

1-1-2007

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TRIPATHI, UMESH NATH; AHMAD, MOHAMMAD SAFI; and VENUBABU, GORIPARTHI (2007) "Synthesis and Spectral Characterisation of Chloro Organotin(IV) di[3(2'-hydroxyphenyl)-5-(4-substituted phenyl) Pyrazolines]," *Turkish Journal of Chemistry*. Vol. 31: No. 1, Article 6. Available at: <https://journals.tubitak.gov.tr/chem/vol31/iss1/6>

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Synthesis and Spectral Characterisation of Chloro Organotin(IV) di[3(2'-hydroxyphenyl)-5-(4-substituted phenyl) Pyrazolines]

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Received 20.09.2006

Chloro organotin(IV) dipyrazolines of the type $R\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2$ [where $\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX} = 3(2'$ -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}] were synthesised by the reaction of RSnCl_3 with sodium salt of pyrazolines in 1:2 molar ratio, in anhydrous benzene. These newly synthesised derivatives were characterised by elemental analysis (C, H, N, Cl and Sn), molecular weight measurement and 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. An octahedral structure around the tin(IV) atom for $\text{RSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2$ is suggested.

Key Words: Organotin(IV), pyrazolines, Sn NMR.

Introduction

The development of a clean procedure for the preparation of heterocyclic compounds is a major challenge in modern heterocyclic chemistry in view of the environmental, practical and economic issues. Pyrazolines are an important class of heterocyclic compounds. They are used industrially as dyes, lubricating oils and antioxidants, and in agriculture as catalysts for decarboxylation reactions as well as inhibitors for plant growth.¹⁻³ The complexation behaviour of 3(2'-hydroxy phenyl)-5-phenylpyrazoline with Ni(II), Co(II) and Cu(II) was investigated in our laboratories.⁴ A perusal of the literature shows nothing about pyrazoline derivatives of tin(IV) or 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

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Tabarelli et al. published a study of the antinociceptive action⁷ of a new series of pyrazolines. Chauhan et al. reported antibacterial and antifungal activities of mixed sulphur 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 a 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 synthesis, spectral characterisation and antimicrobial activity of diorganotin(IV) dipyrazolines.^{11,12} We have also studied the tin(IV) pyrazolines of the type $L\text{SnCl}_3$ and $L_2\text{SnCl}_2$ [where $L = 3(2'\text{-Hydroxyphenyl})\text{-}5(4\text{-X-phenyl})\text{pyrazoline}$ {where $X = \text{H}$ (**a**); CH_3 (**b**); OCH_3 (**c**); Cl (**d**)}. The free ligand and some of the tin(IV) pyrazolines exhibited higher antineurotoxic effects in the brain cells of Swiss albino mice. In the present paper, we describe the results of the synthesis and spectral characterisation of chloro organotin(IV) di[3(2'-hydroxyphenyl)-5-(4-substituted phenyl) pyrazolines].

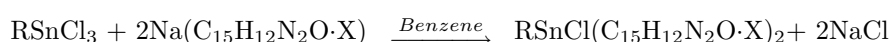
Experimental

Solvents (benzene, acetone and alcohols) were rigorously dried and purified before use by standard methods.¹³ All the chemicals used were of analytical grade. Methyltin trichloride (E. Merck), n-propyltin trichloride (E. Merck) and phenyltin trichloride (Lancaster) were used as received. O-hydroxy acetophenone (CDH) and benzaldehydes (s.d. fine) were used as received.

Synthesis of the $\text{R}\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$

Ligands were prepared as described previously.¹⁴ The new chloro-organotin(IV)

dipyrazolines of the general formula $\text{R}\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$ were prepared by the following route:



[where $\text{R} = \text{Me}, \text{Pr}^n, \text{Ph}$; $\text{X} = \text{H}, -\text{CH}_3, -\text{OCH}_3$ and $-\text{Cl}$]

$\text{Me}\text{SnCl}(\text{C}_{16}\text{H}_{15}\text{N}_2\text{O})_2$: Freshly cut pieces of sodium (0.222 g; 9.66 mmol) were placed in a flask with excess isopropanol and refluxed (approximately 30 min), until a clear solution of sodium isopropoxide was obtained. The benzene solution of 3(2'-Hydroxyphenyl)-5(4-methyl-phenyl) pyrazoline (2.43 g; 9.66 mmol) was then added and the reaction mixture was further refluxed for 1 h, whereby a constant yellow colour was obtained. The reaction mixture was cooled to room temperature and then benzene solution of MeSnCl_3 (1.15 g; 4.83 mmol) was added with constant stirring. The reaction mixture was further stirred at room temperature for 6 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 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.

