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STRUCTURE AND FUNGICIDAL ACTIVITY OF SOME DIORGANOTIN(IV) WITH BENZAMIDOPHENYLALANINE

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ABSTRACT

New diorganotin(IV) complexes of the type Ph_2SnL_2, Bu_2SnL_2 and Me_2SnL_2 of the ligand benzamidophenylalanine (L_H). Ligand formed by reaction of benzoyl chloride with phenylalanine in presence of sodium hydroxide. The prepared complexes were characterized by elemental analysis, infrared, conductance measurements and nuclear magnetic resonance (^1H, ^{13}C and ^{119}Sn NMR) spectral data. From the spectral measurements, monomer structures, 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, Physolospora piricola and Fusarium oxysporum. Moreover, the Ph_2SnL_2 show a higher inhibition percentage then diorganotin carboxylate.

Keywords: diorganotin(IV), carboxylate, spectral study, fungicidal activity.

INTRODUCTION

The interest in organotin compounds in general and organotin carboxylates in particular continues to grow because of their biological activity and potential antineoplastic and antituberculosism agents [1-3], PVC stabilizers [4-6] and anti-tumour drugs [7] as well a polymer catalysts [8].

Vast studies have been focused on organotin carboxylates and many of them have been characterized recently either by single crystal structure determination or by spectroscopy [9]. This paper describe the preparation and characterization of benzamidophenylalanine (L_H) and its complexes,
Diphenyltin (IV) bis(benzamidophenylalanine) (Ph_2SnL_2), Dibutyltin (IV) bis(benzamidophenylalanine) (Bu_2SnL_2) and Dimethyltin (IV) bis(benzamidophenylalanine) (Me_2SnL_2).

MATERIALS AND METHODS

Synthesis of benzamidophenylalanine

A one gram of phenylalanine 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 shaked 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.

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 added of petroleum ether, dried at 60 ºC and recrystallized from Ethanol.

Instrumentation

Elemental C, H and N analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000-370) 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 ^oC using Inolop-Cond Level 1 WTW, atomic absorption measurements of the prepared complexes were obtained using Shimadzu 680cc-flame. The ^1H, ^{13}C and ^{119}Sn nuclear magnetic resonance spectra were recorded on a jeo l400 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 DISCUSSIONS

The ligand was prepared by the reaction of benzoyl chloride with phenylalanine 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 9-19 ohm^{-1} cm^2 mol^{-1}, suggesting their non-electrolytic nature. The data of CHNS 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	90	165-166	71.31 (71.36)	5.54 (5.61)	6.86 (5.20)	-
Ph_2SnL_2	White	80	110-112	64.98 (65.28)	4.78 (4.73)	4.23 (3.46)	14.57 (14.66)
Bu_2SnL_2	White	77	133-135	61.85 (62.43)	6.112 (6.03)	4.86 (3.64)	15.32 (15.43)
Me_2SnL_2	White	84	101-103	60.04 (59.58)	4.938 (5.00)	5.29 (4.09)	17.10 (17.32)

Infra-red spectroscopy

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3688 cm^{-1}, 3326 cm^{-1}, 1623 cm^{-1} and 1344 cm^{-1} assigned to υ (OH), υ (N-H), υ (COO) asym. And υ (COO) sym. group respectively.

The COO stretching vibrations are important to predict the bonding mode of the ligand. According to Lebl et al. [10] the values of Δυ [Δυ = υ asym.(COO) - υ sym.(COO)] can be divided into 3 groups ; (a) In compounds where Δυ(COO) > 350 cm^{-1}, the carboxylate group binds in a monodentate fashion. However, other very weak intra- and intermolecular interactions cannot be excluded. (b) When Δυ (COO) < 200 cm^{-1}, the carboxylate groups of these compounds can be considered to be bidentate. (c) In compounds where Δυ (COO) > 200 cm^{-1} and < 350 cm^{-1} an intermediate state between monodentate and bidentate (anisobidentate) occurs. It has also been suggested that the Δυ (COO) value in the chelating mode is less than the Δυ (COO) in a bridging mode [11].

From the preceding discussion it is proposed that in the investigated compounds, have chelating-type carboxylates. The disappearance of the hydrogen from hydroxyl group on complexation indicate the complexation is through the oxygen atom. The bands for υ (Sn-C) and υ (Sn-O) are assigned in the range of (553-568) and (445-467) cm^{-1} respectively. The IR data of the complexes are shown in Table-2. The Table lists the stretching frequency (υ) for some of the characteristics groups exhibited by the ligand and complexes.

The presence of only one Sn-C band indicates that the two R groups are in trans axial position [12]. According to group theoretical predictions the trans-SnO_4C_2 system should exhibit one Sn-O and one Sn-C vibration and the cis isomer two Sn-C and four Sn-O stretching vibrations in the IR spectra [13].

Table-2. Characteristic absorption bands of ligand and its complexes.

