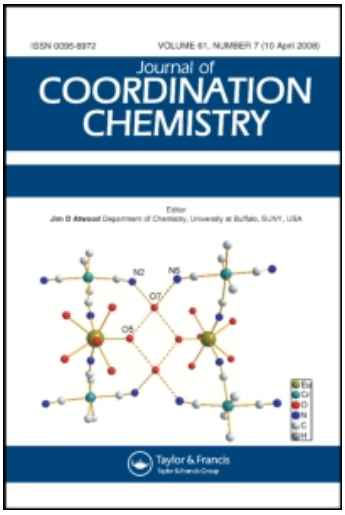

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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

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To cite this Article Tripathi, U. N. , Ahmad, M. Safi , Venubabu, G. and Ramakrishna, P.(2007) 'Synthesis, spectral and antimicrobial studies of triorganotin(IV) 3(2'-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates', Journal of Coordination Chemistry, 60: 16, 1709 — 1720
To link to this Article: DOI: 10.1080/00958970601110865
URL: http://dx.doi.org/10.1080/00958970601110865

Journal of Coordination Chemistry
Vol. 60, No. 16, 15 August 2007, 1709–1720

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

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(*Received 30 August 2006; in final form 25 September 2006*)

Triorganotin(IV) pyrazolinates of the type $R_3Sn(C15H_{12}N_2O \cdot X)$ [where $C_{15}H_{12}N_2O \cdot X =$ 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_3SnCl with the sodium salt of pyrazolines in a 1 : 1 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 studies [IR and multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn)]. The bidentate behaviour of the ligands was confirmed by IR, ^{1}H and ^{13}C NMR spectral data. Trigonal bipyramidal structure around tin(IV) atom for $R_3Sn(C_{15}H_{12}N_2O \cdot X)$ has been suggested. The free pyrazoline and a few triorganotin(IV) pyrazolinates have also been screened for their antibacterial and antifungal activities. Some triorganotin(IV) pyrazolinates exhibit higher antibacterial and antifungal effects than free pyrazoline and some of the antibiotics.

Keywords: Organotin(IV); Pyrazolinates; Antimicrobial activity

1. Introduction

Pyrazolines are an important class of heterocyclic compounds, used in industries as dyes, lubricating oils, antioxidants and in agriculture as catalysts for decarboxylation as well as inhibitors for 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 shows nothing about pyrazolinate derivatives of tin(IV) or organotin(IV).

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

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ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601110865

In continuation to our previous work, it was thought worthwhile to study the complexation behaviour of 3(2′-hydroxyphenyl)-5-phenylpyrazoline and substituted pyrazolines with tin(IV) and organotin(IV). We have studied the synthesis, spectral characterization and antimicrobial activity of diorganotin(IV) dipyrazolinates [10, 11]. We have also studied the tin(IV) pyrazolinates of the type $LSnCl_3$ and L_2SnCl_2 [where L = 3(2′-hydroxyphenyl)-5(4-X-phenyl)pyrazoline {where X = H (a); CH_3 (b); OCH_3 (c); Cl (d)}]. The free ligand and some of the tin(IV) pyrazolinates exhibit higher antineurotoxic effects in brain cells of *Swiss albino mice*. In the present article we describe the results of synthesis, spectral characterization and antimicrobial studies of triorganotin(IV)3(2′-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolinates.

2. Experimental

Solvents (benzene, acetone and alcohols) were rigorously dried and purified before use by standard methods [12]. All the chemicals used were of analytical grade quality. Trimethyltin chloride (Merck), tripropyltin-*n*-chloride (Merck) and triphenyltin chloride (Lancaster) were used as received. *o*-Hydroxy acetophenone (CDH) and benzaldehydes (s.d.fine) were used as received.

