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Synthesis, Characterization and Biological Studies of Organotin(IV) Carboxylates

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Organotin(IV) carboxylate of the type $R_2SnCl(L_I)$, $R_2Sn(L_{II})_2$ (where, R = Ph, Bu; L = 1-naphthoxyacetate, 2-naphthoxyacetate) have been synthesized by the reaction of dichlorodiorganotin(IV) with sodium salt of ligand in 1:1 and 1:2 molar ratio. All the complexes have been characterized by spectral studies (IR, ^1H, ^{13}C and ^{119}Sn NMR) and elemental analysis. On the basis of these studies, it was observed that the ligands behaved as bidentate coordinating through carboxylate oxygen atom. The ligands and carboxylate complexes were evaluated for *in vitro* antimicrobial activity against fungi *Aspergillus niger*, *Candida albicans* and against bacteria gram negative *Escherichia coli* and gram positive *Staphylococcus aureus*. The organotin(IV) carboxylate complexes were found to be more potent than the parent ligands.

Key Words: Organotin(IV) carboxylates, Napthoxyacetic acid, NMR, IR.

INTRODUCTION

Organotin(IV) compounds with nitrogen, oxygen and sulphur donor ligands have been receiving increasing attention due to the wide spectrum of biological activities such as antimicrobial[1-4] antiinflammatory[5,6] cardiovascular[7,8] antituberculosis[9,10] and environmental applications. The considerable developments over recent decades in the use of organotin compounds as reagents or intermediates in organic synthesis prompted the preparation of many new organotin compounds[11]. Organotin carboxylates have been the subject of interest because of their biochemical and commercial applications[12]. In general the biochemical activity of organotin(IV) carboxylates is greatly influenced by the structure of the molecule and coordination number of tin atom[13]. Therefore, recognition of the importance between the biological properties and the structure of organotin(IV) carboxylates[14] have together spurred on the study of carboxylate of tin. Studies on organotin(IV) complexes having carboxylate ligands with additional donor atoms available for coordination to tin have revealed a new structural type which may lead to complexes with different activity such as naphthoxyacetic acid. In this communication we have designed a series of diorganotin dichlorides with 1-naphthoxyacetate ion and 2-naphthoxyacetate ion in 1:1 and 1:2 molar ratio and studied the effect of coordination on antimicrobial activity to explore their use as potential biocidal agents.

EXPERIMENTAL

All the operations were carried out in an inert atmosphere on a vacuum line by using Schlenk technique. The solvent used were of analytical grade and were dried by standard techniques. During the course of synthesis, tin and chloride in the complexes were determined gravimetrically as tin oxide and silver chloride, respectively[15]. Elements (carbon, hydrogen) were estimated on Perkin-Elmer 2400 instrument.

The FTIR spectra [4000-400 cm^{-1}] were obtained in KBr pellets on Perkin-Elmer spectrum RX1 instrument. ^{1}H, ^{13}C and ^{119}Sn NMR were recorded on Bruker Avance II 400 MHz instrument with tetramethyl silane and tetramethyl tin as internal /external standards at SAIF, Chandigarh.

Reaction of dichlorodiorganotin with sodium salt of naphthoxyacetic acid in 1:1 molar ratio: The dichlorodiorganotin(IV) and sodium salt of naphthoxyacetic acid were dissolved in dry benzene and stirred for 2 h under dry nitrogen atmosphere. The mixture was then filtered to remove NaCl formed during the reaction. The solvent from the filtrate was gradually removed by evaporation under vacuum until solid product was obtained. The desired compound was recrystallized from diethyl ether. All other organotin(IV) derivatives of 1-naphthoxyacetic acid and 2-naphthoxyacetic acid were synthesized analogously as described above in the desired molar ratio. The analytical data of the compounds is given in Table-1.

Antimicrobial activity: The microbiocidal activity of the ligands and complexes was evaluated against bacteria *viz*., *Escherichia coli* and *Staphylococcus aureus* using two fold serial dilution technique[16] to determine the minimum inhibitory concentration (MIC) values. Fresh culture were obtained by inoculation of respective bacteria in nutrient broth-IP followed by incubation at 37 ± 1 ºC. The complexes in DMSO to give a concentration of 100 µg/mL (stock solution). The stock solution of sythesized complexes was serially diluted in the tube containing 1 mL of sterile double strength nutrient broth-IP to get a concentration of 0.15-5.00 µg/mL and then inoculated with 100 µL of suspension of respective organisms in sterile saline (*S. aureus, E. coli*). The inoculated tubes were incubated at 37 ± 1 ºC for 24 h and minimum inhibitory concentration (MIC) were determined. The antifungal activity of synthesized ligands and their organotin(IV) complexes against the fungal species *Aspergillus niger* and *Candida albicans* was determined by serial dilution method using sabouraud dextrose broth-IP following the incubation condition of 25 ± 1 ºC for a period of 7 days, except *C. albicans* (37 ± 1 ºC for a period of 36 h). The conventional bactericide tetracycline, chloramphenicol, kanamycin, cefazoline sodium and cefotaxime and fungicide cycloheximide, carbendazim and fluconazole were used as standard for comparing the activity of the compound.

