Synthesis, Spectroscopic Characterization and *in vitro* Antibacterial Study of Diorganotin(IV) Complexes of 5-(4-Carboxy-Phenylazo)-2-Hydroxy-Benzoic Acid

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ABSTRACT: *Diorganotin(IV) complexes [$(R_2Sn)_2HL$] [where, R = methyl-, butyl- and L = 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid] were synthesized by reacting sodium salt of the ligand [Na_2HL] with dimethyl or dibutyltin(IV) dichlorides in anhydrous methanol using 2:1 metal-ligand ratio. The complexes were characterized by elemental analysis, UV, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy, and Mass spectrometry techniques. The coordination geometry of the complexes was determined using ^{119}Sn NMR spectroscopy and was found to be tetrahedral in solution state. The molecular mass and the proposed structure of the complexes have been predicted by the molecular ion peaks in EI-MS spectra of the complexes. The antibacterial activity of the complexes was investigated by screening against different bacteria with respect to standard drug, Gentamycin.*

KEYWORDS: *Diorganotin(IV) complexes; Carboxylate; NMR spectroscopy; Antibacterial activity.*

INTRODUCTION

Organotin(IV) carboxylates are a very interesting part of organotin chemistry owing to their structural variety [1,2] and potential biological activity as such anti-fungal, anti-bacterial, anti-tumor, and anti-malarial, urease inhibition, anti-proliferative, anti-tuberculosis properties, and cytotoxicity [3-9]. The wide range of coordination behavior of tin and the geometries of the complexes provides the spatial arrangement of ligand which is capable to attack the biological molecules in different ways [3,4]. The structural varieties of the organotin(IV) carboxylates is due to the higher coordination ability of tin and also its tendency to be involved in either weak or strong intra- and inter-molecular coordination [10-13]. The carboxylate ligands also play a significant role in diversifying the structures of organotin(IV) complexes as they can coordinate to tin atoms in a different mode of coordination such as monodentate, chelating bidentate, and bridging bidentate fashions [14-18]. Organotin(IV) complexes of azo-carboxylates are also very interesting because of their structural variety and significant biological activities [14,15]. The structural diversity exhibited by organotin(IV) carboxylates are monomers, dimers, tetramers, oligomeric ladder, hexameric drums, macrocyclic, cluster and cage structures etc. [19-23]. Among the organotin(IV) carboxylates, the study of diorganotin(IV) carboxylates are also very interesting due to their structural diversity and potential biological activity [24-26].

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1021-9986/2021/3/898-905 8/$/5.08

Earlier we reported triorganotin(IV) complexes of 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid and their *in vitro* antimicrobial activity [18]. However, this ligand system was not explored in case of diorganotin(IV) complexes. In my present report, I have included the synthesis, spectroscopic characterization and *in vitro* antibacterial activity of diorganotin(IV) complexes $[(R_2Sn)_2HL]$ [where, R = methyl-, butyl- and L = 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid]. The complexes were synthesized by refluxing sodium salt of the ligand in anhydrous methanol with diorganotin(IV) dichlorides following 2:1 metal-ligand ratio. The complexes have been characterized by elemental analysis, UV, IR, ^{1}H, ^{13}C, ^{119}Sn NMR spectroscopy and Mass spectrometry techniques. The coordination geometry of the complexes has been predicted by ^{119}Sn NMR spectroscopy in the solution state. The molecular mass and the proposed structure of the synthesized complexes have been predicted by the EI-MS spectral study. The *in vitro* antibacterial activity of the complexes were screened against different bacteria with reference to standard drug and reported in this work.

EXPERIMENTAL SECTION

Materials and method

Diorganotin(IV) dichlorides [dimethyltin(IV) dichloride and dibutyltin(IV) dichloride],*para*-amino benzoic acid and salicylic acid were obtained from MERCK and used without further purification. The solvents used in this work were dried and purified following the standard procedures [27]. Carbon, hydrogen, and nitrogen analysis were carried out on a Perkin Elmer 2400 series II instrument. UV-Visible spectra of the ligand and the complexes were recorded on a UV-1800 Shimadzu spectrophotometer in N,N-dimethyl formamide solution from 200 to 800 nm and IR spectra were obtained from Shimadzu FT-IR-8400S spectrophotometer from 4000 to 400 cm^{-1} range using KBr disks. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 spectrometer measuring at 400.13, 100.62, and 149.18 MHz frequency respectively. For ^{1}H and ^{13}C NMR spectroscopy, tetramethylsilane was used as reference set at 0.00 ppm while tetramethyltin at 0.00 ppm was employed as reference for ^{119}Sn NMR spectroscopy. JeolGCMate II GC-MS spectrophotometer was used for Mass spectrometry.

