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RESEARCH ARTICLE

Triorganotin(IV) Complexes of Schiff Base Derived from Glycine: Synthesis, Characteristic Spectral Studies and Antifungal Activity

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Abstract: A series of triorganotin(IV) complexes of *N*-(2-hydroxy-1-naphthylidene) glycine (**1**), having general formula [Ph_3Sn(Hhngl)] (**2**), [Bu_3Sn(Hhngl)] (**3**), [Me_3Sn(Hhngl)] (**4**), [where H_2hngl= *N*-(2-hydroxy-1-naphthylidene) glycine] were synthesized by reacting of triorganotin(IV) chloride with the ligand, with the aid of sodium iso-propoxide in appropriate stiochiometric ratios (1:1, 1:2). All the complexes exhibit good antifungal activity against four pathogenic fungi namely, *Aspergillus niger*, *Aspergillus flavus*, *Penicillium* sp. and *Fusarium* sp.

Keywords: Triorganotin complexes, Schiff base, Spectroscopic studies, Antifungal activity

Introduction

Organotin(IV) complexes show a spectrum of biological effects and have been extensively studied in various biological fields[1-6]. It is worth noting that, for a long time, organotin(IV) complexes have been widely used in a variety of industrial and beneficial use in agricultural applications[7-9].

The organotin(IV) complexes of Schiff bases have received notable attention in view of their structural chemistry and remarkable biological activities[10-12]. Regarding this, the conformation and geometry and biological activity of organotin(IV) complexes of Schiff bases have been investigated. In the present study, we have synthesized some triorganotin(IV) complexes as potential antifungal agents.

Experimental

All the reagents, *viz*., 2-hydroxy-1-naphthaldehyde (Aldrich), triphenyltin(IV) chloride (Merck), tributyltin(IV) chloride (Merck), trimethyltin(IV) chloride (Merck) were used as received. All the chemicals and solvents used, were dried and purified by standard methods,

and moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. The melting points were determined in open capillaries with electronic melting point apparatus. C, H and N analysis of ligand and complexes were carried on a VarioEL, CHNS elemental analyzer. The tin content in the synthesized complexes were determined gravimetrically as SnO_2. Infrared spectra of the solid compounds were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer in the range 4000-500 cm^{-1} from KBr discs and 500-200 from CsI discs. ^1H NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer at SAIF, Punjab University, Chandigarh, India, using DMSO or $CDCl_3$ as a solvent and TMS as the internal standard. Molecular weight determinations were carried out by the Rast camphor method. The Conductivity Measurement was performed using conductometer Eco Testr EC Low in DMSO having 10^{-3} M at room temp. The antifungal activity of ligand and their diorganotin(IV) complexes were evaluated by poison food technique.

*Synthesis of Schiff base (**1**)*

Schiff bases were prepared by condensation of hot aqueous (25 mL) solution of glycine (0.975 g; 0.013 mol) and 2-hydroxy-1-naphthaldehyde (2.238 g; 0.013 mol), dissolved in ethanol (50 mL). The reaction mixture was refluxed for about 2 h (Scheme I) and yellow brown polycrystalline precipitate was obtained after standing overnight. It was purified by repeated washing with aqueous-ethanol (1: 2) and dried in vacuum over fused $CaCl_2$.

Synthesis of complexes

*$[Ph_3Sn(Hhngl)]$ **(2)***

The solution of triphenyltin(IV) isopropoxide (2.045 g, 0.005 mol) and H_2hngl (1.031 g, 0.0045 mol) was stirred for half an hour and then refluxed on a wax bath for 8-10 h. The isopropanol liberated, was removed azeotropically with benzene and the product was dried under reduced pressure. The oily product thus obtained was solidified and purified by trituration with petroleum ether (b.p. 60-80 ^{0}C).

*$[Bu_3Sn(Hhngl)]$ **(3)***

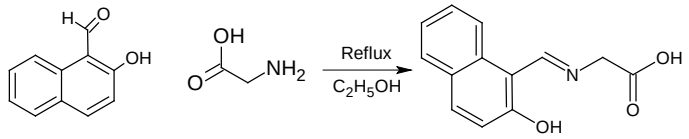
Complex **3** was prepared in the similar way as complex 2. Tributyltin(IV) isopropoxide (1.745 g, 0.005 mole) and H_2hngl (1.031 g, 0.0045 mole).

*$[Me_3Sn(Hhngl)]$ **(4)***

Complex **4** was prepared in the similar way as complex **2** Trimethyltin(IV) isopropoxide (1.115 g, 0.005 mole) and H_2hngl (1.031 g, 0.0045 mole).

