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ORIGINAL ARTICLE

Synthesis, spectroscopic studies and fungicidal activity of some diorganotin(IV) with 2-[(phenylcarbonyl)amino]propanoato

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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 2-[(phenylcarbonyl)amino]propanoic acid (HL) ligand formed by reaction of benzoyl chloride with alanine in presence of sodium hydroxide. The prepared complexes were characterized by infrared, nuclear magnetic resonance (^{1}H, ^{13}C, ^{119}Sn NMR) spectral data and elemental analysis and conductance measurements. From the spectral measurements, monomer structures for the complexes were proposed. Bidentate and Octahedral geometry was proposed for the complexes prepared. Bioassay result *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.

1. Introduction

In the past 3 decades the chemistry of tin compounds has gained considerable importance, both in basic research and in industrial applications. There are many interesting aspects of inorganic and organic tin chemistry discussed in various reviews (Chandrasekhar et al., 2002). Organotin compounds have gained an edge over other organometallics due to their bioavailability in the ecosystem and entrance into the food chain, the fact they are less harmful to the environment and their pharmaceutical applications, including antitumour and anticancer uses. For these reasons, tin and its derivatives are in commercial use more than any other element (Shahid et al., 2003; Hussain et al., 2009).

Organotin carboxylates have attracted considerable attention due to their wide applications in many fields (Tian et al., 2005), such as biological activity and potential antineoplastic and antituberculosis agents (Yousif et al., 2009a; Arks and Balko, 2005) PVC stabilizers (Thoonen et al., 2004; Kuzelova and Vymazal, 1999; Tabassum and Pettinari, 2006) and anti-tumour drugs (Angiolini et al., 2006) as well as polymer catalysts (Katsoulakou et al., 2008). Vast studies have been

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focused on organotin carboxylates and many of them have been characterized recently either by single crystal structure determination or by spectroscopy (Masood et al., 2004; Pellerito et al., 2010). As a continuation of our series on the synthesis and characterization of organotin carboxylates (Yousif et al., 2009b; Hameed et al. 2009; Farina et al. 2009a; Najeeb et al., 2009; Farina et al., 2009b), we report the diverse fields of applications of organotin complexes, we have synthesized new ligand 2-[(phenylcarbonyl)amino]propanoic acid and its complexes, diphenyltin(IV)bis(2-[(phenylcarbonyl) amino]propanoato) (Ph_2SnL_2), dibutyltin(IV)bis(2-[(phenylcarbonyl)amino]propanoato) (Bu_2SnL_2) and dimethyltin(IV) bis(2-[(phenylcarbonyl)amino]propanoato) (Me_2SnL_2).

2. Experimental

2.1. Synthesis of 2-[(phenylcarbonyl)amino]propanoic acid

One gram of alanine was dissolved in (25 ml) of 5% NaOH solution in a conical flask. To this mixture, benzoyl chloride (2.25 ml) was added in five portions in (0.5 ml increments) and shaken vigorously until all the chloride reacted, acidified with diluted hydrochloric acid and the crude product was washed with cold ether. Finally, the desired product was recrystallized from ethanol.

2.2. 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 h with a 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, dried at 60 °C and recrystallized from ethanol.

2.3. Instrumentation

Elemental C, H and N analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000–370) 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 680 cc-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.

3. Results and discussion

The ligand was prepared by the reaction of benzoyl chloride with alanine 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 the adsorbent. The conductance of these complexes has been recorded in DMF at room temperature in the range 7–18 $ohm^{-1}\,cm^2\,mol^{-1}$, 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.

3.1. Infra-red spectroscopy

The FTIR spectrum of the ligand, shows characteristic stretching absorption bands at 3371 cm^{-1}, 3328 cm^{-1}, 1611 cm^{-1} and 1332 cm^{-1} assigned to υ(OH), υ(N–H), υ(COO) asym. and υ(COO) sym. groups, respectively.

The COO stretching vibrations are important to predict the bonding mode of the ligand. According to Lebl et al. the values of $\Delta\upsilon$ [$\Delta\upsilon = \upsilon$ asym.(COO)$-\upsilon$ sym.(COO)] can be divided into three groups (Reeves and White, 1983); (a) In compounds where $\Delta\upsilon$(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 $\Delta\upsilon$ (COO) < 200 cm^{-1}, the carboxylate groups of these compounds can be considered to be bidentate. (c) In compounds where $\Delta\upsilon$ (COO) > 200 cm^{-1} and < 350 cm^{-1} an intermediate state between monodentate and bidentate (anisobidentate) occurs. It has also been suggested that the $\Delta\upsilon$ (COO) value in the chelating mode is less than the $\Delta\upsilon$ (COO) in a bridging mode (Shahid et al., 2009). From the preceding discussion it is proposed that the investigated compounds have chelating-type carboxylates. The disappearance of hydrogen from the hydroxyl group on complexation indicates that the complexation is through the oxygen atom. The bands for υ(Sn–C) and υ(Sn–O) are assigned in the range of (531–556) and (443–447) 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.

