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Synthesis, spectral and antimicrobial studies of diorganotin(IV)3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates

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Diorganotin(IV) dipyrazolinates of the type $R_2Sn(C_{15}H_{12}N_2OX)_2$ [where $C_{15}H_{12}N_2OX$ = 3(2′-Hydroxyphenyl)-5(4-X-phenyl)pyrazoline {where X = H (a); CH_3 (b); OCH_3 (c); Cl (d) and R = Me, Pr^n and Ph}] have been synthesized by the reaction of R_2SnCl_2 with sodium salt of pyrazolines in 1 : 2 molar ratio, in anhydrous benzene. These newly synthesized derivatives have been characterized by elemental analysis (C, H, N, Cl and Sn), molecular weight measurement as well as spectral [IR and multinuclear NMR (^1H, ^{13}C and ^{119}Sn)] studies. The bidentate behaviour of the pyrazoline ligands was confirmed by IR, ^1H and ^{13}C NMR spectral data. A distorted *trans*-octahedral structure around tin(IV) atom for $R_2Sn(C_{15}H_{12}N_2OX)_2$ has been suggested. The free pyrazoline and diorganotin(IV) dipyrazolinates have also been screened for their antibacterial and antifungal activities. Some diorganotin(IV) dipyrazolinates exhibit higher antibacterial and antifungal effect than free ligand and some of the antibiotics. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: organotin(IV); pyrazolinates; antimicrobial activity

INTRODUCTION

The development of a clean procedure for the preparation of heterocyclic compounds is a major challenge of modern heterocyclic chemistry in view of the environmental, practical and economic issue. Pyrazolines are an important class of heterocyclic compounds. They are used in industry as dyes, lubricating oils, antioxidants and in agriculture as catalysts for the decarboxylation reaction as well as inhibitors of plant growth.[1–3] Complexation behaviour of 3(2′-hydroxy phenyl)-5-phenylpyrazoline with Ni(II), Co(II) and Cu(II) have been investigated in our laboratories.[4] Perusal of literature, however, shows nothing about pyrazolinate derivatives of tin(IV) and organotin(IV).

Octahedral tin(IV) complexes are potential antitumour and antiviral agents.[5] The use of organotin(IV) halides as anti-inflammatory agents against different types of oedema in mice is of fundamental interest.[6] Tabarelli *et al.* have recently published a study of antinociceptive action[7] of a new series of pyrazolines. Chauhan *et al.* have reported antibacterial and antifungal activities of mixed sulfur ligand complexes of tin(IV).[8] Organotin(IV) complexes such as tetra-n-butyltin-bis-3,6-dioxaheptanoato, -bis-3,6,9-trioxadecanoato-distannoxane and di-*n*-butyl and triphenyltin derivatives of 4-carboxybenzo-15-crown-5 also exhibit very pronounced *in vitro* cytotoxic properties.[9,10]

In continuation of our previous work, it was thought worthwhile to study the complexation behaviour of 3(2′-hydroxyphenyl)-5(4-X-phenyl)pyrazoline and substituted pyrazolines with tin(IV) and organotin(IV). We have studied the tin(IV) pyrazolinates of the type $LSnCl_3$ and L_2SnCl_2 [where L = 3(2′-Hydroxyphenyl)-5(4-X-phenyl)pyrazoline; X=H (**a**); CH_3 (**b**); OCH_3 (**c**); Cl (**d**)]. The free ligand and some of the tin(IV) pyrazolinates exhibited higher antineurotoxic effect in brain cells of *Swiss albino mice*. In the present paper we are describing the results of synthesis, spectral characterization and antimicrobial studies of diorganotin(IV)3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates.

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EXPERIMENTAL

Materials

Solvents (benzene, acetone and alcohols) were rigorously dried and purified before use by standard methods.[11] All the chemicals used were of analytical grade quality. Dimethyl tindichloride (E. Merck), di-*n*-propyltin dichloride (E. Merck) and diphenyltin dichloride (Lancaster) were used as received. *O*-hydroxy acetophenone (CDH) and benzaldehydes (s.d. fine chemicals) were used as received.