Results and Discussion

The Schiff base was prepared by adopting earlier reported method (Scheme 1)[13]. A new methodology has been used to synthesized triorganotin(IV) complexes. Organotin complexes were usually prepared by reacting organotin hydroxide or organotin oxide to corresponding ligand and also by reacting organotin halide to sodium or potassium salt of ligand. In present study, we have replaced halogen of triorganotin with isopropoxide group by reacting them to sodium isopropoxide (Scheme 2). The triorganotin isopropoxides were isolated and reacted to ligand. These reactions proceed with the liberation of isopropanol, which is fractionated out azeotropically and estimated to monitor the completion of reaction. Owing to highly hydroscopic nature of the triorganotin(IV) alkoxides, all the reactions would be carried out under strictly anhydrous condition. The structure of complexes was confirmed by their physiochemical analysis such as elemental, azeotropic, gravimetric analysis and conductivity measurement. The precise information about their structure is obtained from IR and ^1H NMR spectral measurements.



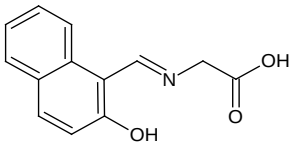
Scheme 1

$$R_3SnCl + NaOPri \xrightarrow[Reflux]{Benzene} R_3Sn(OPri) + NaCl \quad (1)$$

(R= Me, Bu and Ph; $NaOPr^i$ =sodium isopropoxide)

$$R_3Sn(OPri) + H_2hngl \xrightarrow[1:_1/\ Reflux]{Benzene/Toluene} R_3Sn(OPri)(Hhngl) + (CH_3)_2CHOH \quad (2)$$

R = Me, Bu, Ph, H_2hngl =



Scheme 2

Elemental analysis

Experimental and calculated elemental compositions of the complexes are given in Table 1. The analytical data are in good agreement with the proposed stoichiometry of the complexes.

Table 1. Analytical details of the various tin- and organotin(IV) complexes of *N*-(2-hydroxy-1-naphthylidene) glycine

S.No.	Ligand/ Complexes	Yield %	Colour	M.P. ^{0}C	Elemental Analysis % Obsd. (Calcd.)				Molar Conductivity, μS cm^{-1}
					C	H	N	Sn	
1	H_2hngl	72	Yellow	65	68.44 (68.12)	4.84 (4.80)	5.89 (6.11)		
3	[Ph_3Sn(Hhngl)]	71	Green	> 300	64.37 (64.33)	4.38 (4.32)	2.37 (2.42)	20.58 (20.52)	16
4	[Bu_3Sn(Hhngl)]	76	Dark Brown	> 300	57.88 (57.92)	7.14 (7.17)	2.70 (2.66)	22.90 (22.94)	06
5	[Me_3Sn(Hhngl)]	78	Green	> 300	48.98 (49.01)	4.85 (4.87)	3.57 (3.54)	30.28 (30.32)	06

Molar conductance

Molar conductance of the synthesized complexes showed very low values indicating their non-electrolytic nature[14].

Infrared spectra

The characteristic infrared frequencies of the triorganotin(IV) complexes are given in Table 2. The IR spectra of the triorganotin complexes display a broad vibrational band at 3400-3413 cm^{-1} which is assignable[15-16], to the unbonded –OH stretching of the phenolic group.

Table 2. IR spectral data of ligand and triorganotin(IV) complexes of *N*-(2-hydroxy-1 naphthylidene) glycine (in cm^{-1})

S.No.	Ligand/ Complexes	ν(OH)	ν(C=N)	ν_{as}(COO)	ν_s(COO)	Δν	ν(Sn-O)	ν(N→Sn)	ν_{as}(Sn-C)/ν_s(Sn-C)
1	H_2hngl	3500-2300 br		1640vs	1397s				
2	[Ph_3Sn(Hhngl)]	3411br	1607s	1642s	1400m	242	524m	418m	278s, 245s, 226s
3	[Bu_3Sn(Hhngl)]	3413br	1590s	1637vs	1408m	229	549m*	413w	549m*
4	[Me_3Sn(Hhngl)]	3400br	1590s	1636vs	1394m	242	501w	467w	528w, 487m

*s: strong; m: medium; w: weak; br: broad; *merge*

These complexes give a strong asymmetric stretching frequencies ν_{as}(COO) near 1636-1642 cm^{-1} and a weaker symmetrical stretching frequencies ν_s(COO) near 1394-1408 cm^{-1} . The magnitude of ν_{as}- ν_s (Δν) separation has been used to explain the type of boding of carboxylate group to the tin metal[17]. The magnitude of ν_{as}- ν_s (Δν) for these complexes are above 200 cm^{-1}, indicating the monodentate bonding of the carboxylate group to the tin metal. In triorganotin(IV) complexes, ν(C=N) band, display between 1590-1607 cm^{-1}, is considerably shifted towards lower frequencies with respect to that of the free Schiff base (around 1620 cm^{-1}), indicating the coordination of the azomethine nitrogen to the triorganotin(IV) moiety.

The bonding of the carboxylate group to the tin metal is further confirmed by the appearance of a band at 501-549 cm^{-1}, assignable to the Sn-O stretching frequency[18]. In the lower frequency region, the band observed in the region 413-467 has been assigned to the νSn←N vibration[19-22]. The far IR spectra of triphenyltin(IV) complex shows bands at 278 cm^{-1} and at 226 cm^{-1}, which may be assigned[23] to the ν_{as}(Sn-C) and ν_s(Sn-C), respectively, whereas the corresponding peaks at 528 cm^{-1} and at 487 cm^{-1}, have also been[23] assigned in the spectra of trimethyltin(IV) complex. In the case of tributyltin(IV) complex the appearance of *ν*(Sn-C) bands are not certain due to the overlapping of Sn-O stretching vibration.

