

## Synthesis, Structural and Fungicidal Studies of Some Diorganotin(IV) with Benzamidoleucine

<sup>1</sup>Yang Farina, <sup>2</sup>Hadeel Adil, <sup>3</sup>Ahmed Ahmed, <sup>1</sup>Abdualbasit Graisa, <sup>2</sup>Emad Yousif

<sup>1</sup>School of Chemical Science & Food Technology, University Kebangsaan Malaysia, Malaysia

<sup>2</sup>Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

<sup>3</sup>Polymer Research Unit, College of Science, Al-Mustansiryah University, Baghdad, Iraq

**Abstract:** New diorganotin(IV) complexes of the type  $\text{Ph}_2\text{SnL}_2$ ,  $\text{Bu}_2\text{SnL}_2$  and  $\text{Me}_2\text{SnL}_2$  of the ligand benzamidoleucine( $\text{L}_H$ ). Ligand formed by reaction of benzoyl chloride with leucine in presence of sodium hydroxide. The prepared complexes were characterized by elemental analysis, infrared, conductance measurements and nuclear magnetic resonance ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR) spectral data. From the spectral measurements, monomer structures for the complexes were proposed. Bidentate and Octahedral geometry was proposed for the complexes prepared. Preliminary in vitro tests for fungicidal activity show that all prepared compounds display good activity to *Gibberela*, *Cercospora arachidicola*, *Physalospora piricola* and *Fusarium oxysporum*.

**Key words:** diorganotin(IV), carboxylate, spectral studies, fungicidal activity

### INTRODUCTION

Diorganotin carboxylates derived from carboxylic acids are among the most extensively studied class of compounds owing to their rich structural chemistry. The diverse structural motifs known in this family of compounds are attributed to the ambidentate character of the carboxylate ligands. Steric and electronic attributes of organic substitution on tin and/or the carboxylate moiety impart significant influence on the structural characteristics in tin carboxylates. Information on the structures of organotin carboxylates continues to accumulate, and at the same time new applications of such compounds are being discovered in industry, ecology and medicine. Recently, much attention has also been focused on their use as metal-based drugs (Shankar et al. 2007; Deak & Tarkanyi 2006; Demertzi 2006).

In order to obtain a better insight into how the organotin species behave inside biological system, it is necessary to study their coordination behaviour with ligands that can occur in the biological medium. In view of this, here we report the synthesis and structural studies of benzamidoleucine ( $\text{L}_H$ ) and its complexes, Diphenyltin(IV) bis(benzamidoleucine) ( $\text{Ph}_2\text{SnL}_2$ ), Dibutyltin(IV) bis(benzamidoleucine) ( $\text{Bu}_2\text{SnL}_2$ ) and Dimethyltin(IV) bis(benzamidoleucine) ( $\text{Me}_2\text{SnL}_2$ ).

### MATERIALS AND METHODS

#### 1.1 Synthesis of Benzamidoleucine:

A one gram of leucine was dissolved in (25ml) of 5% NaOH solution in a conical flask. To this mixture benzoyl chloride (2.25mL) was added in a five portions in (0.49 ml increments) and shaken vigorously until all the chloride has reacted. Acidified with diluted hydrochloric acid and the crude product was washed with cold ether. Finally, the desired product was recrystallized from Ethanol.

#### 1.2 Preparation of Complexes:

Complexes were synthesized by dissolving the free ligand (2 mmol) in hot toluene and adding the diorganotin salts (1 mmol) to the solution. The solution was refluxed for 6 hours with magnetic stirrer and then cooled and filtered. The filtrate was reduced under vacuum to a small volume and solid was precipitated by the addition of petroleum ether then filtered, dried at 60 °C and recrystallized from Ethanol.

**Corresponding Author:** Yang Farina, Emad Yousif, Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

### 3. Instrumentation:

Elemental C, H and N analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000-370)  $\text{cm}^{-1}$  cut were recorded as potassium bromide discs using a Perkin-Elmer spectrophotometer GX, molar conductance measurements were made in anhydrous DMF at 25 °C using Inolop-Cond Level 1 WTW, atomic absorption measurements of the prepared complexes were obtained using Shimadzu 680cc-flame. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  nuclear magnetic resonance spectra were recorded on a jeol 400 MHz spectrometer, relative to the internal standard tetramethylsilane (TMS). Melting points were determined in open capillary tubes using an electrothermal 9300 digital melting point apparatus.