Synthesis of 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid (H_3L)

Synthetic procedure of 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid (H_3L) was reported earlier [18]. Yield: 70%; m.p. 235-237ºC. *Anal.* Calc. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.49; N, 9.79%; Found: C, 58.26; H, 3.38; N, 9.57%. UV-visible (DMF) λ_{max}(nm): 246, 395. IR (cm^{-1}): 1680 ν_{asy} (COO); 1609, 1593, 1410, 1378, 1348.

Synthesis of sodium salt of 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid), (Na_2HL)

Preparation of sodium salt of H_3L was mentioned in the earlier report [18]. Yield: 56%; m.p. 210ºC. *Anal.* Calc. for $C_{14}H_8N_2O_5Na_2$: C, 50.90; H, 2.48; N, 8.48. Found: C, 51.18; H, 2.55; N, 8.35%. IR (cm^{-1}): 1590 ν_{asy}(COO); 1480, 1383, 1483, 1254.

*Synthesis of dimethyltin(IV) complex of 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid, $[Me_2Sn]_2HL$ (**1**)*

Compound(**1**) was synthesized by refluxing sodium salt of ligand, (Na_2HL) with dimethyltin(IV) dichloride as 1:2 molar ratio in anhydrous methanol. The yellow crystalline compound was obtained after recrystallization from chloroform. Yield: 48%; m.p. 161-162°C. *Anal*. Calc. for $C_{18}H_{20}N_2O_5Sn_2$: C, 37.16; H, 3.47; N, 4.82. Found: C, 37.38; H, 3.41; N, 4.74%. UV-visible (DMF) λ_{max}(nm): 260, 360, 460. IR (KBr, cm^{-1}): 1600 ν_{asy}(COO), 1471 ν_{sym} (COO), 129 $\Delta\nu$(ν_{asy}COO -ν_{sym}COO), 1562 ν_{asy}(COO), 1427 ν_{sym}(COO), 135 $\Delta\nu$(ν_{asy}COO -ν_{sym}COO), 578(Sn-C), 480 ν(Sn–O). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H, Ligand skeleton: 11.19 [s, 1H, (OH)], 8.15 [1H, H-2], 7.96 [m, 2H, H-3´ & H-5´], 7.89 [s, 1H, H-6], 7.26 [m, 2H, H-2´ & H-6´], 7.13 [1H, H-5] ppm. Sn-CH_3 skeleton: 1.24 [s, 6H, (Sn-CH_3)], 1.18 [s, 6H, (Sn-CH_3)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 177.18 [CO_2], 172.20 [CO_2], 164.54 [C-4], 155.02 [C-1´], 144.57 [C-1], 132.78 [C-4´], 131.47 [C-3´ & C-5´], 129.92 [C-6], 128.57 [C-2], 126.56 [C-3], 122.17 [C-2 & C-6], 118.24 [C-5]; Sn-Me skeleton: 13.69, 12.39 [Sn-CH_3] ppm. ^{119}Sn NMR ($CDCl_3$, 149 MHz): 116.16, 137.24 ppm.EI-MS: MW calculated for $C_{36}H_{40}N_4O_{12}Sn_4$, 581.7; found: 582.0; (m/z): 582.0 (4) $[C_{36}H_{40}N_4O_{12}Sn_4]^+$; other prominent peaks: 549.7.1 (5), 508.0 (5), 205.2 (40), 185.3 (53), 155.3 (38), 120.5 (20).