Physical measurements

Chlorine was estimated by Volhard's method and tin was determined gravimetrically as tin dioxide.¹⁵ 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 (tetramethyl silane) and TMT (tetramethyl tin) as internal standards, respectively. Molecular weights were determined on a Knoauer Vapour Pressure osmometer in CHCl_3 at 45 $^\circ\text{C}$. The elemental analysis (C, H and N) was estimated by Coleman CHN analyser.

Results and discussion

All the compounds are light yellow to brown solids, non-hygroscopic and stable at room temperature. These are 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 $^\circ\text{C}$ shows the monomeric nature of these compounds. The elemental analysis (C, H, N, Cl, and Sn) data are in accordance with the stoichiometry proposed for respective compounds.

Infrared spectra

Infrared spectral data of these compounds are summarized in Table 2. All compounds exhibit bands of medium intensity in the region 3324-3318 cm^{-1} due to $\nu(\text{N-H})$ stretching vibrations and bands in the region 1626-1620 cm^{-1} due to $\nu(\text{C=N})$ stretching vibrations.⁴ The band present in the region 1014-1008 cm^{-1} in **3**, **7** and **11** may be assigned to $\nu(\text{C-O})$ stretching, indicating the presence of an $-\text{OCH}_3$ group. The signal due to $\nu(\text{O-H})$ (originally present at $\sim 3080 \text{ cm}^{-1}$ in free pyrazolines) is completely missing from the spectra of complexes. All compounds exhibit bands of medium intensity in the region 542-280 cm^{-1} and 297-293 cm^{-1} due to $\nu(\text{Sn-C})$ ¹⁶ and $\nu(\text{Sn-Cl})$ ¹⁷ stretching vibrations, respectively.

The presence of new bands (in comparison to free pyrazolines) in the region 498-487 and 399-395 cm^{-1} has been assigned to $\nu(\text{Sn-O})$ and $\nu(\text{Sn-N})$ stretching vibrations, respectively^{16,18}. The appearance of these 2 new bands and absence of a hydroxyl band suggest that the pyrazoline behaves as a monobasic bidentate ligand.

Multinuclear NMR spectroscopy

The ^1H NMR chemical shifts of these compounds are listed in Table 3. In the ^1H NMR spectra, the aromatic protons of chloro organotin(IV) dipyrazolates were observed as a complex pattern in the region δ 8.1-6.5 ppm.¹⁹ The peak due to the hydroxyl proton (originally present at $\delta \sim 11.00$ ppm in free pyrazolines) is completely missing from the spectra of the complexes, suggesting bonding through the hydroxyl oxygen atom. The appearance of a peak at δ 5.4-5.1 ppm as a broad singlet could be assigned to the N-H group (originally present at δ 5.4-5.0 ppm in free pyrazolines), suggesting the non-involvement of the N-H group in bond formation. The skeletal protons of a 5-membered ring observed at δ 3.4-3.1 ppm as a triplet and at

Table 1. Synthetic, analytical and physical data for $\text{RSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$.

S.No.	Reactants (in g)		Molar Ratio	Products	Yield % (g.)	MP (°C)	Mol. Wt. Found (Calcd.)	Analysis(%): Found (Calcd.)				
	RSnCl_3	Sodium Ligand						C	H	N	Sn	Cl
1.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	91 (2.82)	236	647 (643.43)	56.74 (57.86)	4.48 (4.50)	8.69 (8.70)	17.68 (18.44)	5.43 (5.50)
2.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	83 (2.68)	170	674 (671.45)	58.56 (59.02)	4.83 (4.91)	8.25 (8.34)	17.75 (17.67)	5.29 (5.27)
3.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	88 (2.98)	156	697 (703.43)	55.24 (56.34)	4.71 (4.69)	7.87 (7.96)	16.95 (16.87)	4.87 (5.03)
4.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	79 (2.71)	213	707 (712.33)	51.73 (52.26)	3.84 (3.79)	7.76 (7.86)	15.92 (16.66)	13.87 (14.92)
5.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{Pr}^{\text{III}}\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	84 (2.72)	146	675 (671.45)	60.12 (59.02)	4.95 (4.91)	8.41 (8.34)	16.54 (17.67)	5.29 (5.27)
6.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{Pr}^{\text{III}}\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	78 (2.62)	174	705 (699.47)	59.24 (60.09)	5.19 (5.28)	8.13 (8.00)	16.86 (16.96)	4.91 (5.06)
7.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{Pr}^{\text{III}}\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	85 (3.00)	153	726 (731.45)	58.11 (57.46)	5.10 (5.05)	7.58 (7.65)	15.78 (16.22)	4.76 (4.84)
8.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{Pr}^{\text{III}}\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	81 (2.89)	195	737 (740.35)	52.79 (53.53)	4.12 (4.18)	7.49 (7.56)	16.25 (16.03)	14.45 (14.36)
9.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	84 (2.85)	203	710 (705.48)	61.35 (61.28)	4.22 (4.39)	7.83 (7.93)	17.13 (16.82)	5.19 (5.02)
10.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	93 (3.29)	254	726 (733.50)	61.37 (62.21)	4.65 (4.77)	7.71 (7.63)	15.98 (16.18)	4.76 (4.83)
11.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	88 (3.24)	196	768 (765.48)	58.49 (59.62)	4.48 (4.57)	7.26 (7.31)	15.67 (15.50)	4.57 (4.63)
12.	1.15 (4.83)	0.222 (9.66)	1:2:2	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X})_2$	82 (3.06)	227	776 (774.38)	54.72 (55.83)	3.79 (3.74)	7.18 (7.23)	14.77 (15.32)	13.69 (13.73)

