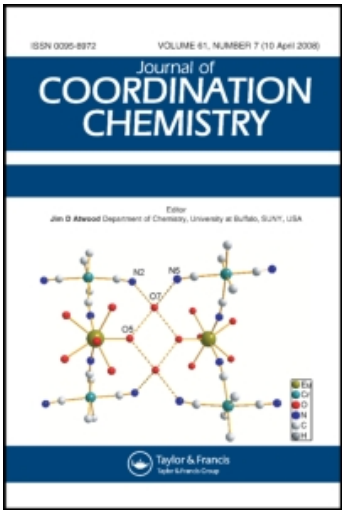

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectral and antimicrobial studies of chlorodiorganotin(IV)[3(2'-hydroxyphenyl)-5-(4-substitutedphenyl) pyrazolinates]

U. N. Tripathi[a]; Mohd. Safi Ahmad[b]; G. Venubabu[b]; P. Ramakrishna[c]
[a] Department of Chemistry, D.D.U. Gorkhpur University, Gorakhpur, UP, India [b] School of Studies in Chemistry, Vikram University, Ujjain, MP, India [c] IEMPS, Vikram University, Ujjain, MP, India

To cite this Article Tripathi, U. N. , Ahmad, Mohd. Safi , Venubabu, G. and Ramakrishna, P.(2007) 'Synthesis, spectral and antimicrobial studies of chlorodiorganotin(IV)[3(2'-hydroxyphenyl)-5-(4-substitutedphenyl) pyrazolinates]', Journal of Coordination Chemistry, 60: 16, 1777 — 1788
To link to this Article: DOI: 10.1080/00958970601183391
URL: http://dx.doi.org/10.1080/00958970601183391

Journal of Coordination Chemistry
Vol. 60, No. 16, 15 August 2007, 1777–1788

Taylor & Francis
Taylor & Francis Group

Synthesis, spectral and antimicrobial studies of chlorodiorganotin(IV)[3(2′-hydroxyphenyl)-5-(4-substitutedphenyl) pyrazolinates]

U. N. TRIPATHI*†, MOHD. SAFI AHMAD‡,
G. VENUBABU‡ and P. RAMAKRISHNA§

†Department of Chemistry, D.D.U. Gorkhpur University, Gorakhpur, 273 001, UP, India
‡School of Studies in Chemistry, Vikram University, Ujjain, 456 010, MP, India
§IEMPS, Vikram University, Ujjain, 456 010, MP, India

(*Received 18 March 2006; revised 14 June 2006; in final form 15 June 2006*)

Chlorodiorganotin(IV)pyrazolinates of the type $R_2SnCl(C_{15}H_{12}N_2O \cdot X)$ [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 reaction of R_2SnCl_2 with the sodium salt of pyrazolines in 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 and spectral studies [IR and multinuclear NMR (^1H, ^{13}C and ^{119}Sn)]. The bidentate behavior of the ligands was confirmed by IR, ^1H and ^{13}C NMR spectral data. Trigonal bipyramidal structure around tin(IV) for $R_2SnCl(C_{15}H_{12}N_2O \cdot X)$ is suggested. The free pyrazoline and some chlorodiorganotin(IV) pyrazolinates have been screened for their antibacterial and antifungal activities. Some chlorodiorganotin(IV) pyrazolinates exhibit higher antibacterial and antifungal effect than free pyrazoline and some 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 behavior 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) and 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

*Corresponding author. Email: un_tripathi@yahoo.com

ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970601183391

agents against different types of Oedema in mice is of fundamental interest [8]. Tabarelli *et al*. have recently published a study of antinociceptive action [9] of a new series of pyrazolines.

In continuation of our work, we examine the complexation 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]. We have also studied 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 tin(IV) pyrazolinates exhibit higher antineurotoxic effects in brain cells of *Swiss albino mice*. In the present article we describe the synthesis, spectral characterization and antimicrobial studies of chlorodiorganotin(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 [11]. All the chemicals used were of analytical grade. Dimethyltin dichloride (E. Merck), *n*-dipropyltin dichloride (E. Merck) and diphenyltin dichloride (Lancaster) were used as received. *O*-hydroxy acetophenone (CDH) and benzaldehydes (s.d.fine) were used as received.