Physical measurements

Chlorine was estimated by Volhard's method and tin was determined gravimetrically as tin dioxide.[12] Infrared spectra were recorded as nujol mulls using CsI cells on Perkin Elmer Model 557 FT-IR spectrophotometer in the range $4000-200\ \text{cm}^{-1}$. ^1H NMR spectra were recorded at room temperature in C_6D_6 on a Bruker DRX-300 spectrometer, operated at 300.1 MHz using TMS (tetramethylsilane) as internal standard. The proton decoupled ^{13}C NMR spectra and proton decoupled ^{119}Sn NMR spectra were recorded at room temperature in C_6D_6 on a Bruker DRX-300 spectrometer, operated at 75.45 and 111.95 MHz for ^{13}C and ^{119}Sn, using TMS (tetramethyl silane) and TMT (tetramethyl tin) as internal standards, respectively. Molecular weights were determined on a Knauer Vapour Pressure osmometer in $CHCl_3$ at 45 °C. The elemental analysis (C, H and N) was estimated using a Coleman CHN analyzer.

Synthesis of the complexes

Ligands were prepared by reported procedure.[13] The new organotin(IV) complexes of the general formula $R_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$ were prepared by the following route.

Synthesis of $R_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$

Diorganotin(IV) dipyrazolinates were synthesized by the reaction of diorganotin dichloride with sodium salts of pyrazolines in 1 : 2 molar ratio:

$$R_2SnCl_2 + 2Na(C_{15}H_{12}N_2O{\cdot}X) \xrightarrow{\text{Benzene}} R_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2 + 2NaCl$$

where R = Me, Pr^n, Ph; X = H, —CH_3, —OCH_3 and —Cl.

$Me_2Sn(C_{15}H_{13}N_2O)_2$

Freshly cut pieces of sodium (0.2221 g; 9.66 mmol) were taken in a flask with excess of isopropanol and refluxed (~30 min), until a clear solution of sodium isopropoxide was obtained. The benzene solution of 3(2′-hydroxyphenyl)-5(4-X-phenyl)pyrazoline (2.29 g; 9.66 mmol) was then added and the reaction mixture was further refluxed for 1 h, after which a constant yellow colour was obtained. The reaction mixture was cooled to room temperature and then benzene solution of anhydrous R_2SnCl_2 (1.06 g; 4.83 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for 4 h, until the colour of the reaction mixture underwent a change. The reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. The light brown coloured solid thus obtained was re-precipitated from benzene and dried in vacuum. The analytical details are summarized in Table 1.

Antimicrobial studies

Agar disc diffusion technique was used for the screening of *in vitro* antimicrobial activity.[14] Inocula of bacteria were prepared in nutrient broth and fungi in potato dextrose agar slant. The molten Muller Hinton medium was poured in sterile Petri dish (9 cm in diameter) to a depth of 4 mm. The medium was left to solidify. Then it was seeded with respective test organisms; 8 mg of each sample to be tested were dissolved in 1 ml acetone solvent. Discs of diameter 5 mm of Whatmann filter paper no. 42 were cut and sterilized. The filter paper discs were immersed in the solution of sample, after soaking; the disc was removed and left in a sterile Petri dish to permit the solvent to evaporate. After about 10 min the paper discs were transferred to seeded agar plate. Five discs were kept on the seeded agar plates. Finally the dishes were incubated at 37 °C for 24 h (for bacteria) and at 30 °C for 72 h (for fungi), where clear inhibition zones were detected around each disc (Fig. 1).

A disc soaked in acetone alone was used as a control under the same conditions and no inhibition zone was observed for acetone. Each distinct inhibition zone was measured as diameter in millimetres; both antibacterial and antifungal activities were calculated as a mean of three replicates.

