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Synthesis, characterization and fungicidal activity of some diorganotin(IV) with 2-thioacetic-5-phenyl-1,3,4-oxadiazole

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ABSTRACT

Complexes of the type R_2SnL_2, where R = phenyl, butyl and methyl and L_H = 2-thioacetic-5-phenyl-1,3,4-oxadiazole, have been synthesized and characterized by physico-chemical (elemental analysis, and electrolytic conductance) and spectral (UV-Visible, IR and (^{1}H, ^{13}C and ^{119}Sn NMR) techniques. Monomer structures for the complexes, 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 shows a higher inhibition percentage then diorganotin carboxylate**.**

| diorganotin(IV) | 2-thioacetic-5-phenyl-1,3,4-oxadiazole | fungicidal activity |

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1. 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-tumor drugs [7] as well as 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 [9-10]. As part of our investigation dealing with the study of diorganotin(IV) species derived from new carboxylate base ligand, we describe herein the synthesis and structural analysis of 2-thioacetic-5-phenyl-1,3,4-oxadiazole (L_H) and its complexes, diphenyltin(IV) bis(2-thioacetic-5-phenyl-1,3,4-oxadiazole) (Ph_2SnL_2), dibutyltin(IV) bis(2-thioacetic-5-phenyl-1,3,4-oxadiazole) (Bu_2SnL_2) and dimethyltin(IV) bis(2-thioacetic-5-phenyl-1,3,4-oxadiazole) (Me_2SnL_2).

2. EXPERIMENTAL

2.1 Synthesis of 2-thioacetic -5-phenyl-1,3,4-oxadiazole

A mixture of ethyl benzoate (0.1 mole) and hydrazine hydrate (0.1 mole) was refluxed for two hours, ethanol (50 ml) was added and refluxed for 5 hours. The precipitate benzoyl hydrazine which separated on cooling was filtered and washed with cold methanol. To a solution of benzoyl hydrazine (0.02 mole) in ethanol (100ml) at 0°C were added carbon disulfide (0.04 mol) and potassium hydroxide (0.02 mole) and the mixture was refluxed for (7) hours. Then the solvent was evaporated and the residue dissolved in water and acidfied with dilute hydrochloric acid. The precipitate was filtered and crystallized from (ethanol) to give 2-mercapto-5-phenyl 1,3,4-oxadiazole which react with one equivalent of chloroacetic acid in the presence of KOH as a basic media to give 2-thioacetic-5-phenyl-1,3,4-oxadiazole (Figure 1) the final product was recrystallized from methanol.

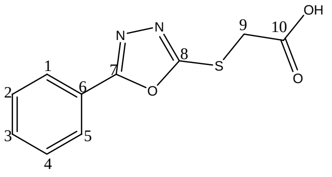

Figure 1: Suggested structure for the prepared ligand.

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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 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, dried at 60 ºC and recrystallized from ethanol**.**

2.3 Measurements

Elemental C, H, S and N analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000-370) cm^{-1} 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. Ultraviolet was accomplished using Shimadsu-UV-Vis spectrophotometer UV-2450, DMSO used as solvent.

3. RESULTS & DISCUSSION

All chemicals and reagents were of reagent-grade quality. 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole was prepared by reaction of one mole of 2-mercapto-5-phenyl 1,3,4-oxadiazole with one mole of chloroacetic acid in the presence of KOH. The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent. Melting point, elemental analysis and ms-molecular peak masses of all the compounds studied are tabulated in Table (1). The data of CHNS and metal analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values. The conductance of these complexes has been recorded in DMF at room temperature in the range 9-15 ohm^{-1} cm^{2} mol^{-1}, suggesting their non-electrolytic nature.

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

Compound	Color	Melting point ^{0}C	Found(Calcd.)%					
			C	H	N	S	M	m/e
L_H	White	162-164	50.84 (50.84)	3.41 (3.41)	11.14 (11.86)	13.17 (13.57)	–	236
Ph_2SnL_2	White	110-111	51.55 (51.70)	2.94 (3.25)	8.01 (7.54)	8.31 (8.63)	16.22 (15.97)	743
Bu_2SnL_2	White	145-147	47.14 (47.81)	4.34 (4.59)	8.10 (7.96)	9.97 (9.12)	17.12 (16.88)	704
Me_2SnL_2	White	138-139	42.91 (42.67)	2.98 (3.26)	9.83 (9.05)	10.83 (10.36)	18.98 (19.17)	619

3.1 Infra-Red Spectroscopy

The FTIR spectrum for HL^{1}, shows a characteristic stretching absorption bands at 3468 cm^{-1}, 1633 cm^{-1}, 1315 cm^{-1}, 1606 cm^{-1}, 1187 cm^{-1} and 1066 cm^{-1} assigned to hydroxyl group, υ(COO) asym., υ(COO) sym., C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching 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]. The bands for υ(Sn-C) and υ(Sn-O) are assigned in the range of (554 - 570) and (430 - 466) cm^{-1} respectively [12] . 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. Major bands in the electronic spectra of the ligand and their tin(IV) complexes also are given in Table 2. The spectrum of the ligand exhibits bands at 205 and 276 nm attributable to the intra-ligand π → π* transition. These bands shift to longer wavelengths in the spectra of tin complexes.