2.1. *Synthesis of $R_2SnCl(C_{15}H_{12}N_2O \cdot X)$*

Ligands were prepared by reported procedure [12]. The new chlorodiorganotin(IV) pyrazolinates of the general formula $R_2SnCl(C_{15}H_{12}N_2O \cdot X)$ were prepared by the following route:

$$R_2SnCl_2 + Na(C_{15}H_{12}N_2O \cdot X) \xrightarrow{\text{Benzene}} R_2SnCl(C_{15}H_{12}N_2O \cdot X) + NaCl$$

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

2.1.1. $Pr^n_2SnCl(C_{15}H_{13}N_2O)$. 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. The 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 solution. The reaction mixture was cooled to room temperature and then a benzene solution of $Pr^n_2SnCl_2$ (1.33 g; 4.83 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for 6 h, till the color of the reaction mixture changed. Reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate. The brown colored solid thus obtained was reprecipitated from benzene and dried in vacuum.

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

Table 1. Synthetic and analytical data for $R_2SnCl(C_{15}H_{12}N_2O \cdot X)$.[a]

Compd No.	Compound	Yield (%)	M.p. (°C)	Analysis Found (Calcd) (in%) C	H	N	Sn	Cl	Mol. wt. Found (Calcd)
1	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	91	142	47.51 (48.46)	4.35 (4.50)	6.57 (6.64)	27.38 (28.19)	8.34 (8.41)	419 (421.30)
2	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	86	168	48.23 (49.66)	4.71 (4.82)	6.51 (6.43)	26.54 (27.26)	8.05 (8.14)	431 (435.31)
3	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	81	161	48.16 (47.90)	4.75 (3.65)	6.16 (6.20)	25.49 (26.29)	7.76 (7.85)	449 (451.30)
4	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	84	174	43.86 (44.79)	3.85 (3.94)	6.05 (6.14)	26.16 (26.04)	14.62 (15.55)	457 (455.75)
5	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	79	99	51.72 (52.61)	5.74 (5.65)	5.79 (5.84)	23.47 (24.76)	7.24 (7.39)	469 (477.34)
6	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	90	128	52.64 (53.77)	5.79 (5.90)	5.54 (5.69)	23.65 (24.15)	7.28 (7.21)	487 (491.35)
7	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	85	111	54.11 (52.07)	5.68 (5.71)	5.63 (5.51)	22.58 (23.39)	6.84 (6.98)	510 (507.34)
8	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	91	137	47.78 (49.27)	5.12 (5.08)	5.49 (5.47)	23.42 (23.19)	13.66 (13.85)	507 (511.79)
9	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	88	194	60.12 (59.45)	4.16 (4.21)	4.49 (5.13)	21.45 (21.76)	6.35 (6.49)	543 (545.40)
10	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	84	226	58.76 (60.11)	4.38 (4.46)	5.12 (5.00)	20.12 (21.21)	6.27 (6.33)	560 (559.41)
11	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	80	179	59.31 (58.44)	4.38 (4.34)	4.78 (4.86)	20.85 (20.62)	6.21 (6.16)	571 (575.40)
12	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	78	191	54.85 (55.92)	3.83 (3.79)	4.76 (4.82)	19.73 (20.46)	12.43 (12.22)	574 (579.85)

[a]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**.

3. Physical measurements

Chlorine was estimated by Volhard's method and tin was determined gravimetrically as tin dioxide [13]. 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 (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 (tetramethylsilane) and TMT (tetramethyltin) as internal standards. Molecular weights were determined on a Knoauer Vapour Pressure osmometer in $CHCl_3$ at 45°C. The elemental analysis (C, H and N) was obtained by using a Coleman CHN analyzer.

3.1. *Antimicrobial studies*

Agar disk diffusion technique was used for the screening of *in vitro* antimicrobial activity [14].