## RESULTS AND DISCUSSION

The ligand was prepared by the reaction of benzoyl chloride with leucine in presence of sodium hydroxide. Table (1) shows the physical data for the ligand and the prepared complexes. The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent. The conductance of these complexes has been recorded in DMF at room temperature in the range 7-15  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , suggesting their non-electrolytic nature. The data of CHN and Tin analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values.

**Table 1:** Physical data for preparation ligand and the complexes prepared.

compound	Color	%Yield	M.P, °C	Found(Calcd.)%			
				C	H	N	Sn
$L_H$	White	87	184-186	65.41(66.36)	7.44(7.28)	6.36(5.95)	-
$\text{Ph}_2\text{SnL}_2$	White	75	161-162	61.13(61.56)	5.09(5.71)	3.68(3.78)	16.41(16.01)
$\text{Bu}_2\text{SnL}_2$	White	81	173-175	57.77(58.21)	7.36(7.18)	3.97(3.99)	17.22(16.92)
$\text{Me}_2\text{SnL}_2$	White	67	169-171	54.30(54.48)	5.19(6.02)	5.21(4.54)	19.11(19.23)

### 4.1 Infra-Red Spectroscopy:

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3317  $\text{cm}^{-1}$ , 1715  $\text{cm}^{-1}$  and 1029  $\text{cm}^{-1}$  assigned to OH, C=O and C-O group respectively. The reaction between this ligand with Diorganotin(IV) gave different types of complexes. In the free ligand, the bands at 1715  $\text{cm}^{-1}$  and 1029  $\text{cm}^{-1}$  were assigned to the stretching of C=O and C-O of the hydroxyl in the carboxylate group. On complexation these bands were shifted to a lower frequency region (Farina et al. 2008). This shift is probably due to the complexation of the metal to the ligand through oxygen of the carbonyl group, the disappearance of the hydrogen from hydroxyl group on complexation indicate the complexation is through the oxygen atom. The bands for  $\nu(\text{Sn-C})$  and  $\nu(\text{Sn-O})$  are assigned in the range of (541-545) and (444-452)  $\text{cm}^{-1}$  respectively (Nath et al. 2008). The IR data of the complexes are shown in Table (2). The Table lists the stretching frequency ( $\nu$ ) for some of the characteristics groups exhibited by the ligand and complexes.

**Table 2:** Characteristic absorption bands of benzamidocysteine and its complexes

compound	O-H	C=O	C-O	Sn-C	Sn-O
$L_H$	3317	1715	1029	-	-
$\text{Ph}_2\text{SnL}_2$	-	1710	1024	545	444
$\text{Bu}_2\text{SnL}_2$	-	1709	1023	541	452
$\text{Me}_2\text{SnL}_2$	-	1707	1025	543	451

### 4.2 Nuclear Magnetic Resonance:

The  $^1\text{H}$ NMR spectra for all compounds were recorded in  $[\text{D}_2\text{H}_6]$  DMSO using tetramethylsilane as the internal standard. The data are tabled in Table 3. The conclusion drawn from  $^1\text{H}$ NMR studies of a few compounds lend further support to suggested formation of benzamidoleucine chelate. Ligand ( $L_H$ ) give a single resonance near  $\delta$  8.66 ppm attributable to the N-H proton. The spectra also exhibit a singlet -OH peaks at 9.88 ppm due to hydroxyl group. The hydroxyl resonances is absent in the spectra of the complexes indicating deprotonation and coordination of Tin to the oxygen. There is a small upfield shift of the aromatic protons resonances of the ligand upon chelation with the diorganotin(IV) moiety (Nieto et al. 2005).