TABLE-1
ANALYTICAL DATA OF ORGANOTIN(IV) COMPLEXES

Complexes	Yield (%)	Elemental analysis (%): found (calcd.)			
		C	H	Sn	Cl
Ph_2SnCl(1- NAA)	75	56.63 (56.56)	3.85 (3.76)	23.50 (23.29)	6.99 (6.96)
Ph_2Sn(1-NAA)$_2$	65	62.40 (62.37)	2.89 (2.76)	17.73 (17.12)	–
Bu_2SnCl(1-NAA)	72	51.30 (51.15)	5.99 (5.79)	25.49 (25.27)	7.62 (7.55)
Bu_2Sn(1-NAA)$_2$	68	58.95 (58.83)	5.77 (5.55)	26.34 (26.18)	–
Me_2SnCl(1-NAA)	72	43.71 (43.62)	4.07 (3.92)	30.36 (30.79)	9.34 (9.20)
Me_2Sn(1-NAA)$_2$	67	55.53 (55.46)	4.62 (4.29)	21.73 (21.62)	–
Ph_2SnCl(2-NAA)	70	56.63 (56.56)	3.82 (3.76)	15.23 (15.08)	6.98 (6.96)
Ph_2Sn(2-NAA)$_2$	68	62.41 (62.37)	2.66 (2.76)	26.49 (26.24)	–
Bu_2SnCl(2-NAA)	69	51.32 (51.15)	5.92 (5.79)	19.34 (19.14)	7.63 (7.55)
Bu_2Sn(2-NAA)$_2$	76	59.93 (58.83)	5.79 (5.55)	15.23 (15.10)	–
Me_2SnCl(2-NAA)	75	43.70 (43.62)	4.10 (3.92)	14.84 (14.61)	9.32 (9.20)
Me_2Sn(2-NAA)$_2$	75	55.54 (55.46)	5.08 (4.92)	14.84 (14.61)	–

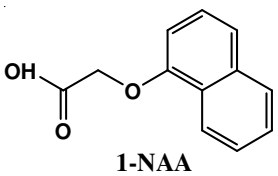
RESULTS AND DISCUSSION

Carboxylates of diorganotin dichloride were synthesized by stirring the dichlorodiorganotin(IV) with sodium salts of naphthoxyacetic acids in 1:1 and 1:2 molar ratios in dry benzene.

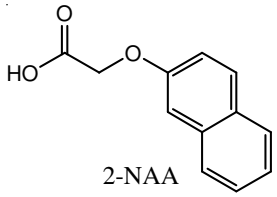
$$R_2SnCl_2 + NaL \xrightarrow[\text{Room temp., 2 h}]{\text{Dry benzene}} R_2Sn(L)Cl + NaCl$$

$$R_2SnCl_2 + 2NaL \xrightarrow[\text{Room temp., 2 h}]{\text{Dry benzene}} R_2Sn(L)_2 + 2NaCl$$

where, L represents the anions of 1-naphthoxyacetic acid (1-NAA) and 2-naphthoxy-acetic acid (2-NAA) R = Bu, Ph].



1-NAA



2-NAA

The complexes were yellow to brown crystalline solids, soluble in chloroform, benzene and dimethyl sulphoxide but insoluble in hexane, heptane and light petroleum.

IR Spectra: The deprotonation of carboxylic acid was evident from the disappearance of a broad band owing to the COOH group in the region 3200-2800 cm^{-1} of the ligand. Which appeared in the free ligand as the ν(O-H) vibration suggested that the ligand was coordinated to tin in the bidentate mode. The strong band at 472-421 cm^{-1} which was assigned to Sn-O stretching mode of vibration was absent in the spectra of the free ligand. The IR spectra can provide useful information concerning the coordinate formation of the carboxyl. The magnitude of $\nu[\nu=\nu_{as}(COO)-\nu_{s}(COO)]$ of about 190-170 cm^{-1} for all complexes was comparable to those for the cooresponding sodium salts, indicated the presence of bidentate carboxyl groups[17]. A band in the 579-542 cm^{-1} region was assigned to the stretching frequency associated with the Sn-C bond[18].