 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** & **12** compounds respectively.

δ 2.6-2.0 ppm as a doublet could be assigned to CH and CH₂ groups,¹⁸ respectively. The CH₃Sn protons give a sharp singlet at δ 0.9-0.6 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 ¹¹⁹Sn and ¹¹⁷Sn isotopes.^{20,21} The resonances due to propyl tin protons are observed in the region δ 2.2-0.6 ppm. The signals due to C₆H₅Sn overlap with the signals of aromatic protons of ligand and are observed at δ 8.1-6.5 ppm as a complex multiplet; therefore aromatic signals could not be assigned individually. Compounds **1-8** show ²J(¹¹⁹Sn, ¹H) values between 84 and 95 Hz. The values of the coupling constants are strongly indicative of 6-coordinated structures^{22,23} and this confirms the bidentate behaviour of ligands in these compounds.

Table 2. IR spectral data (cm⁻¹) for chloro organotin(IV) dipyrazolates.

S. No.	Compound	$\nu(\text{N-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-O})$	$\nu(\text{Sn-N})$	$\nu(\text{Sn-Cl})$
1	MeSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3320	1620	-	541	498	396	296
2	MeSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3322	1624	-	538	491	397	295
3	MeSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3318	1621	1008	540	493	395	294
4	MeSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3318	1623	-	539	488	399	297
5	Pr ⁿ SnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3320	1620	-	540	490	397	293
6	Pr ⁿ SnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3322	1626	-	542	491	397	295
7	Pr ⁿ SnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3321	1621	1010	536	493	395	297
8	Pr ⁿ SnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3318	1620	-	541	489	399	293
9	PhSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3322	1624	-	280	491	397	296
10	PhSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3320	1623	-	284	487	396	295
11	PhSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3324	1626	1014	283	493	395	293
12	PhSnCl(C ₁₅ H ₁₂ N ₂ O·X) ₂	3321	1621	-	285	495	399	297

where X = H in **1**, **5** and **9**; CH₃ in **2**, **6** and **10**; OCH₃ in **3**, **7** and **11**; Cl in **4**, **8** and **12** compounds respectively.

The proton decoupled ¹³C NMR spectra (Table 3) of chloro organotin(IV) dipyrazolates show the presence of all important signals with reference to free pyrazolines. The assignments were made on the basis of available literature along with the spectra of the free pyrazolines. The signal observed in the region δ 135.9-126.1 ppm as a multiplet could be assigned to aromatic carbon.¹⁹ The signal observed at δ 165.8-165.1 ppm due to imino carbon of the 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 9.7-9.6 ppm could be assigned to the MeSn group. The signals observed at δ 25.9-25.5 ppm, 28.8-28.3 ppm and 12.5-12.1 ppm may be assigned to α C, β C and γ C of the PrⁿSn group. The signals due to the PhSn group overlap with the signals of aromatic carbons of the ligand and are observed at δ 135.9-126.1 ppm as a complex pattern. All 8 compounds (**1-8**) show ¹J(¹¹⁹Sn, ¹³C) values between 675 and 695 Hz. The values of the coupling constants are strongly indicative of 6-coordinated tin.²²⁻²⁴

Table 3. ^1H NMR and ^{13}C NMR data (in δ ppm) for chloro organotin(IV) dipyrazolates.