3.2. Nuclear magnetic resonance

The ^{1}H NMR spectra for all compounds were recorded in [$^{2}H_6$] DMSO using tetramethysilane as the internal standard. The data are compiled in Table 3. The conclusion drawn from ^{1}H NMR studies of a few compounds lend further support to

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

Compound	Color	%Yield	M.P. (°C)	Found (calcd.) (%)			
				C	H	N	Sn
HL	White	85	165–166	62.32(62.17)	5.81(5.74)	7.17(7.25)	–
Ph_2SnL_2	White	78	142–145	57.65(58.47)	4.99(4.60)	4.12(4.26)	17.71(18.06)
Bu_2SnL_2	White	81	157–156	53.79(54.48)	6.44(6.20)	3.82(4.54)	19.93(19.23)
Me_2SnL_2	White	73	171–172	50.06(49.56)	4.06(4.92)	5.53(5.25)	22.41(22.27)

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)
HL	3771	1611	1332	–	–
Ph_2SnL_2	–	1540	1323	531	444
Bu_2SnL_2	–	1539	1318	534	443
Me_2SnL_2	–	1546	1320	556	447

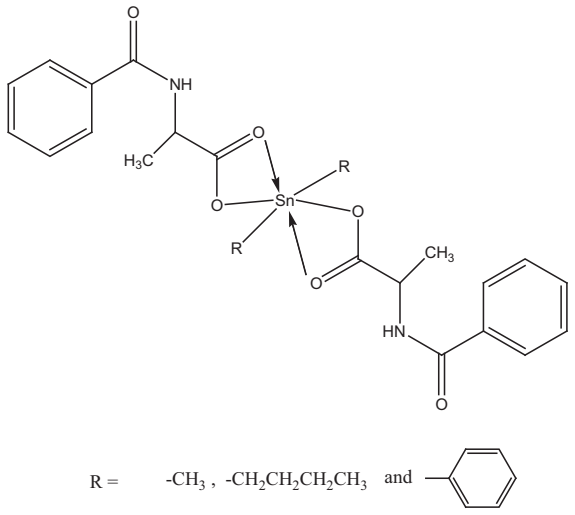
Table 3 ^{1}H NMR spectral data (δ, ppm) of the ligand and complexes.

Compound	O–H	N–H	C–H aromatic	C–(2)H aliphatic
HL	9.24	8.71	7.51–7.81	3.86
Ph_2SnL_2	–	8.69	7.44–7.77	3.82
Bu_2SnL_2	–	8.68	7.46–7.81	3.84
Me_2SnL_2	–	8.67	7.31–7.78	8.81

suggested the formation of 2-[(phenylcarbonyl)amino]propanoic acid chelate. Ligand (HL) gives a single resonance near δ 8.71 ppm attributable to the N–H proton. The spectra also exhibit a singlet –OH peak at 9.24 ppm due to hydroxyl group. The hydroxyl resonance 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 (Yousif et al., 2009a). 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 for the Me_2SnL_2. In dibutyltin(IV) complex the butyl protons appears as a multiplet and a triplet in the range of 1.55–0.72 ppm due –$CH_2CH_2CH_2CH_3$ group. The aromatic protons in Ph-Sn appears in the 7.06–7.17 ppm.

Table 4 shows the most relevant ^{13}C and ^{119}Sn NMR data. Due to scant solubility of the ligand and its complexes in the $CDCL_3$, their spectra were recorded in [$^2H_6$] DMSO. The C═O resonance group of the complexes at (160.22–160.31) ppm where shifted downfield compared with the position in the free ligand, which appeared at 165.32 ppm. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to the metal ion. This observation lends further evidence that the complexation occurred through the oxygen atoms of the carboxylate group. ^{119}Sn NMR spectra for the complexes were recorded in [$^2H_6$] DMSO. Diorganotin(IV) complexes gave resonance at −442.86, −436.83 and −431.49 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 appears, as usual, at a 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 (−442.86 ppm), probably reflects the greater shielding ability of the phenyl group.

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



R = -CH_3 , -$CH_2CH_2CH_2CH_3$ and

3.3. Biological activity

On the other hand, the newly prepared compounds were screened for their *in vitro* antifungal activity against *Gibberela*, *Cercospora arachidicola*, *Physolospora piricola* and *Fusarium oxysporum* in DMF by the serial plate dilution method (Reeves and White, 1983). All the fungal strains were clinical isolates, identified with conventional morphological and biochemical methods. Sabouraud's agar media was prepared by dissolving peptone (1 g), D-glucose (4 g), and agar (2 g) in distilled water (100 ml) and adjusting the pH to 5.7. Normal saline was used to make a suspension of the spore of fungal strain for lawning. A loopful of a particular fungal strain was transferred to 3 ml saline to get a suspension of the corresponding species. Agar media (20 ml) was poured into each petri dish. Excess suspension was decanted and the plates were dried by placing in an incubator at 37 °C for 1 h. Antifungal activity was determined by measuring the diameter of the inhibition zone. The zone of inhibition observed after respective incubation was measured and percent inhibition of the compounds were calculated. The results are presented in the Table 5 and show that all compounds display certain activity to *P. piricola* at a low concentration. Moreover, the Ph_2SnL_2 is more active than the other diorganotin derivatives. In addition, Ph_2SnL_2 shows

Table 4 ^{13}C 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
HL	165.32	170.43	127.74–131.55	42.65	
Ph_2SnL_2	160.22	165.26	126.86–133.76	41.64	−442.86
Bu_2SnL_2	160.24	166.14	126.25–131.94	42.13	−436.83
Me_2SnL_2	160.31	164.19	127.4–131.44	41.38	−431.49

Table 5 Fungicidal activities of prepared compounds.

Compound	Inhibition ratio (%) (50 ppm)		
	Me_2SnL_2	Bu_2SnL_2	Ph_2SnL_2
Gibberela	17.9	20.1	23.3
Cercospora arachidicola	33.8	57.1	36.8
Physolospora piricola	48.4	57.3	80.7
Fusarium oxysporum	11.6	26.2	65.3

the highest inhibition percentage for *P. piricola* (80.7%) *in vitro*. (Table 5).

4. Conclusion

The ligand 2-[(phenylcarbonyl)amino]propanoic 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 a 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, C. arachidicola, P. piricola* and *F. oxysporum*.

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