2.1. *Synthesis of $R_3Sn(C_{15}H_{12}N_2O \cdot X)$*

Ligands were prepared by reported procedure [13]. The new triorganotin(IV) pyrazolinates of general formula $R_3Sn(C_{15}H_{12}N_2O \cdot X)$ were prepared by the following route:

$$R_3SnCl + Na(C_{15}H_{12}N_2O \cdot X \xrightarrow{\text{Benzene}} R_3Sn(C_{15}H_{12}N_2O \cdot X) + NaCl$$

[where R = Me, Pr^n, Ph; X = H, $-CH_3$, $-OCH_3$ and $-Cl$]

2.1.1. $Ph_3Sn(C_{15}H_{13}N_2O)$. Freshly cut pieces of sodium (0.111 g; 4.83 mmol) were taken in a flask with excess isopropanol and refluxed (~1/2 h), till a clear solution of sodium isopropoxide was obtained. A benzene solution of 3(2′-hydroxyphenyl)-5-phenyl pyrazoline (1.14 g; 4.83 mmol) was then added and the reaction mixture was further refluxed for 1 h, giving a yellow colour. The reaction mixture was cooled to room temperature and then benzene solution of Ph_3SnCl (1.86 g; 4.83 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for 6 h, till the colour of the reaction mixture underwent a change. Reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. The brown coloured solid thus obtained was reprecipitated from benzene and dried in vacuum.

All compounds were prepared by the same method; analytical results are presented in table 1.

Table 1. Synthetic and analytical data for $R_3Sn(C_{15}H_{12}N_2O \cdot X)$.

Compd no.	Compound	Yield (%)	M.p. (°C)	Analysis found (Calcd) (%) C	H	N	Sn	Cl	Mol. Wt. Found (Calcd)
1	$Me_3Sn(C1_5H_{12}N_2O \cdot X)$	87	111	52.13 (53.92)	5.31 (5.48)	6.77 (6.98)	28.55 (29.60)	–	403 (400.86)
2	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	92	127	56.10 (55.00)	5.82 (5.78)	6.71 (6.74)	27.59 (28.60)	–	409 (414.87)
3	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	79	134	42.87 (42.96)	5.37 (5.57)	6.35 (6.49)	26.81 (27.54)	–	433 (430.86)
4	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	84	116	47.78 (49.66)	5.01 (4.82)	6.41 (6.43)	27.31 (27.26)	8.11 (8.14)	437 (435.31)
5	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	91	99	57.99 (59.44)	7.06 (7.01)	5.81 (5.77)	24.12 (24.47)	–	480 (484.92)
6	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	82	133	61.23 (60.17)	7.11 (7.21)	5.56 (5.61)	21.98 (23.78)	–	495 (498.93)
7	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	85	154	60.03 (58.31)	6.87 (6.99)	5.81 (5.77)	24.12 (24.47)	–	516 (514.92)
8	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	94	119	54.26 (55.49)	6.28 (6.35)	5.35 (5.39)	21.17 (22.85)	7.01 (6.82)	514 (519.37)
9	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	77	183	65.29 (67.51)	4.81 (4.76)	4.79 (4.74)	18.76 (20.21)	–	589 (587.01)
10	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	89	171	68.18 (67.94)	4.79 (4.99)	4.58 (4.65)	18.69 (19.74)	–	596 (601.02)
11	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	95	214	67.24 (66.18)	4.77 (4.86)	4.49 (4.53)	18.27 (19.23)	–	620 (617.01)
12	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	86	360	61.95 (63.77)	4.24 (4.34)	4.42 (4.50)	20.10 (19.09)	4.97 (5.70)	618 (621.46)

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

3. Physical measurements

Chlorine was estimated by Volhard's method and tin was determined gravimetrically as tin dioxide [14]. Infrared spectra were recorded as nujol mulls using CsI cells on a Perkin-Elmer Model 557 FT-IR spectrophotometer in the range 4000–200 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 (tetramethyl silane) 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 and TMT (tetramethyl tin) as internal standards, respectively.

Molecular weights were determined on a Knoauer Vapour Pressure osmometer in $CHCl_3$ at 45°C. The elemental analysis (C, H and N) was estimated by using a Coleman CHN analyzer.

3.1. *Antimicrobial studies*

Agar disc diffusion technique was used for the screening of *in vitro* antimicrobial activity [15].