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

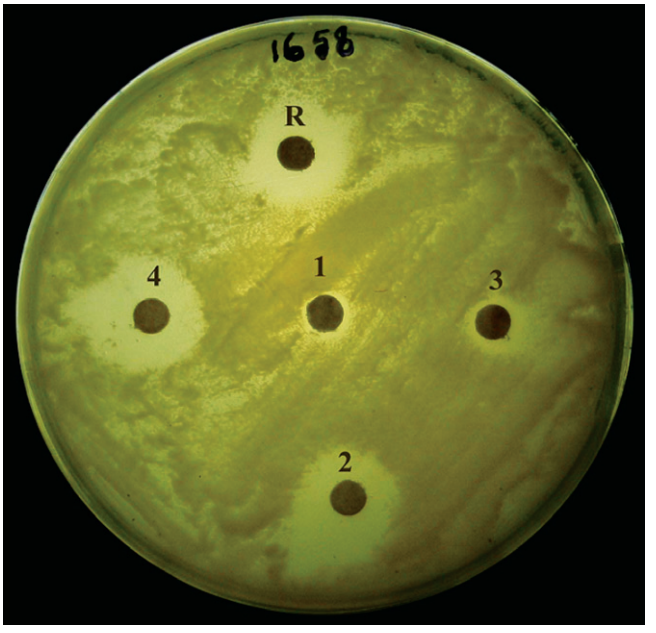

Figure 1. Antibacterial activity against *Citrobacter freundii*, 1 = free pyrazoline [3(2′-Hydroxyphenyl)-5-phenyl pyrazoline], 2 = compound **1**, 3 = compound **5**, 4 = compound **9** and R = chloramphenicol.

Petri dish (9 cm in diameter) to get a depth of 4 mm. The medium was left to solidify. After it was seeded with respective test organisms. 8 mg of each sample to be tested was dissolved in 1 mL of acetone. Disks of Whatmann filter article no. 42 (5 mm) were cut and sterilized. The filter paper disks were immersed in solution of sample. After soaking the paper was removed and left in a sterile Petri dish to permit the solvent to evaporate. After about 10 min the article disks were transferred to a seeded agar plate. 5 disks 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 inhibition zones were detected around each disk (figure 1).

A disk soaked in acetone alone was used as a control under the same conditions and no inhibition zone was observed. 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 compounds are light yellow to brown colored solids, non-hygroscopic and 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 at 45°C shows monomeric nature of these compounds. The elemental analysis (C, H, N, Cl, and Sn) data agrees with stoichiometry proposed for the 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 3319–3311 cm^{-1} due to ν(N–H) stretching vibrations and bands in the region 1645–1638 cm^{-1} due to ν(C=N) stretching vibrations [4]. The band in the region 1016–1014 cm^{-1} in **3**, **7** and **11** may be assigned to ν(C–O) stretching indicating the presence –OCH_3. 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 540–280 cm^{-1} and 298–291 cm^{-1} due to ν(Sn–C) [15] and ν(Sn–Cl) [16] stretching vibrations, respectively.

The presence of new bands (in comparison to free pyrazolines) in the region 499–487 and 396–393 cm^{-1} has been assigned to ν(Sn–O) and ν(Sn–N) stretching vibrations, respectively [15, 17]. The appearance of these two new bands and missing of hydroxyl band suggests that the pyrazoline is a monobasic bidentate ligand.

4.2. *Multinuclear NMR spectroscopy*

The ^{1}H NMR chemical shifts of these compounds are listed in table 3. The aromatic protons of chlorodiorganotin(IV) pyrazolinates were observed as a complex pattern in the region δ 8.3–6.7 ppm [18]. The peak due to hydroxyl proton (originally present at $\delta \sim 11.00$ ppm in free pyrazolines) is absent from the spectra of complexes suggesting 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 N–H group (originally present at δ 5.4–5.0 ppm in free pyrazolines) suggesting the non involvement of N–H group in coordination. The skeletal protons of the five-membered ring are observed at δ 3.7–3.3 ppm as a triplet and at δ 2.5–1.9 ppm as a doublet, assigned to CH and CH_2 groups [18], respectively. 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 [19, 20]. The resonances due to propyl tin protons are observed in the region δ 2.0–0.6 ppm. The signals due to C_6H_5Sn overlap