Table 2: Characteristic absorption bands of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole and its complexes

Compound	**υ(O-H) cm^{-1}**	**υ(COO) asym cm^{-1}**	**υ(COO) sym cm^{-1}**	**υ(Sn-C) cm^{-1}**	**υ(Sn-O) cm^{-1}**	**UV (λmax) nm**
L_H	3468	1633	1351	-	-	205,276
Ph_2SnL_2	-	1590	1341	570	455	234,285
Bu_2SnL_2	-	1596	1341	554	466	236.289
Me_2SnL_2	-	1594	1345	564	430	224,284

3.2 Nuclear Magnetic Resonance

The data of proton NMR of the 2-thioacetic-5-phenyl-1,3,4-oxadiazole and its complexes displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the complexes. The observed changes are the evidences of complexion had happened because the chemical shift of a compound is heavily depended on its electronic environment. The spectra also exhibit a singlet –OH peaks at 9.58 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. The δ 7.59-7.96 ppm resonance signal protons of the aromatic ring shifted to the higher field upon complexation, while the downfield shift of the protons in C9 of the aliphatic group shifted from δ 3.88 (in the free ligand to 3.32-3.34 (in the Sn complexes). However, we were able to detect all proton and carbon signals separately. ^{1}H NMR data for the ligand and the complexes are reported in Table 3. The complexes Ph_2SnL_2, $Bu_2SnL_2$and Me_2SnL_2 show additional signals. The methyltin ($Sn-CH_3$) occurs at 1.26, 1.23 and 1.21 ppm as the sharp singlet integrated 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 1.42-0.81 ppm due –$CH_2CH_2CH_2CH_3$ group. The aromatic protons in Ph-Sn appear in the 7.78-8.61 ppm [11].

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

*	**L_H**	**Ph_2SnL_2**	**Bu_2SnL_2**	**Me_2SnL_2**
1	7.96	7.94	7.95	7.93
2	7.94	7.66	7.93	7.68
3	7.59	7.58	7.57	7.61
4	7.94	7.66	7.67	7.68
5	7.96	7.94	7.93	7.93
9	3.88	3.32	3.33	3.34

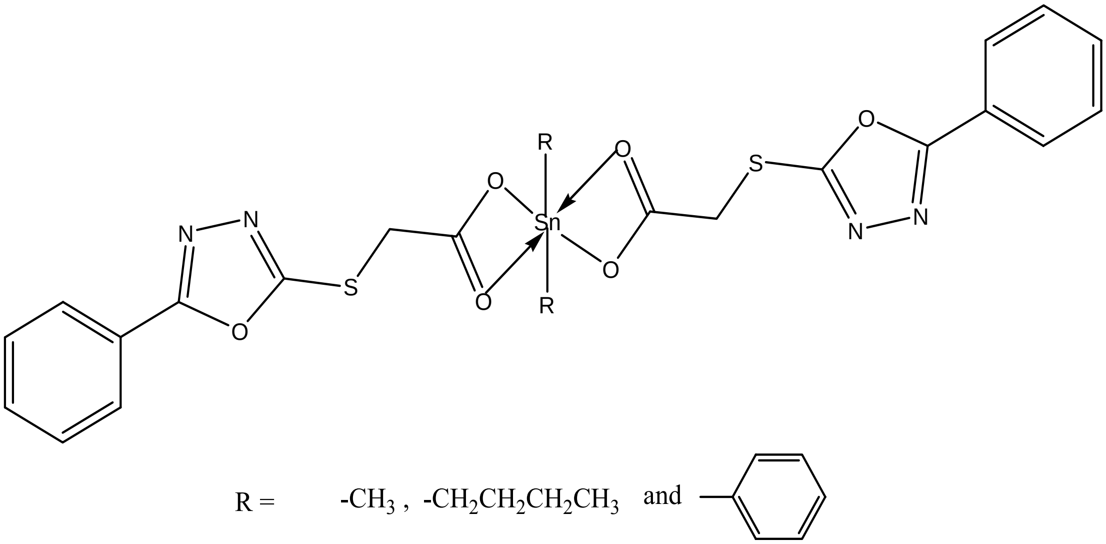
- H-atom attached to the C-atom numbered as δ(^{1}H)

Table 4 shows the most relevant ^{13}C and ^{119}Sn NMR data. Their spectra were recorded in [$^2H_6$] DMSO. The C=O resonance group of the complexes at (170.21-170.91) ppm were shifted downfield compared with the position in the free ligand which appeared at 168.69ppm. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion [12]. 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 -452.64, -422.25 and -432.64 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 -452.64 ppm, probably reflects the greater shielding ability of the phenyl group.

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

C-atom no	L_H	Ph_2SnL_2	Bu_2SnL_2	Me_2SnL_2
1	126.31	126.33	126.36	126.36
2	129.42	129.47	129.44	129.41
3	131.87	131.88	131.85	131.83
4	129.42	129.47	129.45	129.41
5	126.31	126.32	126.35	126.36
6	123.12	122.13	122.26	122.24
7	164.43	164.45	164.41	164.43
8	164.6	164.62	164.63	164.63
9	39.69	39.93	39.91	39.65
10	168.15	170.21	170.34	170.91

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



3.3 Biological activity

Preliminary in vitro tests for fungicidal activity of ligand and complexes have been carried out by the fungi growth inhibition method [13]. These compounds were 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* (84.1%) in vitro.

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

Compound	**Inhibition Ratio (%) (50ppm)**		
	Me_2SnL_2	Bu_2SnL_2	Ph_2SnL_2
Gibberela	18.2	21.3	23.4
Cercospora arachidicola	23.4	33.4	35.4
Physolospora piricola	38.1	44.5	84.1
Fusarium oxysporum	12.4	18.4	55.4

4. CONCLUSION

The ligand benzamidalanine was successfully synthesized. The ligand was treated to different diorganotin(IV) oxide metal salts to afford the corresponding complexes. It may be concluded that the ligand coordinated through carboxylate to the tin atom leading to the formation of four member 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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