Inoculums of bacteria were prepared in nutrient broth and fungi in potato dextrose agar slant. The molten Muller Hinton medium was poured into a sterile

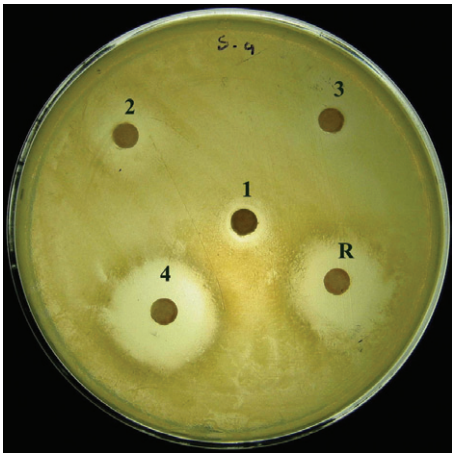

Figure 1. Antibacterial activity against *Staphylococcus aureus*, 1 = free ligand [3(2′-hydroxyphenyl)-5-phenyl pyrazoline], 2 = compound **1**, 3 = compound **5**, 4 = compound **9** and R = tetracycline.

petri dish (9 cm in diameter) to get a depth of 4 mm. The medium was left to solidify. Thereafter, it was seeded with respective test organisms. About 8 mg of each sample to be tested was dissolved in 1 mL of acetone and 5 mm discs of Whatmann filter paper no. 42 were cut and sterilized. The filter paper discs were immersed in a 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 minutes the paper discs were transferred to seeded agar plate. About 5 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 or inhibition zones were detected around each disc (figure 1).

A disc soaked in acetone alone was used as a control under the same conditions and there was no observed inhibition zone for acetone. Each distinct inhibition zone was measured as diameter in mm, both antibacterial and antifungal activity can be calculated as a mean of three replicates.

4. Results and discussion

All the compounds are light yellow to brown solids, non-hygroscopic, stable at room temperature, soluble in common organic (benzene, chloroform, acetone) and coordinating (methanol, tetrahydrofuran, dimethylformamide and dimethylsulphoxide) solvents. The molecular weight measurement in dilute chloroform solution at 45°C shows these compounds as monomers. The elemental analyses (C, H, N, Cl and Sn) are in accord with proposed compounds.

4.1. *Infrared spectra*

The infrared spectral data of these compounds are summarized in table 2. All compounds exhibit bands of medium intensity in the region 3325–3318 cm^{-1} due to

Table 2. IR spectral data (in cm^{-1}) for triorganotin(IV) pyrazolinates.

Sl no.	Compound	ν(N–H)	ν(C=N)	ν(C–O)	ν(Sn–C)	ν(Sn–O)	ν(Sn–N)
1	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	3320	1642	–	546	527	395
2	$Me_3Sn(C1_5H_{12}N_2O \cdot X)$	3321	1644	–	550	531	398
3	$Me_3Sn(C1_5H1_2N_2O \cdot X)$	3323	1641	1012	548	527	397
4	$Me_3Sn(C1_5H1_2N_2O \cdot X)$	3325	1638	–	545	530	398
5	$Pr^n_3Sn(C1_5H1_2N_2O \cdot X)$	3323	1640	–	548	529	396
6	$Pr^n_3Sn(C1_5H_{12}N_2O \cdot X)$	3320	1639	–	546	529	397
7	$Pr^n_3Sn(C1_5H1_2N_2O \cdot X)$	3318	1644	1016	550	527	395
8	$Pr^n_3Sn(C1_5H1_2N_2O \cdot X)$	3323	1641	–	544	530	398
9	$Ph_3Sn(C1_5H1_2N_2O \cdot X)$	3325	1642	–	548	531	399
10	$Ph_3Sn(C1_5H_{12}N_2O \cdot X)$	3323	1640	–	545	533	397
11	$Ph_3Sn(C1_5H1_2N_2O \cdot X)$	3320	1644	1010	550	527	395
12	$Ph_3Sn(C1_5H1_2N_2O \cdot X)$	3322	1638	–	546	527	396

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.

