of parent acids and complexes **1-4** are given in Table-1. Inhibition zones with a diameter less than 10 mm are considered as weak; larger than 10 mm but less than 16 mm are considered as moderate and finally larger than 16 mm and above are active[7,23]. Based on this study, complexes **2** and **4** which were derivatives of triphenyltin(IV) were found to be more active compared to the diorganotin(IV) complexes (**1** and **3**) and parent acids against *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* but lower compared to the reference drugs. Based on the structural-activity study, complexes **2** and **4** were found to be more active due to both complexes were obtained as simple a monomer, four-coordinated and exhibited tetrahedral (sp^3) in solution form whereas complexes **1** and **3** obtained as a bulky molecule with a complicated structure which in turn restrict their mobility to the target cell or active site. Moreover, based on the data in Table-1 showed that complexes **2** and **4** were completely inactive against *Klebsiella pneumoniae* bacterial strains in this study.

TABLE-1
PRELIMINARY *IN VITRO* ANTIBACTERIAL SCREENING ACTIVITY OF PARENT ACID AND COMPLEXES **1-4**

Complexes	Inhibition zone (mm)				
	Bacillus subtilis	*Escherichia coli*	*Klebsiella pneumoniae*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*
3-CH_3-4-NO_2-C_6H_3COOH	8	8	9	11	12
1	9	7	10	7	11
2	18	–	–	22	17
4-CH_3-3-NO_2-C_6H_3COOH	11	9	10	12	11
3	12	7	9	20	13
4	20	8	–	22	17
Chloramphenicol	29	–	23	34	30
Doxycycline	34	24	21	40	28
Rifampicin	25	24	23	29	37

Agar well diffusion method (*in vitro*) = 1.0 mg/mL; reference drug = chloramphemicol, doxycycline and rifampicin.

Conclusion

Complexes **1-4** have been successfully synthesized. The structural as well as the coordination number of tin(IV) moieties of complexes **1-4** have been successfully characterized quantitatively and qualitatively. Based on the preliminary *in vitro* antibacterial screening activity, complexes **2** and **4** [triphenyltin(IV)] showed better activity compared to complexes **1** and **3** [diorganotin(IV)] but lower activity compared to the reference drugs.

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