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

Sl. No.	Compound	ν(N–H)	ν(C=N)	ν(C–O)	ν(Sn–C)	ν(Sn–O)	ν(Sn–N)	ν(Sn–Cl)
1	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3319	1638	–	539	497	393	298
2	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3313	1638	–	536	499	396	294
3	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3317	1642	1016	537	499	395	293
4	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3317	1640	–	540	496	394	295
5	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3311	1645	–	538	494	393	291
6	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3315	1641	–	536	497	396	294
7	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3313	1640	1014	536	498	395	293
8	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3317	1638	–	539	495	394	296
9	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3313	1640	–	280	490	394	293
10	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3315	1638	–	283	487	393	291
11	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3312	1642	1015	284	488	396	296
12	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	3317	1645	–	286	491	395	295

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**.

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

Sl. No.	Chemical shift (in δ ppm)		Coupling Constants (in Hz)[b]	θ (in °)
	$(C_{15}H_{12}N_2O \cdot X)$[a]	R–Sn		
1	7.7–6.9 (9H, m, Ar–H) 5.5 (1H, s, NH) 3.3 (1H, t, CH) 2.0 (2H, d, CH_2)	0.8 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 68$	118.1
2	7.9–7.0 (8H, m, Ar–H) 5.1 (1H, s, NH) 3.5 (1H, t, CH) 2.3 (2H, d, CH_2) 1.3 (CH_3)	0.9 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 70$	119.9
3	7.8–6.9 (8H, m, Ar–H) 5.3 (1H, s, NH) 3.7 (1H, t, CH) 2.1 (2H, d, CH_2) 4.2 (3H, s, OCH_3)	0.8 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 71$	120.8
4	7.7–6.7 (8H, m, Ar–H) 5.4 (1H, s, NH) 3.6 (1H, t, CH) 2.2 (2H, d, CH_2)	0.7 (CH_3)	$^{2}J(^{119}Sn,^{1}H) = 66$	116.4
5	7.8–6.8 (9H, m, Ar–H) 5.5 (1H, s, NH) 3.3 (1H, t, CH) 2.4 (2H, d, CH_2)	1.2 (αCH_2) 1.8 (βCH_2) 0.7 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 72$	121.8
6	7.9–6.9 (8H, m, Ar–H) 5.3 (1H, s, NH) 3.7 (1H, t, CH) 2.3 (2H, d, CH_2) 0.9 (CH_3)	1.1 (αCH_2) 1.9 (βCH_2) 0.7 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 74$	123.9
7	7.5–6.7 (8H, m, Ar–H) 5.1 (1H, s, NH) 3.5 (1H, t, CH) 2.5 (2H, d, CH_2) 4.1 (3H, s, OCH_3)	1.4 (αCH_2) 2.0 (βCH_2) 0.6 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 64$	116.1
8	7.7–6.7 (8H, m, Ar–H) 5.4 (1H, s, NH) 3.7 (1H, t, CH) 2.4 (2H, d, CH_2)	1.3 (αCH_2) 1.8 (βCH_2) 0.6 (γCH_3)	$^{2}J(^{119}Sn,^{1}H) = 71$	120.8
9	7.9–7.1 (9H, m, Ar–H) 5.3 (1H, s, NH) 3.6 (1H, t, CH) 2.0 (2H, d, CH_2)	7.9–7.1 (m, C_6H_5)		
10	8.1–7.3 (8H, m, Ar–H) 5.3 (1H, s, NH) 3.3 (1H, t, CH) 1.9 (2H, d, CH_2) 0.8 (CH_3)	8.1–7.3 (m, C_6H_5)		
11	8.3–7.5 (8H, m, Ar–H) 5.5 (1H, s, NH) 3.7 (1H, t, CH) 2.1 (2H, d, CH_2) 4.3 (3H, s, OCH_3)	8.3–7.5 (m, C_6H_5)		
12	7.9–6.8 (8H, m, Ar–H) 5.1 (1H, s, NH) 3.5 (1H, t, CH) 2.3 (2H, d, CH_2)	7.9–6.8 (m, C_6H_5)		

[a]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**;
[b]m = complex multiplet, s = singlet, d = doublet, t = triplet.

with the signals of aromatic protons of ligand (δ 8.3–6.7 ppm) and could not be assigned individually. Compounds **1–8** show $^{2}J(^{119}\text{Sn}, ^{1}\text{H})$ values between 62–74 Hz. The values of coupling constants are strongly indicative of five-coordinate structures [19, 21, 22], confirming the bidentate behavior of ligands in these compounds.