S. No.	^1H NMR Chemical shift (in δ ppm)		Coupling constants (in Hz)	^{13}C NMR Chemical shift (in δ ppm)		Coupling constants (in Hz)	
	($\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X}$)	R-Sn		($\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}\cdot\text{X}$)	R-Sn		
1	7.6-6.9 (18H, m, Ar-H)	0.7 (CH ₃)	$^2\text{J}(^{119}\text{Sn}, ^1\text{H}) = 84$	135.9-129.8 (Ar-C)	9.6 (CH ₃)	$^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 679$	
	5.1 (2H, s, NH)			165.6 (C=N)			
	3.1 (2H, t, CH)			42.9 (CH)			
	2.3 (4H, d, CH ₂)			26.3 (CH ₂)			
2	7.6-6.7 (16H, m, Ar-H)	0.9 (CH ₃)	$^2\text{J}(^{119}\text{Sn}, ^1\text{H}) = 87$	135.7-128.9 (Ar-C)	9.6 (CH ₃)	$^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 681$	
	5.2 (2H, s, NH)			165.3 (C=N)			
	3.2 (2H, t, CH)			43.2 (CH)			
	2.4 (4H, d, CH ₂)			26.1 (CH ₂)			
3	7.5-6.8 (16H, m, Ar-H)	0.6 (CH ₃)	$^2\text{J}(^{119}\text{Sn}, ^1\text{H}) = 89$	135.7-129.4 (Ar-C)	9.7 (CH ₃)	$^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 675$	
	5.1 (2H, s, NH)			165.3 (C=N)			
	3.4 (2H, t, CH)			42.8 (CH)			
	2.3 (4H, d, CH ₂)			26.3 (CH ₂)			
4	4.2 (6H, s, OCH ₃)		$^2\text{J}(^{119}\text{Sn}, ^1\text{H}) = 85$	50.8 (OCH ₃)		$^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 677$	
	7.7-7.0 (16H, m, Ar-H)	0.7 (CH ₃)		135.5-129.6 (Ar-C)	9.6 (CH ₃)		
	5.2 (2H, s, NH)			165.7 (C=N)			
	3.1 (2H, t, CH)			42.7 (CH)			
5	7.6-6.9 (18H, m, Ar-H)	1.4 (αCH_2)*	$^2\text{J}(^{119}\text{Sn}, ^1\text{H}) = 90$	135.6-128.9 (Ar-C)	25.7 (αC)*	$^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 687$	
	5.4 (2H, s, NH)	2.1 (βCH_2)		163.5 (C=N)	28.8 (βC)		$^2\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 38$
	3.1 (2H, t, CH)	0.6 (γCH_3)		42.6 (CH)	12.1 (γC)		
	2.4 (4H, d, CH ₂)			26.4 (CH ₂)			$^3\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 108$
7.3-6.8 (16H, m, Ar-H)	1.2 (αCH_2)	135.8-128.7 (Ar-C)	25.5 (αC)	$^1\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 69$			
5.2 (2H, s, NH)	2.0 (βCH_2)	165.7 (C=N)	28.3 (βC)		$^2\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 40$		
3.3 (2H, t, CH)	0.9 (γCH_3)	43.6 (CH)	12.1 (γC)	$^3\text{J}(^{119}\text{Sn}, ^{13}\text{C}) = 110$			