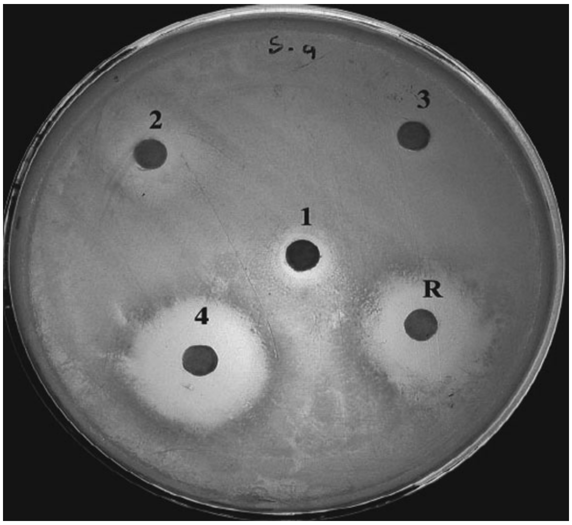

Figure 1. Antibacterial activity against *Staphylococcus aureus*; 1 = free pyrazoline [3(2′-hydroxyphenyl)-5-phenyl pyrazoline]; 2 = compound **1**; 3 = compound **5**; 4 = compound **9**; and R = tetracycline.

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Table 1. Physical and analytical data for $R_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$

Compound no.	Compound	Yield (%)	M.P. (°C)	Molecular weight found (calculated)	Analysis(%): found (calculated)				
					C	H	N	Sn	Cl
1	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	82	179	627 (622.99)	61.23	5.11	8.93	18.96	—
					(61.68)	(5.13)	(8.98)	(19.05)	
2	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	86	123	647 (651.01)	62.81	5.55	8.54	18.28	—
					(62.72)	(5.52)	(8.60)	(18.23)	
3	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	91	184	686 (682.99)	59.39	5.25	8.17	17.27	—
					(59.78)	(5.27)	(8.19)	(17.37)	
4	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	85	147	685 (691.89)	55.93	4.29	8.13	17.08	10.20
					(55.54)	(4.33)	(8.09)	(17.15)	(10.24)
5	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	80	163	673 (679.03)	63.29	5.85	8.16	17.54	—
					(63.67)	(5.89)	(8.24)	(17.47)	
6	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	78	118	712 (707.05)	64.16	6.20	7.89	16.81	—
					(64.54)	(6.22)	(7.92)	(16.78)	
7	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	84	156	744 (739.03)	61.38	5.98	7.53	15.97	—
					(61.75)	(5.95)	(7.57)	(16.06)	
8	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	90	206	742 (747.93)	58.18	5.06	7.47	15.84	9.39
					(57.80)	(5.08)	(7.48)	(15.86)	(9.47)
9	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	91	174	741 (747.09)	67.12	4.85	7.43	15.79	—
					(67.51)	(4.81)	(7.49)	(15.88)	
10	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	88	234	779 (775.11)	67.77	5.12	7.18	15.27	—
					(68.17)	(5.16)	(7.22)	(15.31)	
11	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	84	189	812 (806.13)	65.18	4.92	6.89	14.81	—
					(65.55)	(4.96)	(6.94)	(14.72)	
12	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	81	211	819 (815.99)	61.47	4.19	6.87	14.56	8.61
					(61.86)	(4.16)	(6.86)	(14.65)	(8.68)

where X = H in **1, 5** and **9**; CH_3 in **2, 6** and **10**; OCH_3 in **3, 7** and **11**; Cl in **4, 8** and **12** compounds respectively.

RESULTS AND DISCUSSION

All the compounds are light yellow to brown coloured solids, non-hygroscopic and stable at room temperature. These are soluble in common organic (benzene, chloroform, acetone) and coordinating (methanol, tetrahydrofuran, dimethylformamide and dimethylsulfoxide) solvents. The molecular weight measurement in dilute chloroform solution at 45 °C shows monomeric nature of these compounds. The elemental analysis (C, H, N, Cl and Sn) data is in accordance with stoichiometry proposed for respective compounds.