**Table 3:**  $^1\text{H}$ NMR spectral data ( $\delta$ , ppm) of the ligand and complexes

compound	O-H	N-H	C-H aromatic	C-(2)H aliphatic
$L_H$	9.88	8.66	7.50-7.89	3.87
$\text{Ph}_2\text{SnL}_2$	-	8.65	7.41-7.81	3.81
$\text{Bu}_2\text{SnL}_2$	-	8.64	7.38-7.80	3.87
$\text{Me}_2\text{SnL}_2$	-	8.63	7.34-7.77	8.84

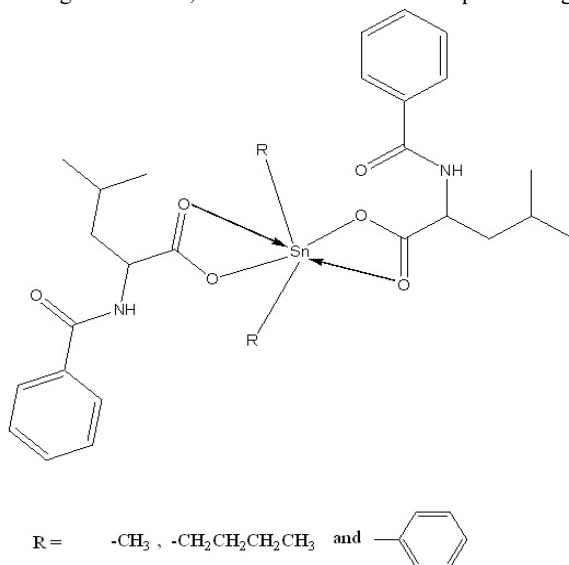
The complexes  $\text{Ph}_2\text{SnL}_2$ ,  $\text{Bu}_2\text{SnL}_2$  and  $\text{Me}_2\text{SnL}_2$  show additional signals. The methyltin ( $\text{Sn}-\text{CH}_3$ ) occurs at 1.34, 1.33 and 1.32 ppm as on the sharp singlet at integrates for the protons accompanied by satellites due to the  $^1\text{H}-^{119}\text{Sn}$  coupling that corresponds to the hydrogen atom of the methyl protons of the  $\text{Me}-\text{Sn}$  for the  $\text{Me}_2\text{SnL}_2$ . In dibutyltin(IV) complex the butyl protons appear as a multiple and a triplet in the range 1.61-0.81 ppm due to  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  group. The aromatic protons in  $\text{Ph}-\text{Sn}$  appear in the range 7.75-8.33 ppm (Farina et al. 2008).

Table 4 shows the most relevant  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR data. Their spectra were recorded in  $[\text{D}_2\text{O}]$  DMSO. The  $\text{C}=\text{O}$  resonance group of the complexes were shifted downfield compared with the position in the free ligand which appeared at 170.57 ppm. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion. This observation lends further evidence that the complexation occurred through the oxygen atoms of the carboxylate group.  $^{119}\text{Sn}$  NMR spectra for the complexes were recorded in  $[\text{D}_2\text{O}]$  DMSO. diorganotin(IV) complexes gave resonance at -457.48, -454.85 and -439.45 ppm related to  $\text{Ph}_2\text{SnL}_2$ ,  $\text{Bu}_2\text{SnL}_2$  and  $\text{Me}_2\text{SnL}_2$  respectively which is well within the range for six-coordinated complexes. In  $\text{Ph}_2\text{SnL}_2$  the  $^{119}\text{Sn}$  resonance appears, as usual, at lower field region than in  $\text{Bu}_2\text{SnL}_2$  and  $\text{Me}_2\text{SnL}_2$  in spite of the greater electron withdrawing capability of the phenyl group. The resonance at (-457.48 ppm), probably reflects the greater shielding ability of the phenyl group (Masood et al. 2004).

**Table 4:**  $^{13}\text{C}$  NMR spectral data ( $\delta$ , ppm) of the ligand and complexes

compound	C=O amide	C=O acid	C-H aromatic	C-H <sub>2</sub> aliphatic	$^{119}\text{Sn}$
$\text{L}_H$	167.85	170.57	128.76-131.87	43.87	
$\text{Ph}_2\text{SnL}_2$	167.81	165.34	127.86-131.86	42.45	-457.48
$\text{Bu}_2\text{SnL}_2$	167.37	165.78	127.87-131.72	41.87	-454.85
$\text{Me}_2\text{SnL}_2$	167.71	165.22	127.42-131.13	42.07	-439.45

On the basis of the preceding discussion, the structure of the complexes suggested as follows:



### 5. Biological Activity:

Preliminary in vitro tests for fungicidal activity of ligand and complexes have been carried out by the fungi growth inhibition method (Zhang et al. 2008). These compounds are dissolved in DMF at a concentration of 50 ppm. The data are summarized in Table 5, and show that all compounds display certain activity to *Gibberella*, *Cercospora arachidicola*, *Physalospora piricola* and *Fusarium oxysporum* at a low concentration.