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

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

The calculated θ values are between 116.1–123.9^{0} for compounds **1–8** and correspond well to the trigonal bipyramidal geometry [21, 22] with equatorial alkyl groups.

The proton decoupled ^{13}C NMR spectra (table 4) of chlorodiorganotin(IV) pyrazolinates show the presence of all important signals of free pyrazolines. Assignments have been made on the basis of available literature and spectra of the free pyrazolines. The signal observed in the region δ 137.3–121.5 ppm as a multiplet could be assigned to aromatic carbons [18]. The signal observed at δ 164.1–162.7 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 the involvement of imino nitrogen in coordination. All other signals were found at their respective positions as in free pyrazolines. The peak observed at δ 10.1–9.7 ppm could be assigned to MeSn. Signals at δ 26.3–25.9 ppm, 28.5–28.3 ppm and 12.9–12.7 ppm may be assigned to αC, βC and γC of Pr^{n}Sn.

The signals due to PhSn overlap with the signals of aromatic carbons of the ligand at δ 137.3–121.5 ppm as a complex pattern. Compounds **1–8** show $^{1}J(^{119}\text{Sn}, ^{13}\text{C})$ values between 562–624 Hz. The coupling constants are strongly indicative of five-coordinate tin [21, 22, 24].

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

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

The calculated θ values are 126.1–131.4° for compounds **1–8** suggesting trigonal bipyramidal geometry with equatorial alkyl groups.

The proton decoupled ^{119}Sn NMR spectra (table 5) of all compounds exhibit a sharp ^{119}Sn resonance in the region at δ −113.7 to −149.9 ppm. These values are also strongly indicative of five-coordinate structures [24–26]. The most plausible geometry around tin(IV) in these compounds is trigonal bipyramidal (figure 2).

4.3. *Microbial assay*

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

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

Sl. No.	Chemical shift (in δ ppm)[a]		Coupling Constants (in Hz)	θ (in °)
	($C_{15}H_{12}N_2O \cdot X$)	R–Sn		
1	135.7–123.5 (Ar–C) 43.5 (CH) 27.9 (CH_2)	9.9 (CH_3)	$^1J(^{119}Sn,^{13}C) = 564$	126.2
2	135.9–122.9 (Ar–C) 162.9 (C=N) 43.7 (CH) 27.3 (CH_2) 13.9 (CH_3)	9.8 (CH_3)	$^1J(^{119}Sn,^{13}C) = 568$	126.6
3	136.1–123.8 (Ar–C) 162.7 (C=N) 43.3 (CH) 27.7 (CH_2) 57.8 (OCH_3)	10.1 (CH_3)	$^1J(^{119}Sn,^{13}C) = 562$	126.1
4	135.7–123.8 (Ar–C) 163.8 (C=N) 43.8 (CH) 27.5 (CH_2)	9.7 (CH_3)	$^1J(^{119}Sn,^{13}C) = 570$	126.8
5	135.5–123.1 (Ar–C) 162.9 (C=N) 43.5 (CH) 27.4 (CH_2)	26.1 (αC)[b] 28.5 (βC) 12.9 (γC)	$^1J(^{119}Sn,^{13}C) = 618$ $^2J(^{119}Sn,^{13}C) = 34$ $^3J(^{119}Sn,^{13}C) = 95$	130.9
6	136.1–123.9 (Ar–C) 163.7 (C=N) 43.9 (CH) 27.5 (CH_2) 13.7 (CH_3)	26.2 (αC) 28.3 (βC) 12.8 (γC)	$^1J(^{119}Sn,^{13}C) = 621$ $^2J(^{119}Sn,^{13}C) = 33$ $^3J(^{119}Sn,^{13}C) = 93$	131.2
7	134.9–122.7 (Ar–C) 163.5 (C=N) 42.8 (CH) 27.7 (CH_2) 57.9 (OCH_3)	26.3 (αC) 28.5 (βC) 12.7 (γC)	$^1J(^{119}Sn,^{13}C) = 614$ $^2J(^{119}Sn,^{13}C) = 34$ $^3J(^{119}Sn,^{13}C) = 91$	130.6
8	135.3–124.1 (Ar–C) 164.1 (C=N) 43.3 (CH) 27.7 (CH_2)	25.9 (αC) 28.3 (βC) 12.9 (γC)	$^1J(^{119}Sn,^{13}C) = 624$ $^2J(^{119}Sn,^{13}C) = 32$ $^3J(^{119}Sn,^{13}C) = 94$	131.4
9	135.6–122.7 (Ar–C) 163.8 (C=N) 43.8 (CH) 27.4 (CH_2)	135.6–122.7 (C_6H_5)		
10	137.3–123.9 (Ar–C) 163.3 (C=N) 43.5 (CH) 27.3 (CH_2) 13.8 (CH_3)	137.3–123.9 (C_6H_5)		
11	136.7–121.5 (Ar–C) 162.9 (C=N) 43.7 (CH) 27.5 (CH_2) 57.7 (OCH_3)	136.7–121.5 (C_6H_5)		
12	136.9–122.3 (Ar–C) 163.9 (C=N) 43.8 (CH) 27.9 (CH_2)	136.9–122.3 (C_6H_5)		