Table 2. IR spectral data (cm^{-1}) for diorganotin(IV) dipyrazolinates recorded as nujol mulls in the range 4000–200 cm^{-1}

Sample no.	Compound	ν(N–H)	ν(C=N)	ν(C–O)	ν(Sn–C)	ν(Sn–O)	ν(Sn–N)
1	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3311	1636	—	537	485	389
2	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3312	1640	—	535	487	391
3	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3309	1641	1012	536	490	390
4	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3307	1638	—	533	489	388
5	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3309	1637	—	532	487	391
6	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3312	1640	—	536	485	389
7	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3309	1637	1017	534	489	388
8	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3311	1637	—	537	488	386
9	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3314	1640	—	285	490	393
10	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3312	1641	—	289	492	392
11	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3309	1638	1015	284	487	391
12	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	3307	1640	—	286	488	388

where X = H in **1, 5** and **9**; CH_3 in **2, 6** and **10**; OCH_3 in **3, 7** and **11**; Cl in **4, 8** and **12** compounds, respectively.

Table 3. ^1H NMR data (δ ppm) for diorganotin(IV) dipyrazolinates recorded at room temperature in C_6D_6

Sample no.	Chemical shift (δ ppm)		Coupling constants (in Hz)	θ (deg)
	($C_{15}H_{12}N_2OX$)	R–Sn		
1	7.7–6.8 (18H, m, Ar–H) 5.3 (2H, s, NH) 3.7 (2H, t, CH) 2.2 (4H, d, CH_2)	0.9 (CH_3)	$^2J(^{119}Sn, ^1H) = 79$	129.6
2	7.6–6.7 (16H, m, Ar–H) 5.4 (2H, s, NH) 3.5 (2H, t, CH) 2.3 (4H, d, CH_2) 1.1 (CH_3)	0.7 (CH_3)	$^2J(^{119}Sn, ^1H) = 82$	133.4
3	7.9–7.1 (16H, m, Ar–H) 5.5 (2H, s, NH) 3.5 (2H, t, CH) 2.0 (4H, d, CH_2) 4.1 (6H, s, OCH_3)	0.8 (CH_3)	$^2J(^{119}Sn, ^1H) = 84$	136.1
4	7.8–6.7 (16H, m, Ar–H) 5.3 (2H, s, NH) 3.7 (2H, t, CH) 2.1 (4H, d, CH_2)	0.8 (CH_3)	$^2J(^{119}Sn, ^1H) = 80$	130.8
5	7.7–6.7 (18H, m, Ar–H) 5.1 (2H, s, NH) 3.6 (2H, t, CH) 2.3 (4H, d, CH_2)	1.4 (αCH_2) 2.0 (βCH_2) 0.7 (γCH_3)	$^2J(^{119}Sn, ^1H) = 88$	141.9
6	8.0–7.1 (16H, m, Ar–H) 5.4 (2H, s, NH) 3.3 (2H, t, CH) 2.4–0.9 (4H, d, CH_2) 0.9 (CH_3)	1.2 (αCH_2) 1.8 (βCH_2) 0.6 (γCH_3)	$^2J(^{119}Sn, ^1H) = 93$	149.9
7	7.9–7.0 (16H, m, Ar–H) 5.5 (2H, s, NH) 3.6 (2H, t, CH) 2.3 (4H, d, CH_2) 4.3 (6H, s, OCH_3)	1.1 (αCH_2) 1.9 (βCH_2) 0.7 (γCH_3)	$^2J(^{119}Sn, ^1H) = 81$	132.1
8	7.6–6.5 (16H, m, Ar–H) 5.3 (2H, s, NH) 3.5 (2H, t, CH) 2.5 (4H, d, CH_2)	0.8 (αCH_2) 1.9 (βCH_2) 0.8 (γCH_3)	$^2J(^{119}Sn, ^1H) = 85$	137.1
9	8.2–7.4 (18H, m, Ar–H) 5.1 (2H, s, NH) 3.7 (2H, t, CH) 2.4 (4H, d, CH_2)	8.2–7.4 (m, C_6H_5)		
10	7.9–7.1 (16H, m, Ar–H) 5.4 (2H, s, NH) 3.7 (2H, t, CH) 2.1 (4H, d, CH_2) 0.8 (CH_3)	7.9–7.1 (m, C_6H_5)		
11	7.7–6.9 (16H, m, Ar–H) 5.1 (2H, s, NH) 3.1 (2H, t, CH) 2.3 (4H, d, CH_2) 4.0 (6H, s, OCH_3)	7.7–6.9 (m, C_6H_5)		