ν(N–H) stretching vibrations and bands in the region 1644–1638 cm^{-1} due to ν(C=N) stretching vibrations [4]. In all compounds the signal due to ν(C=N) stretching is found to be shifted to lower wave number in comparison to the spectra of free pyrazolines (at ~1654 cm^{-1}) suggesting involvement of imino nitrogen in coordination. The band present in the region 1016–1010 cm^{-1} in compounds **3**, **7** and **11** may be assigned to ν(C–O) stretching indicating the presence of $–OCH_3$. The signal due to ν(O–H) (originally present at ~3080 cm^{-1} in ligands) is missing from the spectra of complexes. All compounds exhibit bands of medium intensity in the region 550–545 cm^{-1} due to ν(Sn–C) [16] stretching vibrations.

The presence of new bands (in comparison to ligand) in the region 533–527 and 399–395 cm^{-1} have been assigned to ν(Sn–O) and ν(Sn–N) stretching vibrations, respectively [16, 17]. The appearance of these two new bands and absence of hydroxyl band suggests that the pyrazoline behaves as monobasic bidentate ligand.

4.2. *Multinuclear NMR spectroscopy*

The ^1H NMR chemical shifts of these compounds are listed in table 3. In ^1H NMR spectra, the aromatic protons of triorganotin(IV) pyrazolinates were observed as a complex pattern in the region δ 8.1–6.5 ppm [18]. The peak due to hydroxyl proton (originally present at δ ~ 11.00 ppm in free pyrazolines) is absent from the spectra of complexes suggesting bonding through hydroxyl oxygen. The appearance of a peak at δ 5.2–4.7 ppm as a broad singlet could be assigned to N–H group (originally present at δ 5.4–5.0 ppm in free pyrazolines) suggesting non involvement of N–H in bond formation. The skeletal protons of the five-membered ring are observed at δ 3.7–3.3 ppm as a triplet and at δ 2.6–2.2 ppm as a doublet assigned to CH and CH_2 groups [18] respectively. The $(CH_3)_3Sn$ protons give a sharp singlet at δ 0.9–0.7 ppm with double satellite resonances of relative intensity 4–5% on both sides of the main peak (singlet) due to the coupling of the protons with ^{119}Sn and ^{117}Sn isotopes [19, 20]. The resonances due to $(C_3H_7)_3Sn$ protons are observed in the region δ 2.1–0.6 ppm. The signals due to $(C_6H_5)_3Sn$ overlap with the signals of aromatic protons of ligand at δ 8.1–6.7 ppm as a complex multiplet, therefore aromatic signals could not be assigned individually.

Table 3. ^{1}H NMR data (in δ ppm) for triorganotin(IV) pyrazolinates.

