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SYNTHESIS AND FUNGICIDAL ACTIVITY OF SOME DIORGANOTIN(IV) WITH BENZAMIDOCYSTEINE

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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 benzamidocysteine (L_H). Ligand formed by reaction of benzoyl chloride with cysteine 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 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, Physolospora piricola and Fusarium oxysporum*.

Keywords: diorganotin(IV), carboxylate, spectral studies, 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 benzamidocysteine (L_H) and its complexes, Diphenyltin (IV) bis (benzami docysteine) (Ph_2SnL_2), Dibutyltin (IV) bis (benzami docysteine) (Bu_2SnL_2) and Dimethyltin (IV) bis (benzamidocysteine) (Me_2SnL_2).

Materials and methods

Synthesis of benzamidocysteine

A one gram of cysteine 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 addition of petroleum ether then filtered, 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 ^{o}C using Inolop-Cond Level 1 WTW, atomic absorption measurements of the prepared complexes were obtained using Shimadzu 680cc-flame.The ^{1}H, ^{13}C and ^{119}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 cysteine 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 9-16 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, ^{o}C	Found(Calcd.)%				
				C	H	N	S	Sn
L_H	White	77	171-172	52.11 (51.17)	5.45 (4.29)	6.34 (6.63)	15.16 (15.18)	-
Ph_2SnL_2	White	71	152-153	51.43 (51.97)	4.41 (3.78)	4.12 (4.04)	9.19 (9.25)	17.71 (17.12)
Bu_2SnL_2	White	68	161-162	46.49 (47.79)	6.38 (5.24)	3.88 (4.29)	9.84 (9.81)	19.74 (18.17)
Me_2SnL_2	White	83	167-118	42.43 (42.20)	4.06 (3.90)	5.53 (4.92)	10.53 (11.27)	21.09 (20.85)

Infra-Red Spectroscopy

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3310 cm^{-1}, 1710 cm^{-1} and 1026 cm^{-1} assigned to OH, C=O and C-O group respectively. The reaction between this ligand with Diorganotin(IV) gave different types of complexe. In the free ligand, the bands at 1710 cm^{-1}and 1025 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 [10]. 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 υ(Sn-C) and υ(Sn-O) are assigned in the range of (545-554) and (445-449) cm^{-1} respectively [10]. 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.

Table (2)
Characteristic absorption bands of benzamidocysteine and its complexes.

compound	O-H	C=O	C-O	Sn-C	Sn-O
L_H	3310	1710	1025	-	-
Ph_2SnL_2	-	1705	1021	554	445
Bu_2SnL_2	-	1707	1017	545	447
Me_2SnL_2	-	1704	1016	551	449

Nuclear magnetic resonance

The ^{1H}NMR spectra for all compounds were recorded in [$_2H^6$] DMSO using tetramethysilane as the internal standard. The data are tabled in Table (3). The conclusion drawn from ^{1H}NMR studies of a few compounds lend further support to suggested formation of benzamidocysteine chelate. Ligand (L_H) give a single resonance near δ 8.69 ppm attributable to the N-H proton. The spectra also exhibit a singlet –OH peaks at 9.71 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 [12].

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 ^1H-^{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 range1.55-0.72 ppm due–$CH_2CH_2CH_2CH_3$ group. The aromatic protons in Ph-Sn appear in the range 7.78-8.11 ppm [10].

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	9.71	8.69	7.50-7.82	3.88
Ph_2SnL_2	-	8.67	7.35-7.89	3.84
Bu_2SnL_2	-	8.66	7.48-7.78	3.85
Me_2SnL_2	-	8.65	7.43-7.79	8.83

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 (163.76-164.68) ppm where shifted downfield compared with the position in the free ligand which appeared at 171.42 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 [10]. 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 [$^2H_6$]

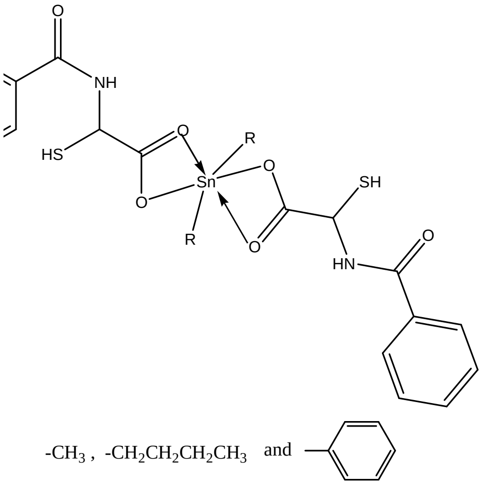
DMSO. diorganotin(IV) complexes gave resonance at -454.76, -445.35 and -443.87 ppm related to Ph_2SnL_2, Bu_2SnL_2 and Me_2SnL_2 respectively which is well within the range for six-coordinated complexes.

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	166.32	171.42	127.76-132.53	42.76	
Ph_2SnL_2	165.25	164.68	127.54-131.65	41.65	-454.76
Bu_2SnL_2	165.65	164.65	126.71-131.75	42.56	-445.35
Me_2SnL_2	165.75	163.76	126.45-131.75	41.64	-443.87

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



Biological activity

Preliminary in vitro tests for fungicidal activity of ligand and complexes have been carried out by the fungi growth inhibition method [11]. 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 *Gibberela*, *Cercospora arachidicola*, *Physolospora piricola* and *Fusarium oxysporum* at a low concentration.

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 (-443.87 ppm), probably reflects the greater shielding ability of the phenyl group.

Table (5)

Fungicidal activities of prepared compounds.

Compound	Inhibition Ratio (%) (50 ppm)		
	Me_2SnL_2	Bu_2SnL_2	Ph_2SnL_2
Gibberela	13.9	27.2	22.5
Cercospora arachidicola	34.1	53.4	31.2
Physolospora piricola	38.4	77.3	73.4
Fusarium oxysporum	12.1	23.1	14.3

Conclusion

The ligand benzamidocysteine 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 *Gibberela, Cercospora arachidicola, Physolospora piricola* and *Fusarium oxysporum*.

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