Table 3. (*Continued*)

	Chemical shift (δ ppm)			
Sample no.	($C_{15}H_{12}N_2OX$)	R–Sn	Coupling constants (in Hz)	θ (deg)
12	8.3–7.7 (16H, m, Ar–H) 5.3 (2H, s, NH) 3.3 (2H, t, CH) 1.9 (4H, d, CH_2)	8.3–7.7 (m, C_6H_5)		

where X = H in **1, 5** and **9**; CH_3 in **2, 6** and **10**; OCH_3 in **3, 7** and **11**; Cl in **4, 8** and **12** compounds, respectively. m = complex pattern, s = singlet, d = doublet, t = triplet.

Infrared spectra

The infrared spectral data of these compounds are summarized in Table 2. All compounds exhibit bands of medium intensity in the region 3314–3307 cm^{-1} due to ν(N–H) stretching vibrations and bands in the region 1641–1636 cm^{-1} due to ν(C=N) stretching vibrations.[4] The band present in the region 1017–1012 cm^{-1} in compounds **3, 7** and **11** may be assigned to ν(C–O) stretching indicating the presence of —OCH_3 group. The signal due to ν(O–H) (originally present at ∼3080 cm^{-1} in free pyrazolines) is completely missing from the spectra of complexes. All compounds exhibit bands of medium intensity in the region 537–284 cm^{-1} due to ν(Sn–C)[15] stretching vibrations.

The presence of new bands (in comparison to free pyrazolines) in the region 492–485 and 393–386 cm^{-1} have been assigned to ν(Sn–O)[15] and ν(Sn–N)[16] stretching vibrations, respectively. The appearance of these two new bands and missing of hydroxyl band suggests that the pyrazoline behaves as monobasic bidentate ligand.

Multinuclear NMR spectroscopy

The ^1H NMR chemical shifts of these compounds are listed in Table 3. In ^1H NMR spectra, the aromatic protons of diorganotin(IV) dipyrazolinates were observed as a complex pattern in the region δ 8.3–6.5 ppm.[17] The peak due to hydroxyl proton (originally present at δ ∼11.00 ppm in free pyrazolines) is completely missing from the spectra of compounds suggesting the bonding through hydroxyl oxygen atom. The appearance of a peak at δ 5.5–5.1 ppm as a broad singlet could be assigned to an N–H group (originally present at δ 5.4–5.0 ppm in free pyrazolines), suggesting the non-involvement of N–H group in bond formation. The skeletal protons of a five-membered ring are observed at δ 3.4–3.1 ppm as a triplet and at δ 2.6–2.0 ppm as a doublet and could be assigned to CH and CH_2 groups, respectively.[17] The CH_3Sn protons give a sharp singlet at δ 0.9–0.7 ppm with double satellite resonances of relative intensity of 4–5% of both sides of the main peak (singlet) due to the coupling of the protons with ^{119}Sn and ^{117}Sn isotopes.[18,19] The resonances due to n-propyltin protons are observed in the region δ 2.0–0.6 ppm. The signals due to C_6H_5Sn overlap with the signals of aromatic protons of ligand and observed at δ 8.3–6.7 ppm as a complex pattern, therefore aromatic signals could not be assigned individually. Compounds **1**–**8** shows $^2J(^{119}Sn, ^1H)$ values between 79–93 Hz. The values of coupling constants are strongly indicative of six-coordinated structures[20,21] and this confirms the bidentate behaviour of ligands in these compounds.