Synthesis of dibutyltin(IV) complex of 5-(4-carboxy-phenylazo)-2-hydroxy-benzoic acid, $[Bu_2Sn]_2HL$ (2)

Brown crystalline compound (**2**) was obtained from chloroform extraction. Yield: 50%; m.p. 69-72°C. *Anal.* Calc. for $C_{30}H_{44}N_2O_5Sn_2$: C, 48.04; H, 5.91; N, 3.73. Found: C, 48.48; H, 5.81; N, 3.65%. UV-visible (DMF) λ_{max}(nm): 265, 360, 455. IR (KBr, cm^{-1}): 1620 ν_{asy}(COO), 1515 ν_{sym}(COO), 105 $\Delta\nu$(ν_{asy}COO -ν_{sym}COO), 1575 ν_{asy} (COO), 1440 ν_{sym}(COO), 135 $\Delta\nu$(ν_{asy}COO -ν_{sym}COO), 590(Sn-C), 500 ν(Sn–O). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H, Ligand skeleton: 11.61 [br, 1H, OH], 8.68 [d, 1H, H-2, *J* = 2.1 Hz], 8.29 [d, 1H, H-6, *J* = 8.4 Hz], 8.08-8.11 [m, 2H, H-3´ and H-5´], 7.90-7.98 [m, 2H, H-2' and H-6'], 7.10 [d, 1H, H-5, *J* =8.7 Hz]; Sn-^{n}Bu skeleton: 1.80 [brm, 8H, H-α and H-β], 1.45 [brm, 4H, H-γ], 0.95 [brm, 6H, H-δ] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C, Ligand skeleton: 178.10 [CO_2], 170.50 [CO_2], 165.15 [C-4], 154.50 [C-1´], 145.23 [C-1], 132.95 [C-4´], 131.50 [C-3´and C-5´], 130.25 [C-6], 128.95 [C-2], 126.59 [C-3], 122.45 [C-2 & C-6], 118.87 [C-5]; Sn-^{n}Bu skeleton: 32.87, 32.25, 27.28, 27.10, 26.59, 26.45 [C-α, C-β and C-γ], 13.53 [C-δ]. ^{119}Sn NMR ($CDCl_3$, 149 MHz): 106.42, 116.32 ppm. EI-MS: MW calculated for $C_{30}H_{44}N_2O_5Sn_2$, (750.1); found: 749.9; (m/z): 749.9 (8) $[C_{30}H_{44}N_2O_5Sn_2]^+$; other prominent peaks: 681.8 (7), 583.6 (9), 566.9 (10), 268.5 (8), 242.3 (8), 158.2 (7).

Antibacterial activity

The bacterial growth inhibition of the compounds was observed using agar well diffusion method [28] with some modification. Escherichia coli (ATCC-11229), Staphylococcus aureus (ATCC-11632), Bacillus subtilus (ATCC-6051), Bacillus cereus (MTCC-430) and Enterococcus faccium (ATCC-35667) were included for antibacterial study. 30 µL (150 µg) and 20 µL (100 µg) of the diorganotin(IV) complexes dissolved in dimethyl sulfoxide were used for the test per well. Gentamycin (5 mL) as reference antibiotic (1 mg/mL) in sterile distilled water was used per well as positive control for the bacteria. A well containing only DMSO (30 µL) was used as a negative control. Culture plates were incubated at 37˚C for 24 hours for bacteria. After incubation of specific time, the diameter of the inhibition zones formed around the wells was measured in millimeter. The MICs of the compounds and reference Gentamycin were determined following the literature procedures [29-31]. MIC is defined as the minimum concentration of drug at which there was no visible growth of the microorganism.

RESULT AND DISCUSSION

Diorganotin (IV) complexes $[(R_2Sn)_2HL]$ [where, R = methyl-, butyl- and L = 5-(4-Carboxy-phenylazo)-2-hydroxy-benzoic acid] were synthesized by refluxing sodium salt of the ligands with appropriate diorganotin(IV) dichlorides in anhydrous methanol in 2:1 metal-ligand stoichiometric ratio. The physical properties and analytical data of the synthesized complexes were described in the Experimental Section, whereas, the reaction scheme for the synthesis of the complexes was given in the reaction "Scheme 1".