[a]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**.
[b]Sn-αCH_2-βCH_2-γCH_3.

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

Sl. No.	Compound[a]	Chemical shift (in δ ppm)
1	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−137.5
2	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−135.2
3	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−133.3
4	$Me_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−138.4
5	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−148.5
6	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−145.7
7	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−149.9
8	$Pr^n_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−143.6
9	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−129.3
10	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−122.9
11	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−130.3
12	$Ph_2SnCl(C_{15}H_{12}N_2O \cdot X)$	−113.7

[a]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**.

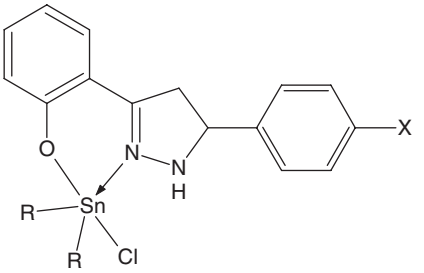

Figure 2. Molecular structure of $R_2SnCl(C_{15}H_{12}N_2O \cdot X)$ (where R = Me, Pr^n, Ph; X = –H, $–CH_3$, $–OCH_3$ and –Cl).

pyrazolinates also exhibited greater antifungal activity towards all tested fungi than the 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 diorganotin with biologically active pyrazoline ligand results in increased activity.

Comparison of the antimicrobial activities of the free pyrazoline and chlorodiorganotin(IV) pyrazolinates with some known antibiotics show:

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

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

Compd	Fungi		Gram (+ve) bacteria		Gram (−ve) bacteria							
No. spp.	*A. niger*	*P. notatum*	*S. aureus*	*B. subtilis*	*C. freundii*	*A. faecalis*	*E. coli*	*K. pneumoniae*	*P. aeruginosa*	*S. typhi*	*P. vulgaris*	*Serratia*
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 are including disk.diameter); **L** = 3(2′-Hydroxyphenyl)-5-phenyl pyrazoline.
[a]The standards are in the form of sterile Hi-Disk cartridges, each disk containing 10 μg of the drug.
[b]R = Terbinafin (antifungal agent) and chloramphenicol (antibacterial agent).

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

5. Conclusions

The present study describes a series of chlorodiorganotin(IV) pyrazolinates. Although it is quite difficult to comment on the molecular structure of these compounds without X-ray crystal structure analysis, a number of tin(IV) structures have been described as trigonal bipyramidal for five coordination [24–26]. Bidentate behavior 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 five-coordinate, trigonal bipyramidal geometry around the tin atom in all compounds.