The coupling constant $^2J(^{119}Sn, ^1H)$ can be used to estimate the C–Sn–C bond angle, θ. Equation (1) yields the θ value:[22]

$$\theta = 0.0161|^2J(^{119}\mathrm{Sn}, ^1\mathrm{H})|^2 - 1.32|^2J(^{119}\mathrm{Sn}, ^1\mathrm{H})| + 133.4 \qquad (1)$$

The calculated θ values are in between 129.6 and 149.9° for compounds **1**–**8**. These values suggest a distorted *trans*-octahedral geometry at tin atom.[20,21]

The proton decoupled ^{13}C NMR spectra (Table 4) of tin(IV) dipyrazolinates show the presence of all important signals with reference to free pyrazolines. The assignments have been made on the basis of available literature along with the spectra of the free pyrazolines. The signals observed in the region δ 137.3–121.9 ppm as a complex pattern could be assigned to aromatic carbon atoms.[17] The signal observed at δ 165.3–162.7 ppm due to imino carbon of C=N group is shifted down field in comparison to the spectra of free pyrazolines (at δ 143.5–142.8 ppm), suggesting the involvement of imino nitrogen in coordination. All other signals were found at their respective positions as in ligand. The peak observed at δ 10.3–9.8 ppm could be assigned to MeSn group. The signals observed at δ 26.7–26.1, 28.6–28.2 and 12.9–12.5 ppm may be assigned to αC, βC and γC of Pr^nSn group. The signals due to PhSn group overlap with the signals of aromatic carbons of ligand and are observed at δ 137.3–122.3 ppm as a complex pattern. All the eight compounds **1**–**8** show $^1J(^{119}Sn, ^{13}C)$ values between 670 and 690 Hz, which are characteristics of six-coordinated tin.[20,21,23]

The coupling constant $^1J(^{119}Sn, ^{13}C)$ can also be used to estimate the C–Sn–C bond angle, θ. Equation (2) yields the θ value;[22]

$$^1J(^{119}\mathrm{Sn}, ^{13}\mathrm{C}) = 11.4\theta - 875 \qquad (2)$$

The calculated θ values are between 135.5 and 137.3° for compounds **1**–**8**. These values also suggest a distorted *trans*-octahedral geometry at the tin atom.

The proton decoupled ^{119}Sn NMR spectra (Table 5) of all compounds have been recorded and exhibit a sharp

Table 4. ^{13}C NMR data (δ ppm) for diorganotin(IV) dipyrazolinates recorded at room temperature in C_6D_6

Sample no.	Chemical shift (δ ppm)		Coupling constants (in Hz)	θ (deg)
	($C_{15}H_{12}N_2O\cdot X$)	R–Sn		
1	136.3–123.9 (Ar–C) 162.7 (C=N) 43.3 (CH) 27.5 (CH_2)	9.8 (CH_3)	$^1J(^{119}Sn, ^{13}C) = 674$	135.9
2	136.1–123.8 (Ar–C) 162.9 (C=N) 43.5 (CH) 27.7 (CH_2) 13.7 (CH_3)	10.3 (CH_3)	$^1J(^{119}Sn, ^{13}C) = 676$	136.0
3	136.1–122.9 (Ar–C) 163.5 (C=N) 43.7 (CH) 27.3 (CH_2) 57.7 (OCH_3)	10.2 (CH_3)	$^1J(^{119}Sn, ^{13}C) = 670$	135.5
4	135.5–123.1 (Ar–C) 163.7 (C=N) 43.9 (CH) 27.4 (CH_2)	9.9 (CH_3)	$^1J(^{119}Sn, ^{13}C) = 672$	135.7
5	136.1–123.7 (Ar–C) 163.5 (C=N) 43.8 (CH) 27.5 (CH_2)	26.3 (αC)[a] 28.5 (βC) 12.8 (γC)	$^1J(^{119}Sn, ^{13}C) = 682$ $^2J(^{119}Sn, ^{13}C) = 41$ $^3J(^{119}Sn, ^{13}C) = 112$	136.6
6	135.5–122.8 (Ar–C) 162.9 (C=N) 43.5 (CH) 27.3 (CH_2) 13.5 (CH_3)	26.5 (αC) 28.3 (βC) 12.9 (γC)	$^1J(^{119}Sn, ^{13}C) = 688$ $^2J(^{119}Sn, ^{13}C) = 38$ $^3J(^{119}Sn, ^{13}C) = 109$	137.1
7	135.1–122.8 (Ar–C) 163.8 (C=N) 43.8 (CH) 27.5 (CH_2) 57.5 (OCH_3)	26.1 (αC) 28.2 (βC) 12.5 (γC)	$^1J(^{119}Sn, ^{13}C) = 684$ $^2J(^{119}Sn, ^{13}C) = 42$ $^3J(^{119}Sn, ^{13}C) = 115$	136.7
8	136.1–124.1 (Ar–C) 163.5 (C=N) 43.5 (CH) 27.7 (CH_2)	26.7 (αC) 28.6 (βC) 12.9 (γC)	$^1J(^{119}Sn, ^{13}C) = 690$ $^2J(^{119}Sn, ^{13}C) = 40$ $^3J(^{119}Sn, ^{13}C) = 110$	137.3
9	136.9–122.3 (Ar–C) 162.9 (C=N) 42.9 (CH) 27.4 (CH_2)	136.9–122.3 (C_6H_5)		
10	136.7–122.8 (Ar–C) 164.1 (C=N) 43.3 (CH) 27.9 (CH_2) 13.7 (CH_3)	136.7–122.8 (C_6H_5)		
11	135.7–123.5 (Ar–C) 163.5 (C=N) 43.5 (CH) 27.9 (CH_2) 57.9 (OCH_3)	135.7–123.5 (C_6H_5)		