UV-Visible spectroscopy

The UV-Visible spectra of the ligand (H_3L) and complexes were recorded in DMF solution (10^{-4} M) at room temperature. The electronic spectrum of the ligand showed absorption bands at 246 and 395 nm which may be assigned to π-π* transition of aromatic ring and n-π* transition of carboxylic acid group, respectively [32]. UV-Visible spectra of the complexes exhibited three absorption bands at 260-265, 360 and at 455-460 nm, respectively. After coordination, π-π*and n-π* transitions were observed at slightly higher wavelength in the complexes. The band observed at 455-460 nm indicates ligand to metal charge transfer [33]. The slight increase of the λ_{max} value from the ligand to the organotin(IV) complexes indicated coordination of the ligand to tin atom [34].

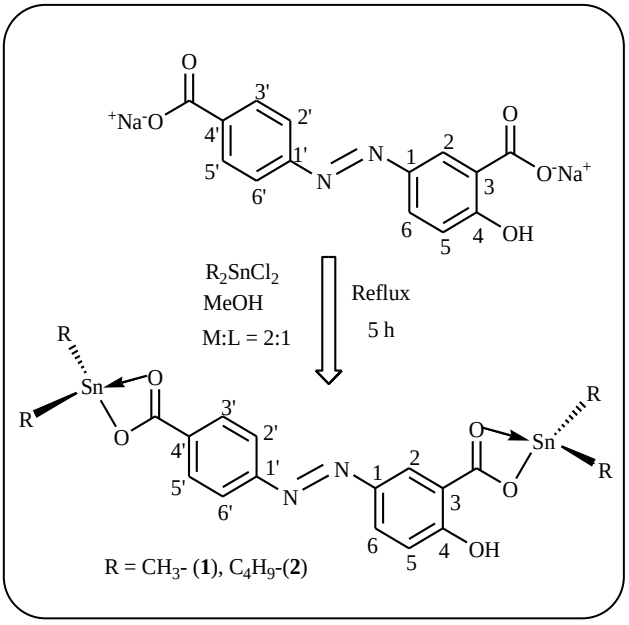
IR Spectroscopy

In the IR spectra of the ligand, the asymmetric [ν_{asy}(COO)] stretching frequencies was observed at 1680 cm^{-1} forthe ligand (H_3L). After coordination, this band was shifted to lower frequency at 1600-1620 cm^{-1} in the complexes. The shift of the band from its position to lower frequency is due to the carboxylate coordination of the ligand to the tin atom [35]. The IR absorption bands for Sn-C and Sn-O in the complexes were observed in the range of 578-590 and 480-500 cm^{-1}, respectively. Generally, the difference between ν_{asy}(COO) and ν_{sym}(COO) absorption frequencies below 200 cm^{-1} indicates bidentate (bridging or chelating) carboxylate moiety, but greater than 200 cm^{-1} is the indication of unidentate carboxylate moiety [36]. The magnitude of $\Delta\nu$

[$\Delta v = v_{asy}(COO) - v_{sym}(COO)$] for the complexes occurring at 105-135 cm^{-1} shows that the carboxylic acid ligand acts aschelating bidentate mode of coordination to the tin atom in the complexes [37-38].

^{1}H, ^{13}C and ^{119}Sn NMR Spectroscopy

The ^{1}H and ^{13}C NMR spectra of the complexes were recorded in $CDCl_3$ and their spectral data were given in the experimental section. The ^{1}H and ^{13}C NMR spectral data of the ligand was mentioned in our earlier report [18]. The spectral data of the reported ligand has been included in present discussion to compare with the spectral data of the synthesized complexes. The ^{1}H NMR spectra of the complexes exhibit a broad singlet at around 11.19 to 11.69 ppm due to the presence of free OH group. This indicates that the OH groups do not coordinate to the tin atom in the complexes [18]. The ligand shows peaks at 7.01 to 8.34 ppm which are due to the presence of aromatic protons, but the synthesized complexes exhibit peaks for aromatic proton in the region 7.13 to 8.76 ppm. The slight change of chemical shift value in the downfield region in the complexes is due to the decrease in electron density of the ligand upon coordination with the tin atom. The two singlet peaks at 1.18 and 1.24 ppm in the upfield region may be assigned to tin-methyl protons in dimethyltin(IV) complex **(1)**. In dibutyltin(IV) complex (**2**), the tin-butyl protons appear as multiplets in the range 0.95 to 1.81 ppm. ^{13}C NMR spectra of the dimethyltin(IV) complex shows two resonance peaks at 172 to 177 ppm due to the carboxylate groups whereas in the free ligand these peaks were observed at 167 to 171 ppm. The increase in chemical shift values of carboxylate groups in the downfield region is a clear indication for the carboxylate coordination to the tin atom [39]. The two signals observed at 12.39 to 13.69 ppm are corresponds to two methyl carbons attached to tin atom. On the other hand, dibutyltin(IV) complex **(2)** shows ^{13}C- resonance peak in the range 13.53 to 32.87 ppm which corresponds to butyl carbons. The observed ^{1}H and ^{13}C NMR signals in the complexes are consistent with the formulation of the synthesized diorganotin(IV) complexes.The geometry and coordination around tin atoms in the complexes was confirmed by recording ^{119}Sn NMR spectra of the complexes in $CDCl_3$. Two broad resonance peaks were observed in the ^{119}Sn NMR spectra of the dimethyltin(IV) complex (**1**) at (137.24, 116.16 ppm) and in dibutyltin(IV) complex (**2**) at (116.32, 106.42 ppm),