Table 3. Continued

7	2.2 (4H, d, CH ₂)	² J(¹¹⁹ Sn, ¹ H) = 95	26.2 (CH ₂)	25.9 (αC) 28.5 (βC) 12.5 (γC)	¹ J(¹¹⁹ Sn, ¹³ C) = 689 ² J(¹¹⁹ Sn, ¹³ C) = 39 ³ J(¹¹⁹ Sn, ¹³ C) = 112
	1.0 (CH ₃)		12.8 (CH ₃)		
	7.7-7.0 (16H, m, Ar-H)		135.4-128.7 (Ar-C)		
8	5.1 (2H, s, NH)	² J(¹¹⁹ Sn, ¹ H) = 93	165.7 (C=N)	25.7 (αC) 28.3 (βC) 12.1 (γC)	¹ J(¹¹⁹ Sn, ¹³ C) = 695 ² J(¹¹⁹ Sn, ¹³ C) = 41 ³ J(¹¹⁹ Sn, ¹³ C) = 106
	3.1 (2H, t, CH)		43.1 (CH)		
	2.4 (4H, d, CH ₂)		26.5 (CH ₂)		
	4.1 (6H, s, OCH ₃)		50.6 (OCH ₃)		
	7.8-7.2 (16H, m, Ar-H)		135.9-128.7 (Ar-C)		
9	5.3 (2H, s, NH)	8.1-6.7 (m, C ₆ H ₅)	165.8 (C=N)	135.9-126.6 (C ₆ H ₅)	
	3.4 (2H, t, CH)		42.5 (CH)		
	2.1 (4H, d, CH ₂)		26.7 (CH ₂)		
	8.1-6.7 (18H, m, Ar-H)		35.9-126.6 (Ar-C)		
	5.4 (2H, s, NH)		165.5 (C=N)		
10	3.4 (2H, t, CH)	7.8-6.5 (m, C ₆ H ₅)	42.8 (CH)	135.8-126.7 (C ₆ H ₅)	
	2.6 (4H, d, CH ₂)		26.4 (CH ₂)		
	7.8-6.5 (16H, m, Ar-H)		135.8-126.7 (Ar-C)		
	5.2 (2H, s, NH)		165.7 (C=N)		
	3.1 (2H, t, CH)		42.5 (CH)		
11	2.1 (4H, d, CH ₂)	7.9-6.5 (m, C ₆ H ₅)	26.6 (CH ₂)	135.9-126.1 (C ₆ H ₅)	
	0.8 (CH ₃)		12.5 (CH ₃)		
	7.9-6.5 (16H, m, Ar-H)		135.9-126.1 (Ar-C)		
	5.2 (2H, s, NH)		165.1 (C=N)		
	3.5 (2H, t, CH)		43.3 (CH)		
12	2.1 (4H, d, CH ₂)	7.9-6.9 (m, C ₆ H ₅)	26.2 (CH ₂)	135.8-126.5 (C ₆ H ₅)	
	4.7 (6H, s, OCH ₃)		50.9 (OCH ₃)		
	7.9-6.9 (16H, m, Ar-H)		135.8-126.5 (Ar-C)		
	5.1 (2H, s, NH)		165.6 (C=N)		
	3.3 (2H, t, CH)		42.9 (CH)		
2.4 (4H, d, CH ₂)	26.4 (CH ₂)				

 where X = H in **1**, **5** and **9**; CH₃ in **2**, **6** and **10**; OCH₃ in **3**, **7** and **11**; Cl in **4**, **8** and **12** compounds respectively ; *Sn-αCH₂-βCH₂-γCH₃.

The proton decoupled ^{119}Sn NMR spectra (Table 4) of all compounds have been reported and exhibit a sharp ^{119}Sn resonance in the region at δ -310.8 to -335.9 ppm. These values are strongly indicative of 6-coordinated structures.²⁴⁻²⁶ The most plausible geometry around the tin(IV) in these compounds is octahedral geometry (Figure).

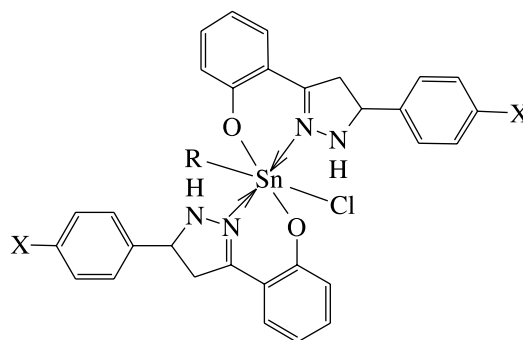


Figure. Molecular structure of $\text{RSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$.
(where $\text{R} = \text{Me}, \text{Pr}^n, \text{Ph}$; $\text{X} = -\text{H}, -\text{CH}_3, -\text{OCH}_3$ and $-\text{Cl}$).

Table 4. ^{119}Sn NMR data (in δ ppm) for chloro organotin(IV) dipyrzolinates.

S. No.	Compound	Chemical shift (in δ ppm)
1	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-325.4
2	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-321.9
3	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-324.7
4	$\text{MeSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-320.6
5	$\text{Pr}^n\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-329.3
6	$\text{Pr}^n\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-332.5
7	$\text{Pr}^n\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-335.9
8	$\text{Pr}^n\text{SnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-331.6
9	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-312.4
10	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-318.7
11	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-310.8
12	$\text{PhSnCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{O} \cdot \text{X})_2$	-317.2

where $\text{X} = \text{H}$ 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.

Conclusions

The present study describes the series of chloro organotin(IV) dipyrzolinates. However, 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 octahedral geometry for 6-coordinated organotin(IV) compounds.²⁴⁻²⁶ However, the bidentate

behaviour of the pyrazoline ligands in these compounds has been confirmed by IR, ^1H NMR and ^{13}C NMR data. The multinuclear NMR (^1H , ^{13}C and ^{119}Sn) data indicating the 6-coordinated octahedral geometry of tin in all these compounds.

Acknowledgements

The authors are grateful 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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