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Table 4. (*Continued*)

Sample no.	Chemical shift (δ ppm)		Coupling constants (in Hz)	θ (deg)
	($C_{15}H_{12}N_2O{\cdot}X$)	R–Sn		
12	137.3 – 123.7 (Ar–C) 165.3 (C=N) 43.7 (CH) 27.3 (CH_2)	137.3 – 123.7 (C_6H_5)		

where X = H in **1, 5** and **9**; CH_3 in **2, 6** and **10**; OCH_3 in **3, 7** and **11**; Cl in **4, 8** and **12** compounds respectively.
[a] Sn–αCH_2–βCH_2–γCH_3.

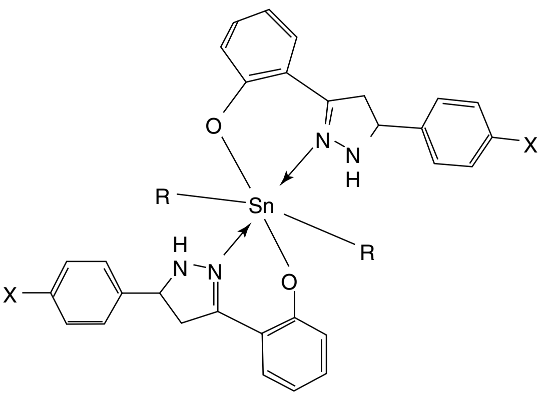

Figure 2. Molecular structure of $R_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$ (where R = Me, Pr^n, Ph; X = $-H$, $-CH_3$, $-OCH_3$ and $-Cl$).

^{119}Sn resonance in the region at δ −342.3 to −384.7 ppm. These values are strongly indicative of six-coordinated[23–25] structures (Fig. 2).

MICROBIAL ASSAY

The antibacterial activities of a free pyrazoline and its three complexes were tested against the bacterial species *Staphylococcus aureus, Bacillus subtilis, Citrobacter freundii, Alcaligenes faecalis, Escherichia coli, Klebsiella pneumoniae, Pseudomonas aeruginosa, Salmonella typhi, Proteus vulgaris* and *Serratia* spp., and the antifungal activity were tested against *Aspergillus niger* and *Penicillium notatum*. The antimicrobial activity of some antibiotics were also tested and compared with free pyrazoline and its tin complexes. The results are listed in Table 6.

The antibacterial studies exhibited that the diorganotin(IV) dipyrazolinates have greater activity towards all tested bacteria than free pyrazolines. The diorganotin(IV) dipyrazolinates also exhibited greater antifungal activity towards all tested fungi than the free pyrazoline.