Sl no.	Chemical shift (in δ ppm)		Coupling constants (Hz)	θ (°)
	($C_{15}H_{12}N_2O \cdot X$)	R–Sn		
1	7.7–6.8 (9H, m, Ar–H) 4.7 (1H, s, NH) 3.5(1H, t, CH) 2.3 (2H, d, CH_2)	0.7 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 65$	116
2	7.5–6.6 (9H, m, Ar–H) 4.8 (1H, s, NH) 3.7(1H, t, CH) 2.4 (2H, d, CH_2) 0.9 (3H, s, CH_3)	0.7 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 64$	115
3	7.8–7.0 (9H, m, Ar–H) 5.1 (1H, s, NH) 3.3 (1H, t, CH) 2.5 (2H, d, CH_2) 4.3 (3H, s, OCH_3)	0.8 (CH_3)	$^{2}J(^{119}Sn^{1}H) = 60$	112
4	7.6–6.5 (9H, m, Ar–H) 4.8 (1H, s, NH) 3.5 (1H, t, CH) 2.6 (2H, d, CH_2)	0.7 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 63$	114
5	7.9–6.7 (9H, m, Ar–H) 4.9 (1H, s, NH) 3.5 (1H, t, CH) 2.4 (2H, d, CH_2)	1.l (αCH_2) 1.8 (βCH_2) 0.7 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 61$	113
6	7.7–6.9 (9H, m, Ar–H) 4.7 (1H, s, NH) 3.7 (1H, t, CH) 2.5 (2H, d, CH_2) 1.9–0.6 (3H, s, CH_3)	1.2 (αCH_2) 1.9 (βCH_2) 0.6 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 60$	112
7	7.5–6.7 (9H, m, Ar–H) 5.0 (1H, s, NH) 3.3(1H, t, CH) 2.6 (2H, d, CH_2) 4.1 (3H, s, OCH3)	1.3 (αCH_2) 2.1 (βCH_2) 0.8 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 66$	116
8	7.9–6.8 (9H, m, Ar–H) 4.8 (1H, s, NH) 3.5(1H, t, CH) 2.2 (2H, d, CH_2)	1.0 (αCH_2) 1.9 (βCH_2) 0.7 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 64$	115
9	7.7–6.8 (9H, m, Ar–H) 4.9 (1H, s, NH) 3.5(1H, t, CH) 2.5 (2H, d, CH_2)	7.7–6.8 (m, C_6H_5)		
10	7.9–7.1 (8H, m, Ar–H) 5.1 (1H, s, NH) 3.7 (1H, t, CH) 2.3 (2H, d, CH_2) 0.9 (3H, s, CH_3)	7.9–7.1 (m, C_6H_5)		
11	8.1–7.1 (8H, m, Ar–H) 5.2 (1H, s, NH) 3.3(1H, t, CH) 2.4 (2H, d, CH_2) 4.2 (3H, s, OCH_3)	8.1–7.1 (m, C_6H_5)		
12	7.6–6.7 (8H, m, Ar–H) 4.9 (1H, s, NH) 3.5 (1H, t, CH) 2.2 (2H, d, CH_2)	7.6–6.7 (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 multiplet, s = singlet, d = doublet, t = triplet.

Compounds **1**–**8** show $^{2}J(^{119}Sn,^{1}H)$ values between 62–73 Hz. The values of coupling constants are strongly indicative of five-coordinate structures [19, 21, 22] confirming bidentate behaviour of ligands in these compounds.

The coupling constant $^{2}J(^{119}Sn,^{1}H)$ can be used to calculate the C–Sn–C bond angle, θ. Equation (1) yields the θ value [23]

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

The calculated θ values are between 112–116° for **1**–**8**. These values correspond well to the trigonal bipyramidal geometry [21, 22].

The proton decoupled ^{13}C NMR spectra (table 4) of triorganotin(IV) pyrazolinates show the presence of all important signals. The assignments have been made on the basis of available literature along with the spectra of the free pyrazolines. The signal observed in the region δ 136.1–120.9 ppm as a multiplet could be assigned to aromatic carbon [18]. The signal observed at δ 163.9–162.8 ppm due to imino carbon of C=N group is shifted downfield in comparison to the spectra of free pyrazolines (at δ 143.5–142.8 ppm) suggesting involvement of imino nitrogen in coordination. All other signals were found at their respective positions as in free pyrazolines. The peak observed at δ 9.9–9.5 ppm could be assigned to Me_3Sn group. The signals observed at δ 25.9–25.5, 28.5–28.1 and 12.9–12.6 ppm may be assigned to αC, βC and γC of $Pr^{n}_{3}Sn$ group. The signals due to Ph_3Sn group overlap with the signals of aromatic carbons of ligand at δ 136.1–120.9 ppm as a complex pattern. All eight compounds, **1**–**8**, show $^{1}J(^{119}Sn, ^{13}C)$ values between 416–425 Hz. The values of coupling constants are strongly indicative of five-coordinate tin [21, 22, 24].

The coupling constants $^{1}J(^{119}Sn,^{13}C)$ can also be used to calculate the C–Sn–C bond angle, θ. Equation (2) yields the θ value [23].

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

The calculated θ values are between 113–114° for compounds **1**–**8**. These values also suggest trigonal bipyramidal geometry.

The proton decoupled ^{119}Sn NMR spectra (table 5) of all these compounds exhibit a sharp ^{119}Sn resonance in the region at δ −130.5 to −165.4 ppm. These values are strongly indicative of five-coordinate structures [24–26]. The most plausible geometry around the tin(IV) in these compounds is trigonal bipyramidal (figure 2).