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

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.

References

[1] J.R. Shah, N.R. Shah. *Ind. J. Chem. A*, **21**, 312 (1982).
[2] J.R. Shah, S.K. Das, R.P. Patel. *J. Indian Chem. Soc*., **50**, 228 (1973).
[3] N.R. Shah, J.R. Shah. *J. Inorg. Nucl. Chem*., **43**, 1583 (1981).
[4] U.N. Tripathi, K.V. Sharma, A. Chaturvedi, T.C. Sharma. *Polish J. Chem*., **77**, 109 (2003).
[5] D.K. Demertzi, P. Tauridou, A. Moukarika, J.M. Tsangaris, C.P. Raptopoulou, A. Tetris. *J. Chem. Soc. Dalton Trans*., **1**, 123 (1995).
[6] M. Kemmer, M. Gielen, M. Biesemans, D. de Vos, R. Willem. *Metal-Based Drugs*, **5**, 189 (1998).
[7] M. Kemmer, L. Ghys, M. Gielen, M. Biesemans, E.R.T. Tiekink, R. Willem. *J. Organomet. Chem*., **582**, 195 (1999).
[8] L. Pellerito, L. Nagy. *Coord. Chem. Rev*., **224**, 111 (2002).
[9] Z. Tabarelli, M.A. Rubin, D.B. Berlese, P.D. Sauzem, T.P. Missio, M.V. Teixeira, A.P. Sinhorin, M.A.P. Martins, N. Zanatta, H.G. Bonacorso, C.F. Mello. *Brazilian J. Med. Bio. Res*., **37**, 1531 (2004).
[10] U.N. Tripathi, G.Venubabu, Mohd. Safi Ahmad, S.S. Rao Kolisetty, A.K. Srivastava. *Appl. Organomet. Chem*., **20**, 669 (2006).
[11] A.I. Vogel. *A Text Book of Quantitative Organic Analysis*, ELBS and Longman, London (1978).
[12] T.C. Sharma, V. Saxena, N.J. Reddy. *Acta Chim*., **93**, 415 (1977).
[13] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, ELBS andLongman, London (1985).
[14] J.H. Benson. *Microbiological Applications (A Laboratory Manual in General Microbiology)*, 5th Edn, p. 459, Wm. C. Brown Publication, Oxford (1990).
[15] X. Song, Q. Xie, X. Fang. *Heteroatom Chem*., **13**, 592 (2002).
[16] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York (1997).
[17] A. Saxena, J.P. Tandon. *Polyhedron*, **3**, 681 (1984).

[18] R.M. Silverstein, F.X. Webster. *Spectrometric Identification of Organic Compounds*, 6th Edn, p. 228, John Wiley & Sons Inc., New York (1998), 232.
[19] H.P.S. Chauhan, A. Bhargava, R.J. Rao. *Indian J. Chem.*, **32**–**A**, 157 (1993).
[20] R.J. Rao, G. Srivastava, R.C. Mehrotra. *J. Organomet. Chem.*, **258**, 155 (1983).
[21] A. Pellerito, T. Fiore, A.M. Giuliani, F. Maggio, L. Pellerito, C. Mansueto. *Appl. Organomet. Chem.*, **11**, 707 (1997).
[22] S. Lencioni, A. Pellerito, T. Fiore, A.M. Giuliani, L. Pellerito, M.T. Cambria, C. Mansueto. *Appl. Organomet. Chem.*, **13**, 145 (1999).
[23] T.P. Lockhart, W.F. Manders. *Inorg. Chem.*, **25**, 892 (1986).
[24] M.S. Singh, K. Tawade. *Indian J. Chem. A*, **41**, 419 (2002).
[25] W. Rehman, M.K. Baloch, A. Badshah. *Braz. Chem. Soc.*, **16**(4), 827 (2005).
[26] N. Bertazzi, G. Bruschetta, G. Casella, L. Pellerito, E. Rotondo, M. Scopelliti. *Appl. Organomet. Chem.*, **17**, 932 (2003).