Scheme 1: Synthesis of diorganotin(IV) complexes.

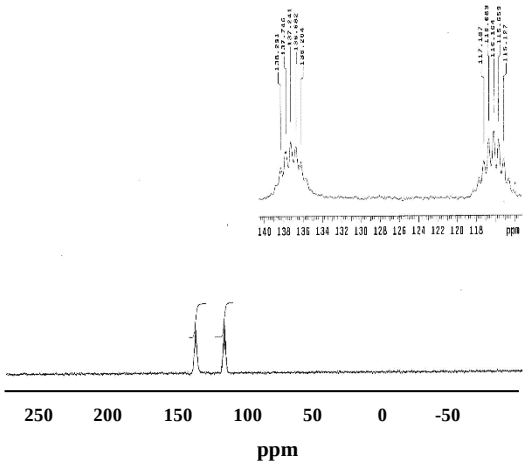


Fig. 1: ^{119}Sn NMR spectrum of $[Me_2Sn]_2HL$ (1).

respectively. ^{119}Sn NMR spectrum of the dimethyltin(IV) complex (**1**) was shown in "Fig. 1". The presence of two resonance peaks in the ^{119}Sn NMR spectra of the complexes indicated the presence of two tin centers which are in different chemical environments. The chemical shift in ^{119}Sn NMR spectra of both the complexes fall within the specified range of four coordinate structure (-60 to +200 ppm) which confirms that the complexes exhibit four coordinate tetrahedral geometry in the solution state [39].

Table 1: Antimicrobial activity of the compounds and the standard drug (zone of inhibition in mm).

Sl. No.	Tested compounds	Amount of samples used per well (µg)	*E. coli*	*B. subtilis*	*B. cereus*	*S. aureus*	*E. faccium*
1	H_3L	150	-	10	8	11	-
		100	-	7	6	8	-
2	$[Me_2Sn]_2HL$**(1)**	150	20	18	20	20	20
		100	18	16	19	18	18
3	$[Bu_2Sn]_2HL$**(2)**	150	22	20	22	20	20
		100	20	18	19	17	18
4	Gentamycin	5	24	22	24	24	20
5	DMSO	-	-	-	-	-	-

For compounds: 30 µL (150 µg) and 20 µL (100 µg) respectively were used per well; for the reference drug: 5µL (5 µg) for Gentamycin was used per well, dash (-) indicated inactivity.

Table 2: Minimum inhibitory concentrations (MICs) of the compounds and the standard drug in (µg/mL).

Sl. No.	Tested compounds	*E. coli*	*B. subtilis*	*B. cereus*	*S. aureus*	*E. faccium*
1	H_3L	-	75	82	65	-
2	$[Me_2Sn]_2HL$ **(1)**	6.5	5.8	5.8	6.0	7.0
3	$[Bu_2Sn]_2HL$ **(2)**	6.0	5.4	5.4	5.4	6.0
4	Gentamycin	5	5	5	5	5

Mass spectrometry

Mass spectrometry technique was employed to give support to the structures of the complexes. The mass spectra of the complexes were determined by the electron ionisation (EI) technique. The molecular ion $[M]^+$peaks of very low intensity were observed for both the complexes. The complexes (**1**)and (**2**) exhibited molecular ion peaks at (m/z) 582 (**1**) and 749.9 (**2**), respectively. The observation of molecular ion peaks in the mass spectra and associated molecular mass of the respective diorganotin(IV) complexes confirmed the proposed tetrahedral structure of the complexes.