**Table 5:** Fungicidal activities of prepared compounds

Compound	Inhibition Ratio (%) (50 ppm)		
	$\text{Me}_2\text{SnL}_2$	$\text{Bu}_2\text{SnL}_2$	$\text{Ph}_2\text{SnL}_2$
<i>Gibberella</i>	14.4	25.3	14.3
<i>Cercospora arachidicola</i>	31.3	61.1	35.2
<i>Physalospora piricola</i>	30.2	69.8	66.9
<i>Fusarium oxysporum</i>	16.2	26.6	20.8

**Conclusion:**

The ligand benzamidoleucine was successfully synthesized. The ligand was treated with different diorganotin(IV) metal salts to afford the corresponding complexes. It may conclude that the ligand coordinated through carboxylate to the Tin atom leading to the formation of four membered ring chelate. Octahedral geometry was proposed for the prepared complexes. Biological activity data have shown that the reported complexes have a significant biological activity against *Gibberella*, *Cercospora arachidicola*, *Physalospora piricola* and *Fusarium oxysporum*.

**REFERENCES**

- Deak, A. and G. Tarkanyi, 2006. "Chiral self-assembly of methyltin(IV)-naproxenates: Combining dative Sn–O bonds, secondary Sn---O interactions and C–H---O hydrogen bonding to make an inter-helical meander-shaped network and a cross-linked Z-shaped ribbon", *Journal of Organometallic Chemistry*, 691: 1693–1702.
- Farina, Y., A. Graisa, M. Kassem and E. Yousif, 2008. "Preparation and spectroscopic studies of diorganotin(IV) Complexes of *N*-phenyl-*m*-nitrobenzohydroxamic acid", *European Journal of Scientific Research*, 22(4): 602-607.
- Kovala, D., 2006. "Recent advances on non-steroidal anti-inflammatory drugs, NSAIDs: Organotin complexes of NSAIDs", *Journal of Organometallic Chemistry*", 691: 1767–1774.
- Masood, H., S. Ali, M. Mazhari, S. Shahzad and K. Shahidi, 2004. "<sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn NMR, Mass, Mossbauer and Biological Studies of Tri-,Di- and Chlorodiorganotin(IV) Carboxylates", *Turkish Journal of Chemistry*, 28: 75 – 85.
- Nath, M., H. Singh, G. Engb and X. Song, 2008. "New diorganotin(IV) derivatives of dipeptides: Synthesis and characteristic spectral studies" , *Spectrochimica Acta Part A*, 71: 529–536.
- Nieto, D., F. Jimenez-Cruz and T. Mancilla, 2005. "Synthesis and characterization of new di-*n*-butyl [bis{dimethyl-2-(3-oxo-5-phenyl(4-substituted)-penten-5-ato)malonates}]tin(IV): The crystal structure of di-*n*-butyl[bis{dimethyl-2-[5-(4-nitrophenyl)-3-oxo-penten-5-ato]malonate}]tin(IV)", *Polyhedron*, 24: 1054–1062.
- Zhang, X., H. Song, Q. Li, X. Liu and L. Tang, 2007. "Synthesis, structure and biological activity of organotin derivatives with pyridylmethylthiobenzoic acid", *Polyhedron*, 26: 3743–3749.
- Shankar, R., A. Singh, G. Hundal, J. Raymond and R. Butcher, 2007. "Synthesis, characterization and structural studies of mixed-ligand di-*n*-butyltin alkanesulfonate derivatives, [n-Bu<sub>2</sub>Sn(X)OS(O)<sub>2</sub>R]<sub>2</sub> [R = Et, n-Pr; X = acac, 4-OMe–O<sub>2</sub>CC<sub>9</sub>H<sub>5</sub>N-2, O<sub>2</sub>CC<sub>9</sub>H<sub>6</sub>N-2, O<sub>2</sub>CC<sub>9</sub>H<sub>6</sub>N-1]", *Journal of Organometallic Chemistry*, 692: 5555–5562.