4.3. *Microbial assay*

The antibacterial activity of a free pyrazoline and three triorganotin(IV) pyrazolinates 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 show that triorganotin(IV) pyrazolinates have greater activity towards all tested bacteria than free pyrazoline. The triorganotin(IV)

Table 4. ^{13}C NMR data (in δ ppm) for triorganotin(IV) pyrazolinates.

Sl no.	Chemical shift (in δ ppm)		Coupling constants (Hz)	θ (°)
	($C_{15}H_{12}N_2O \cdot X$)	R–Sn		
1	135.7–127.3 (Ar–C) 163.6 (C=N) 44.8 (CH) 27.4 (CH_2)	9.7 (CH_3)	$^1J(^{119}Sn,^{13}C) = 416$	113
2	134.8–126.5 (Ar–C) 163.3 (C=N) 43.9 (CH) 27.3 (CH_2) 13.5 (CH_3)	9.5 (CH_3)	$^1J(^{119}Sn,^{13}C) = 424$	114
3	134.9–126.1 (Ar–C) 162.8 (C=N) 43.7 (CH) 27.8 (CH_2) 57.7 (OCH_3)	9.9 (CH_3)	$^1J(^{119}Sn,^{13}C) = 421$	114
4	135.3–127.1 (Ar–C) 163.7 (C=N) 44.5 (CH) 27.1 (CH_2)	9.5 (CH_3)	$^1J(^{119}Sn,^{13}C) = 418$	113
5	134.7–126.4 (Ar–C) 162.9 (C=N) 44.6 (CH) 26.8 (CH_2)	25.9 (αC)* 28.1 (βC) 12.8 (γC)	$^1J(^{119}Sn,^{13}C) = 425$ $^2J(^{119}Sn,^{13}C) = 35$ $^3J(^{119}Sn,^{13}C) = 90$	114
6	135.7–126.6 (Ar–C) 163.5 (C=N) 44.8 (CH) 26.2 (CH_2) 13.7 (CH_3)	25.7 (αC)* 28.3 (βC) 12.9 (γC)	$^1J(^{119}Sn,^{13}C) = 422$ $^2J(^{119}Sn,^{13}C) = 32$ $^3J(^{119}Sn,^{13}C) = 87$	114
7	135.4–126.5 (Ar–C) 162.8 (C=N) 44.7 (CH) 26.6 (CH_2) 57.5 (OCH_3)	25.5 (αC)* 28.1 (βC) 12.6 (γC)	$^1J(^{119}Sn,^{13}C) = 421$ $^2J(^{119}Sn,^{13}C) = 34$ $^3J(^{119}Sn,^{13}C) = 91$	114
8	134.9–126.6 (Ar–C) 163.4 (C=N) 44.6 (CH) 26.7 (CH_2)	25.5 (αC)* 28.5 (βC) 12.7 (γC)	$^1J(^{119}Sn,^{13}C) = 418$ $^2J(^{119}Sn,^{13}C) = 33$ $^3J(^{119}Sn,^{13}C) = 88$	113
9	134.7–121.6 (Ar–C) 162.9 (C=N) 43.9 (CH) 26.8 (CH_2)	134.7–121.6 (C_6H_5)		
10	135.2–121.7 (Ar–C) 163.7 (C=N) 44.5 (CH) 26.2 (CH_2) 13.6 (CH_3)	135.2–121.7 (C_6H_5)		
11	135.8–120.9 (Ar–C) 163.9 (C=N) 44.7 (CH) 26.5 (CH_2) 57.1 (OCH_3)	135.8–120.9 (C_6H_5)		
12	136.1–121.3 (Ar–C) 163.6 (C=N) 44.9 (CH) 26.9 (CH_2)	136.1–121.3 (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.
*Sn-αCH_2-βCH_2-γCH_3.

Table 5. ^{119}Sn NMR data (in δ ppm) for triorganotin(IV) pyrazolinates.