Nevertheless, it is difficult to make an exact structure and activity relationship between antimicrobial activity and the structure of these complexes. It can possibly be concluded that the complexation of biologically active diorganotin moiety with biologically active pyrazoline ligand results in increased activity of these complexes.

Table 5. ^{119}Sn NMR data (in δ ppm) for diorganotin(IV) dipyrazolinates recorded at room temperature in C_6D_6

Sample no.	Compound	Chemical shift (δ ppm)
1	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−364.6
2	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−366.5
3	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−364.3
4	$Me_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−371.4
5	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−381.5
6	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−384.7
7	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−377.4
8	$Pr^n{}_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−379.1
9	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−342.3
10	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−358.2
11	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−354.6
12	$Ph_2Sn(C_{15}H_{12}N_2O{\cdot}X)_2$	−349.9

where X = H in **1, 5** and **9**; CH_3 in **2, 6** and **10**; OCH_3 in **3, 7** and **11**; Cl in **4, 8** and **12** compounds, respectively.

Comparison of the antimicrobial activities of the free pyrazoline and diorganotin(IV) dipyrazolinates with some known antibiotics exhibit the following results:

(1) The diorganotin(IV) dipyrazolinates exhibit greater antibacterial effect towards *Staphylococcus aureus* compared with free pyrazoline and tetracycline.
(2) The diorganotin(IV) dipyrazolinates exhibit a comparable antibacterial effect on *Citrobacter freundii* compared with free pyrazoline and tetracycline.
(3) The diorganotin(IV) dipyrazolinates exhibit a comparable effect towards *Bacillus subtilis* and *Alcaligenes faecalis* compared with free pyrazoline and tetracycline.
(4) The diorganotin(IV) dipyrazolinates exhibit a greater antifungal effect on *Aspergillus niger* compared with free pyrazoline and terbinafin.

From all of the above results we can conclude that some diorganotin(IV) dipyrazolinates exhibit greater antimicrobial effect than free pyrazoline and some antibiotics.

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Table 6. Antimicrobial activity of the free pyrazoline and diorganotin(IV) dipyrazolinates

	Fungi		Gram (+ve) bacteria		Gram (−ve) bacteria							
Compound no.	*A. niger*	*P. notatum*	*S. aureus*	*B. subtilis*	*C. freundii*	*A. faecalis*	*E. coli*	*K. pneumoniae*	*P. aeruginosa*	*S. typhi*	*P. vulgaris*	*Serratia* spp.
L[a]	+	−	+	+	+	+	−	−	−	−	−	−
(**1**)	++	−	++	+	+++	+	−	−	−	−	−	−
(**5**)	++	−	+	+	+	+	−	−	−	−	−	−
(**9**)	+++	−	+++	++	+++	+	−	−	−	−	−	−
R[b]	+++	−	+++	++	+++	+++	−	−	−	−	−	−

Inhibition values beyond control are + = 6–10 mm, ++ = 11–15 mm, +++ = 16–20 mm, ++++ = 21–25 mm and − = not active (the values include disc diameter); **L*** = 3(2′-hydroxyphenyl)-5-phenyl pyrazoline; **1** = compound **1**; **5** = compound **5**; **9** = compound **9**.

[a] **R** = terbinafin (antifungal agent) and tetracycline (antibacterial agent).

[b] The standards are in the form of sterile Hi-Disc cartridges, each disc containing 10 μg of the drug.

CONCLUSIONS

The present study describes the series of diorganotin(IV) dipyrazolinates, although it is quite difficult to comment on the molecular structure of these compounds in solid state without actual X-ray crystal structure analysis of at least one of the products. In a number of tin(IV) complexes the structures have been described as distorted *trans*-octahedral geometry for six-coordinated diorganotin compound.[23–25] However, the bidentate behaviour of the pyrazoline ligands in these compounds has been confirmed by IR, ^{1}H NMR and ^{13}C NMR data. The multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) data indicate the six-coordinated distorted *trans*-octahedral geometry of tin in all these compounds.

The tin compounds exhibit higher antibacterial and antifungal effect than the free pyrazoline and some of the antibiotics tetracycline and antifungal agent terbinafin respectively.

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