^{1}H NMR spectra

Table 3 shows the chemical shifts (δ in ppm) of various protons in metal complexes. The appearance of a signal at δ 9.40-10.81 ppm, in the complexes, may be due to the unbonded phenolic –OH proton[24]. The ^{1}H NMR spectra of the complexes, the signals in the region δ 8.34-9.10 ppm have been assigned to azomethine (-N=CH-) proton[21,24]. The multiplet between δ 7.02-8.34 ppm is assigned to the naphthylidene group protons. The butyl protons attached to the tin in tributyltin(IV) complex observed at appropriate position in accordance to the previously reported values[21,25]. In the triphenyltin(IV) complex, the signals for the phenyl groups attached to tin are observed in the range of δ 7.14-8.00 ppm, in conjugation with naphthylidene group protons. Two signals due to Sn-Me_3 in trimethyltin(IV) complex are observed around δ 0.83 ppm and δ 0.64 ppm[4,26], indicating the presence of methyl groups in two different environment. In the light of above finding, the proposed structure of triorganotin(IV) complexes are shown in Figure 1.

Table 3. ^{1}H NMR Spectral data of ligand and triorganotin(IV) complexes of *N*-(2-hydroxy-1-naphthylidene) glycine (in δ ppm)

S.No.	Ligand/ Complexes	Ar-OH proton	-N=CH- proton	Ar-H protons	Sn-C_4H_9, Sn-CH_3, Sn-C_6H_5 protons
1	H_2hngl	10.79 (s, 1H)	8.60 (s, 1H)	7.11-8.34 (m, 6H)	
2	[Ph_3Sn(Hhngl)]	9.40 (s, 1H)	8.34 (s, 1H)	7.14-8.00 (m, 6H)	7.14-8.00 (m, 15H)
3	[Bu_3Sn(Hhngl)]	10.70 (s, 1H)	9.10 (d, 1H)	7.02-7.88 (m, 6H)	0.80, 1.24 and 1.40-172 (t, tq and m, 27H, Sn-C_4H_9)
4	[Me_3Sn(Hhngl)]	10.81 (s, 1H)	8.36 (d, 1H)	7.13-8.34 (m, 6H)	0.87 (s, 3H), 0.66(s, 3H)

s: singlet; d: doublet; t: triplet: m: multiplet

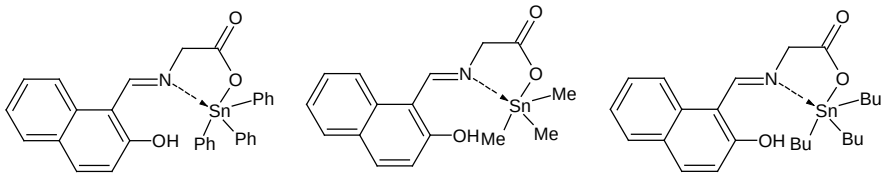


Figure 1. Proposed structure of triorganotin(IV) complexes

Biological activity

The antifungal activity of liand triorganotin(IV) complexes were evaluated by poisoned food technique[27-28]. All these triorganotin(IV) complexes possessed antifungal activity against *Aspergillus niger*, *Aspergillus flavus* and *Penicillium* sp. as shown in Table 4.

Table 4. Antifungal bioassay results[a] (*in vitro*) for triorganotin(IV) complexes of *N*-(2-hydroxy-1-naphthylidene) glycine

S.No.	Complexes	Mycelial growth inhibition, %			
		Aspergillus niger	*Aspergillus flavus*	*Penicillium* sp.	*Fusarium* sp.
1	[Ph_3Sn(Hhngl)]	58.5	62.1	60.2	52.4
2	[Bu_3Sn(Hhngl)]	49.2	46.7	52.1	48.6
3	[Me_3Sn(Hhngl)]	52.5	50.1	55.3	50.1

[a]*Concentration used 2.00 mg ml^{-1} of DMSO*

The complex namely, [Ph_3Sn(Hhngl)] **(2)**, showed more than 60% inhibition of mycelial growth against *Aspergillus flavus* and *Penicillium* sp. The complex [Bu_3Sn(Hhngl)] **(3)** and [Me_3Sn(Hhngl)] **(4)** showed maximum fungicidal activity against *Penicillium* sp. A perusal of tables 4 shows that the triphenyltin(IV) complex, exhibit maximum fungitoxicity than tributyl- and trimethyltin(IV) complexes of H_2hngl.

Conclusion

Based on various studies such as elemental analysis, IR and ^{1}H NMR spectral studies, five-coordinate geometry for triorganotin(IV) complexes are proposed. The triorganotin(IV) complexes show good antifungal activity and the order of antifungal activity of triorganotin(IV) complexes of H_2hngl is Ph>Me>Bu.

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