^{1}H NMR spectra: A singlet appeared at 9.26 ppm in proton NMR spectra of the free ligand disappeared in the spectra of the metal complexes, indicating the deprotonation of the carboxylic acid proton on complexation by diorganotin moiety. The spectra showed that the resonance appeared at 4.78-4.71 ppm for complexes was assigned to the proton of ($O-CH_2$), confirming their formation. The spectra showed that the chemical shifts of the butyl groups appeared as a multiplet in the region 1.80-1.35 ppm. Protons due to phenyl ring appeared as a multiplet in the region 7.75-6.82 ppm. A multiplet in the region 8.32-7.22 ppm was due to protons of napthlene ring (Table-2). The integrated proton ratio for each group was in agreement with the proposed structures.

^{13}C NMR spectra: The ^{13}C NMR spectra of the ligands and their tin complexes were recorded in $CDCl_3$ with a few drops of DMSO-d_6 (Table-3). Although at least two different set of carboxylate groups were present, only single resonance in the range 178.4-177.3 ppm was observed for the COO group in the ^{13}C spectra of complexes. The possible reason is that either accidental magnetic equivalence of the carbonyl carbon atoms or the difference between the two sets of resonance is small to be resolved. The carbon of carboxylate group of the ligands was observed at 195.5-194.5 ppm for HL_I and HL_{II}, respectively and was shifted to 178.4-177.3 ppm was complexation indicating the involvement of oxygen atom of COO group. A single resonance is observed in the range 65.4-65.2 ppm due to carbon of $O-CH_2$ group. Phenyl ring carbon are observed in the range 145.4-125.3 ppm. The peaks at 26.5, 25.6, 25.3, 13.1 ppm are due to ^{1}C, ^{2}C, ^{3}C and ^{4}C carbons of the butyl group ($\equiv Sn-{}^{1}CH_2-{}^{2}CH_2-{}^{3}CH_2-{}^{4}CH_3$) while methyl group attached to tin appeared at 10.7-10.3 ppm (Table-3). The spectra of all organometallic complexes showed a significant downfield shift of all carbon resonances compared with the free ligand. The shift was consequence of the attachment of ligand to the acceptor.

^{119}Sn NMR spectra: Although δ (^{119}Sn) is influenced by several factor, including the aromatic or aliphatic group R bound to the tin atom (and possibly the type of

TABLE-2
^{1}H AND ^{119}Sn NMR SPECTRAL DATA OF METAL COMPLEXES (ppm)

Complexes	$-OCH_2$	Methyl/butyl/phenyl	Naphthalene ring proton	^{119}Sn NMR
Ph_2SnCl (1-NAA)	4.78 (s, 2H)	6.91-7.75 (m, 10H)	7.93-8.32 (m, 10H)	-198.50
$Ph_2Sn(1\text{-}NAA)_2$	4.77 (s, 4H)	6.82-7.75 (m, 10H)	7.93-8.32 (m, 10H)	-375.22
$Bu_2SnCl(1\text{-}NAA)$	4.76 (s, 2H)	1.35-1.80 (m, 9H)	7.22-7.84 (m, 10H)	-115.61
$Bu_2Sn(1\text{-}NAA)_2$	4.75 (s, 4H)	1.35-1.80 (m, 9H)	7.22-7.76 (m, 10H)	-147.63
$Me_2SnCl(1\text{-}NAA)$	4.76 (s, 2H)	0.92-1.43 (s, 6H)	7.22-7.76 (m, 10H)	-115.61
$Me_2Sn(1\text{-}NAA)_2$	4.75 (s, 4H)	0.92-1.54 (s, 6H)	7.22-7.76 (m, 10H)	-147.63
$Ph_2SnCl(2\text{-}NAA)$	4.75 (s, 2H)	6.91-7.75 (m, 10H)	7.93-8.32 (m, 10H)	-198.50
$Ph_2Sn(2\text{-}NAA)_2$	4.76 (s, 4H)	6.82-7.75 (m, 10H)	7.93-8.32 (m, 10H)	-385.60
$Bu_2SnCl(2\text{-}NAA)$	4.71 (s, 2H)	1.35-1.80 (m, 9H)	7.22-7.84 (m, 10H)	-115.61
$Bu_2Sn(2\text{-}NAA)_2$	4.71 (s, 4H)	1.35-1.80 (m, 9H)	7.22-7.74 (m, 10H)	-147.63
$Me_2SnCl(2\text{-}NAA)$	4.74 (s, 2H)	0.92-1.41 (s, 6H)	7.22-7.76 (m, 10H)	-115.61
$Me_2Sn(2\text{-}NAA)_2$	4.75 (s, 4H)	0.92-1.54 (s, 6H)	7.22-7.76 (m, 10H)	-147.63