Antibacterial study

Antibacterial activity of the diorganotin(IV) complexes were determined with reference to standard drug and the result has been listed in the "Table 1". The antibacterial activities of the complexes are found to be higher than that of the ligand. The minimum inhibition concentration (MIC) of the complexes (**1**) and (**2**) were also determined and listed in the "Table 2". The antibacterial activity and minimum inhibition concentration (MIC) for the tested bacteria were byrepresented "Fig. 2" and "Fig. 3". From the result it is clear that the dibutyltin(IV) complex (**2**) has lower value of MIC as compared to that of dimethyltin(IV) complex (**1**). However, the antibacterial activity of the complexes are less but closer to the standard drug, Gentamycin. The activity of the ligand increases upon coordination with the tin in the complexes which may be explained by chelation theory [40]. During chelation, the polarity of the metal ion is decreased significantly due to sharing of positive charge with the donor groups of the ligand. Moreover, due to the delocalization of the π electron cloud over the chelate ring the lipophilic character of the central metal atom increases significantly. The increase in lipophilic character enables the metal ions to infuse the lipid layer across the cell membrane of microorganisms [41].

CONCLUSIONS

Dimethyl and dibutyltin(IV) complexes of 5-(4-Carboxy-phenylazo)-2-hydroxy-benzoic acid (H_3L) were synthesized using standard procedure. The complexes were characterized by elemental analysis, UV, IR, ^1H, ^{13}C, ^{119}Sn NMR spectroscopy and Mass

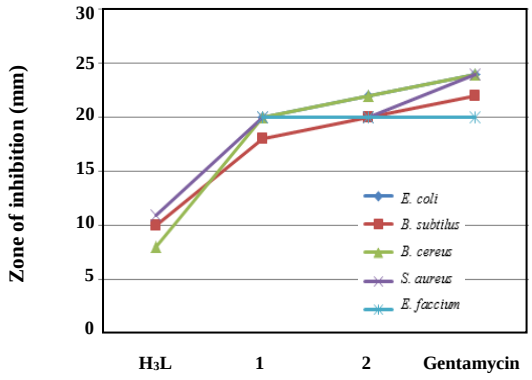


Fig. 2: Comparison of antibacterial activity of the compounds with standard drug.

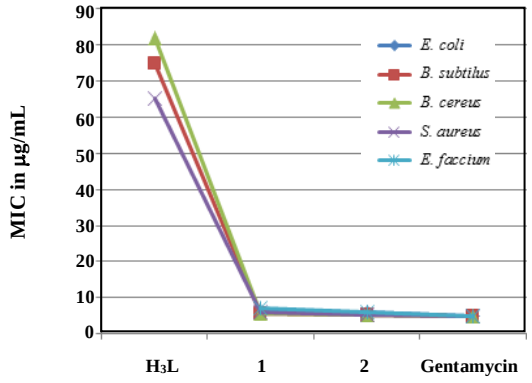


Fig. 3: Minimum inhibition concentrations (MICs) of the compounds and the standard drug.

spectrometry technique. IR spectra of the complexes indicate that in both the complexes the carboxylate oxygen atoms act as a chelating bi-dentate mode of coordination. ^{119}Sn NMR spectra of the complexes confirmed the presence of two different tin centers which adopt 4-coordinate tetrahedral geometry in solution. EI-MS spectra of the complexes in the solution state are in good agreement with the formulation of the molecular structure of the complexes. The antibacterial activity of the complexes is higher than that of the ligand but close to that of the standard drug.

Acknowledgments

IISc, Bangalore for ^{1}H, ^{13}C NMR spectra, SAIF, IIT Bombay for ^{119}Sn NMR, SAIF, IIT Madras for EI-MS spectral study, and Department of Chemistry, NIT Agartala.

Received : Nov. 6, 2019 ; Accepted :Jan. 13, 2020

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