Sl. No.	Compound	Chemical shift (in δ ppm)
1	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	−153.9
2	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	−161.3
3	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	−157.4
4	$Me_3Sn(C_{15}H_{12}N_2O \cdot X)$	−155.8
5	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	−160.7
6	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	−165.4
7	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	−159.8
8	$Pr^n_3Sn(C_{15}H_{12}N_2O \cdot X)$	−157.3
9	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	−130.5
10	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	−138.6
11	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	−153.7
12	$Ph_3Sn(C_{15}H_{12}N_2O \cdot X)$	−141.5

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.

pyrazolinates also exhibit greater antifungal activity towards all tested fungi than free pyrazoline (figure 1).

Nevertheless, it is difficult to make an exact structure and activity relationship between antimicrobial activity and the structure of these complexes. Complexation of biologically active triorganotin with biologically active pyrazoline ligand results in increased activity of the complexes.

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

(a) The triorganotin(IV) pyrazolinates exhibit a comparable antibacterial effect towards *S. aureus* compared to free pyrazoline and chloramphenicol.
(b) The triorganotin(IV) complexes exhibit a greater antibacterial effect towards *C. freundii* compared to free pyrazoline and chloramphenicol.
(c) The triorganotin(IV) complexes exhibit a comparable effect towards *B. subtilis* and *A. faecalis* compared to free pyrazoline and chloramphenicol.
(d) The triorganotin(IV) complexes exhibit a greater antifungal effect towards *A. niger* compared to free pyrazoline and terbinafin.

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

5. Conclusions

The present study describes the series of triorganotin(IV) pyrazolinates. It is quite difficult to comment on the molecular structure of these compounds in solid state without an X-ray crystal structure analysis of at least one products. In a number of tin(IV) complexes the structures have been described as trigonal bipyramidal for coordination number five [24–26]. The bidentate behaviour of the pyrazoline ligands in these compounds has been confirmed by IR, ^{1}H NMR and ^{13}C NMR data. The ^{1}H NMR, ^{13}C NMR and ^{119}Sn NMR data suggest the five-coordinate, trigonal bipyramidal geometry around the tin in all compounds.

Table 6. Antimicrobial activity of the free pyrazoline and triorgnotin(IV) pyrazolinates.

Compd No.	Fungi		Gram (+ve) bacteria		Gram (−ve) bacteria							
	A. niger	*P. notatum*	*S. aureus*	*B. subtilis*	*C. freundi*	*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, and − = not active (the values are including disc diameter); L = 3(2′-hydroxyphenyl)-5-phenyl pyrazoline, **1** = compound **1**, **5** = compound **5**, **9** = compound **9**.

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

[b]R = Terbinafin (antifungal agent) and chloramphenicol (antibacterial agent).

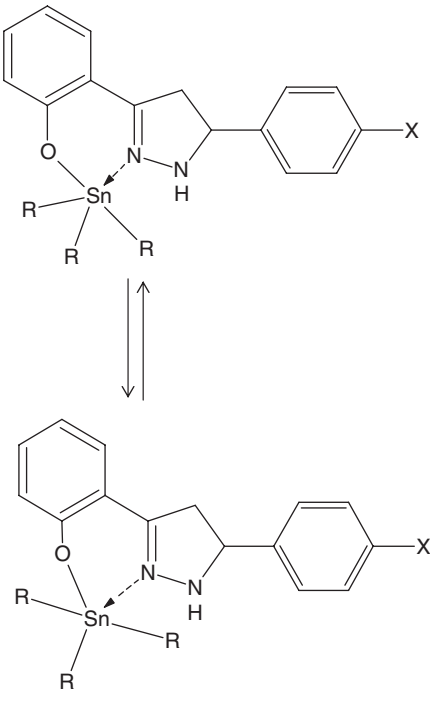

Figure 2. Molecular structure of $R_3Sn(C_{15}H_{12}N_2O \cdot X)$ (where R = Me, Pr^n, Ph; X = –H, $–CH_3$, $–OCH_3$ and –Cl).

The tin compounds exhibit higher antibacterial and antifungal effects than free pyrazoline and the antibiotic chloramphenicol and antifungal agent terbinafin.

Acknowledgements

The authors are thankful to RSIC, CDRI, Lucknow (India); RRL, Jammu (India); Punjab University, Chandigarh (India) and IISc, Bangalore (India) for providing the necessary spectral and analytical data.

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