TABLE-3
^{13}C NMR SPECTRAL DATA OF METAL COMPLEXES (ppm)

Complexes	>COO	$-OCH_2$	Naphthalene ring carbon	Sn-C
HL_1	194.5	57.4	151.1 (C_1), 130.8 (C_2), 127.3 (C_3), 128.5 (C_4), 127.9 (C_5), 128.2 (C_6), 129.5 (C_7), 130.2 (C_8), 135.1 (C_9), 138.9 (C_{10})	–
Ph_2SnCl (1-NAA)	178.3	65.4	155.7 (C_1), 138.5 (C_2), 132.7 (C_3), 130.0 (C_4), 129.6 (C_5), 128.6 (C_6), 129.7 (C_7), 129.2 (C_8), 136.9 (C_9), 139.6 (C_{10})	145.4 (C_1), 135.0 (C_2), 125.3 (C_3), 128.6 (C_4)
$Ph_2Sn(1\text{-}NAA)_2$	178.3	65.4	155.7 (C_1), 138.5 (C_2), 132.7 (C_3), 130.0 (C_4), 129.6 (C_5), 128.6 (C_6), 129.7 (C_7), 129.2 (C_8), 136.9 (C_9), 139.6 (C_{10})	145.4 (C_1), 135.0 (C_2), 125.3 (C_3), 128.6 (C_4)
$Bu_2SnCl(1\text{-}NAA)$	178.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	26.5 (C_1), 25.6 (C_2), 25.3 (C_3), 13.1 (C_4)
$Bu_2Sn(1\text{-}NAA)_2$	177.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	26.8 (C_1), 25.6 (C_2), 25.3 (C_3), 13.3 (C_4)
$Me_2SnCl(1\text{-}NAA)$	177.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	10.3
$Me_2Sn(1\text{-}NAA)_2$	177.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	10.7

HL_{II}	195.5	57.4	151.1 (C_1), 130.8 (C_2), 127.3 (C_3), 128.5 (C_4), 127.9 (C_5), 128.2 (C_6), 129.5 (C_7), 130.2 (C_8), 135.1 (C_9), 138.9 (C_{10})	–
Ph_2 SnCl(2-NAA)	178.4	65.4	155.7 (C_1), 138.5 (C_2), 132.7 (C_3), 130.0 (C_4), 129.6 (C_5), 128.6 (C_6), 129.7 (C_7), 129.2 (C_8), 136.9 (C_9), 139.6 (C_{10})	145.4 (C_1), 135.0 (C_2), 125.3 (C_3), 128.6 (C_4)
$Ph_2Sn(2\text{-}NAA)_2$	178.4	65.4	155.7 (C_1), 138.5 (C_2), 132.7 (C_3), 130.0 (C_4), 129.6 (C_5), 128.6 (C_6), 129.7 (C_7), 129.2 (C_8), 136.9 (C_9), 139.6 (C_{10})	145.4 (C_1), 135.0 (C_2), 125.3 (C_3), 128.6 (C_4)
Bu_2SnCl(2-NAA)	178.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	26.5 (C_1), 25.6 (C_2), 25.3 (C_3), 13.1 (C_4)
$Bu_2Sn(2\text{-}NAA)_2$	177.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	26.8 (C_1), 25.6 (C_2), 25.3 (C_3), 13.3(C_4)
Me_2SnCl(2-NAA)	178.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	10.3
$Me_2Sn(2\text{-}NAA)_2$	178.3	65.2	155.7 (C_1), 138.3 (C_2), 132.5 (C_3), 130.3 (C_4), 129.1 (C_5), 128.3 (C_6), 129.6 (C_7), 129.2 (C_8), 136.7 (C_9), 139.6 (C_{10})	10.7

donor atom of the ligand) or type of geometry around tin atom. The high field chemical shift for the phenyl derivatives being a consequnce of anisotropic shielding effects in addition with the π interaction. The ^{119}Sn NMR spectra of organotin(IV) complexes displayed sharp singlet in the range of -198.50 to -115.61 to ppm and -385.60 to -375.22 ppm (Table-2) clearly indicating the *penta*- and *hexa*-coordinated states around the tin atom for 1:1 and 1:2 molar reactions and is well in agreement with reported values[19]. On the basis of result discussed so far, including the analytical and spectral data, the following structures of 1:1 and 1:2 complexes having around tin atom have been proposed in Figs. 1 and 2.