Compound	υ(O-H)	υ(COO) asym	υ(COO) sym	υ(Sn-C)	υ(Sn-O)
L_H	3688	1623	1344	-	-
Ph_2SnL_2	-	1532	1336	568	445
Bu_2SnL_2	-	1535	1335	553	467
Me_2SnL_2	-	1540	1337	556	451

NMR spectroscopy

The ^{1H}NMR spectra for all compounds were recorded in [$_2H^6$] DMSO using tetramethysilane as the internal standard. The data are compiled in Table-3. The conclusion drawn from ^{1H}NMR studies of a few compounds lend further support to suggested formation of benzamidoalanine chelate. Ligand (L_H) gives a single resonance near δ 8.47 ppm attributable to the N-H proton. The spectra also exhibit a singlet - OH peaks at 9.11 ppm due to hydroxyl group. The hydroxyl resonances is absent in the spectra of the complexes indicting 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 [14] the complexes Ph_2SnL_2, $Bu_2SnL_2$and Me_2SnL_2 Show additional signals. The methyltin (Sn-CH_3) accurse at 1.35, 1.33 and 1.31 ppm as on the sharp singlet at integrates for the protons accompanied by satellites due to the ^{1}H-^{119}Sn coupling that corresponds to the hydrogen atom of the methyl protons of the Me-Sn for the Me_2SnL_2. In dibutyltin(IV) complex the butyl protons appears as a multiple and a triplet in the range 1.45-0.89 ppm due-$CH_2CH_2CH_2CH_3$ group. The aromatic protons in Ph-Sn appear in the range 7.23-7.31 ppm [15].

Table-3. ^{1H}NMR spectral data (δ,ppm) of the ligand and complexes.

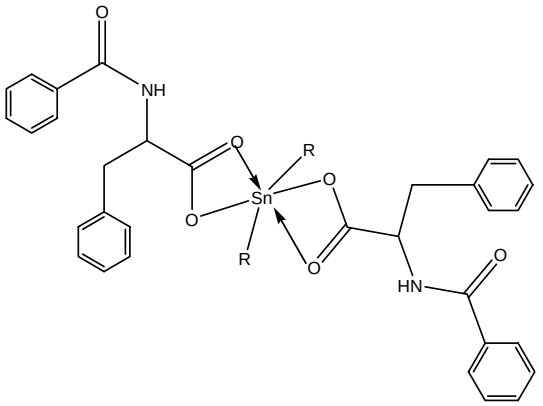
Compound	O-H	N-H	C-H aromatic	C-(2)H aliphatic
L_H	9.11	8.74	7.41-7.85	3.92
Ph_2SnL_2	-	8.43	7.40-7.81	3.81
Bu_2SnL_2	-	8.61	7.37-7.81	3.87
Me_2SnL_2	-	8.73	7.36-7.83	3.88

Table-4 shows the most relevant ^{13}C and ^{119Sn}NMR data, their spectra were recorded in [$^2H_6$] DMSO. The C=O resonance group of the complexes at (174.10-175.54) ppm where shifted downfield compared with the position in the free ligand which appeared at 179.64 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 [14]. This observation lends further evidence that the complexation occurred through the oxygen atoms of the carboxylate group. ^{119Sn}NMR spectra for the complexes were recorded in [$^2H_6$] DMSO. Diorganotin(IV) complexes gave resonance at -445.22, -433.22 and -431.65 ppm related to Ph_2SnL_2, Bu_2SnL_2 and Me_2SnL_2 respectively which is well within the range for six-coordinated complexes. In Ph_2SnL_2 the ^{119}Sn resonance appear, as usual, at lower field region than in Bu_2SnL_2 and Me_2SnL_2 in spite of the greater electron withdrawing capability of the phenyl group. The resonance at (-445.22 ppm), probably reflects the greater shielding ability of the phenyl group.

Table-4. ^{13C}NMR spectral data (δ,ppm) of the ligand and complexes.

Compound	C=O amide	C=O acid	C-H aromatic	C-H_2 aliphatic	^{119}Sn
L_H	164.43	179.64	124.41-130.65	41.44	
Ph_2SnL_2	162.33	175.54	126.13-133.55	42.07	-445.22
Bu_2SnL_2	163.43	174.18	124.43-131.65	42.11	-433.22
Me_2SnL_2	164.31	174.10	127.52-132.87	42.34	-431.65

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



R = -CH_3 , -$CH_2CH_2CH_2CH_3$ and 

Biological activity

Preliminary in vitro tests for fungicidal activity of ligand and complexes have been carried out by the fungi growth inhibition method [16]. 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 Physolospora piricola at a low concentration. Moreover, the Ph_2SnL_2 are more active than the other diorganotin derivatives. In addition, Ph_2SnL_2 shows the highest inhibition percentage for Physolospora piricola (83.6%) in vitro.

Table-5. Fungicidal activities of prepared compounds.

Compound	Inhibition Ratio (%) (50ppm)		
	Me_2SnL_2	Bu_2SnL_2	Ph_2SnL_2
Gibberela	20.4	30.2	22.4
Cercospora arachidicola	43.4	60.4	44.3
Physolospora piricola	50.2	80.1	83.6
Fusarium oxysporum	30.5	50.4	70.3

CONCLUSIONS

The ligand benzamidophenylalanine acid was successfully synthesized. The ligand was treated with different diorganotin(IV) 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 Gibberela, Cercospora arachidicola, Physolospora piricola and Fusarium oxysporum.

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