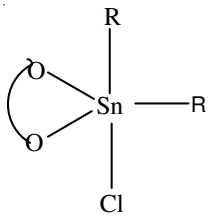


Fig. 1. Five coordinated structure of $R_2SnCl(L)$

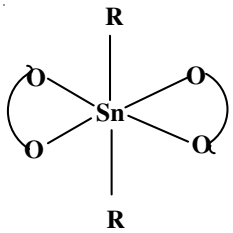


Fig. 2. Six coordinated structure of $R_2Sn(L)_2$

Antimicrobial assay: The *in vitro* growth inhibitory activity against fungi, *viz*., *A. niger*, *C. albicans* and bacteria *E. coli* and *B. subtilis* were evaluated for ligand HLI and HLII and their tin complexes. From the fungicidal and bactericidal data as reported in Table-4 it may be concluded that (i) diphenyl organotin(IV) complex is found to be more active, which may be due to the fact that the bulkiness of R group increases the lipophilicity, coupled with the polarity of Sn-C bond which gives boost to the bioactivity of these complexes and is of the order Ph > Bu > Me.

TABLE-4
in vitro ANTIMICROBIAL ACTIVITY* OF LIGANDS AND THEIR ORGANOTIN(IV) COMPLEXES (MIC IN μg/mL)

Complexes/ligands	Fungi		Bacteria	
	A. niger	*C. albicans*	*E. coli*	*S. aureus*
HL_1	50.00	50.00	25.00	50.00
HL_2	25.00	50.00	50.00	25.00
Ph_2SnCl(1-NAA)	6.25	12.50	12.50	6.25
Ph_2Sn(1-NAA)$_2$	6.25	6.25	3.12	12.50
Bu_2SnCl(1-NAA)	12.50	25.00	12.50	12.50
Bu_2Sn(1-NAA)$_2$	12.50	12.50	6.25	12.50
Me_2SnCl(1-NAA)	12.50	12.50	12.50	25.00
Me_2Sn(1-NAA)$_2$	6.25	12.50	12.50	12.50
Ph_2SnCl(2-NAA)	6.25	6.25	6.25	12.50
Ph_2Sn(2-NAA)$_2$	3.12	6.25	3.12	6.25
Bu_2SnCl(2-NAA)	12.50	25.00	12.50	12.50
Bu_2Sn(2-NAA)$_2$	12.50	12.50	12.50	12.50
Me_2SnCl(2-NAA)	12.50	12.50	25.00	25.00
Me_2Sn(2-NAA)$_2$	12.50	12.50	12.50	6.25

*The MIC of standard drugs for antibacterial activity (tetracycline, chloramphenicol, kanamycin, cefazoline sodium and cefotaxime) and antifungal activity (cycloheximide, carbendazim and fluconazole) were found to be < 3.12 μg/mL.

(ii) Most of the complexes show lower MIC values in comparison to the parent compounds against all the bacteria and fungi used, signifying the greater activity of the complexes. The activity of the ligand was enhanced on complexation with organotin halides. This may be explained by chelation theory in which chelation reduces the polarity of the central metal atom because of sharing of its positive charge with the donor group and possible π electron delocalization with in the whole chelate ring. This chelation increases the lipophilic nature of metal complex, which favours the permeation of the complexes through lipid layer of cell membrane. Compound inhibit the growth of fungi and bacteria to greater extent as concentration is increased. Also, the complexes of organotin chlorides were found to be more potent than free ligand. (iii) Tin complexes containing Sn-Cl bond are less reactive as compared to others which indicates that as the number of carboxylate group increases activity increases. This is probably due to increase in number of donor atom which interfere the cell process. (iv) Conventional fungicide and bactericide

showed inhibition at concentration less 3.12 ppm. No compounds better inhibitory action than the conventional fungicide and bactericide used. Some of the compounds have toxicity near to the conventional fungicide against bacteria *Bacillus subtilis* and fungi *Aspergillus niger* and *Candida albicans*.

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