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Studies on some Diorganotin(IV) Complexes of Bis- and Tris-Pyrazolyl and Bis-Pyridyl Methanes and Pyridyl Pyrazoles

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Abstract

A series of complexes of the type $[R_2SnCl_2\overset{\frown}{NN}]$ (where R = Me, Et or Pr^n and $\overset{\frown}{NN}$ = bis(1-pyrazolyl)methane (pz_2CH_2), tris(1-pyrazolyl)methane (pz_3CH), bis(3,5-dimethyl-1-pyrazolyl)methane [$(Me_2pz)_2CH_2$], 1-(2-pyridyl)pyrazole (pzpy)). 1-(2-pyridyl)3,5-dimethylpyrazole ((Me_2pz)py) and bis(2-pyridyl)methane (py_2CH_2) have been prepared and characterized by elemental analyses, IR, NMR and ^{119}Sn Mössbauer spectroscopic techniques. They are non-electrolytes in acetonitrile. The IR and ^{119}Sn Mössbauer spectral data indicate a six-coordinate *trans*-R_2Sn structure. The complexes containing pz_2CH_2, pz_3CH and $(Me_2Pz)_2CH_2$ ligands dissociate in chloroform solution into reactant molecules, while the other complexes retain a six-coordinate geometry. Only two pyrazolyl ligands in pz_3CH complexes coordinate to the tin atom.

Introduction

During the last two decades, molecular complexes formed by the Lewis acid–base interaction of organotin moieties with primarily nitrogen and to a lesser extent with phosphorous, oxygen and sulphur donor mono- or poly-dentate ligands [1, 2] have been studied quite extensively. The resulting complexes of the type $[R_{4-n}SnX_nL_2]$ (when $n = 2$) generally show hexacoordination with more or less distorted octahedral geometry around the central tin atom depending on the nature of R, X and L, with the possibility of *cis* and *trans* isomerism.

Diorganotin complexes containing nitrogen donor ligands are particularly of interest as the *cis*-halo complexes are comparable to that of the well known antitumour platinum complexes. Recently some of these complexes derived from chelating nitrogen donor ligands with *cis*-halogen geometry were found to show antitumour activity [3, 4]. The majority of studies made with diorganotin(IV) complexes containing nitrogen donor ligands involved symmetrical bipyridine-type ligands.

Since the discovery of polypyrazolylalkanes by Trofimenko in 1966 [5, 6] and latter pyridylpyrazoles [7], their coordination behaviour towards transition metal ions and metal carbonyls has been studied [8, 9]. In many instances properties of the resulting complexes were quite different from those containing bipyridine type ligands. The coordination chemistry of such ligands with main group elements has received little attention [10]. In view of this it was considered worthwhile to prepare diorganotin(IV) complexes derived from such ligands and to study their stereochemistry. The present work describes the preparation and properties of diorganotin dichloride complexes containing bis(1-pyrazolyl)methanes, bis(2-pyridyl)methane, tris(1-pyrazolyl)methane and 1-(2-pyridyl)pyrazoles.

Experimental

Dialkyltin dichloride, R_2SnCl_2 (R = Me, Et, Pr^n), were prepared by the Kocheshkov coproportionation reaction of tetraalkyltins with $SnCl_4$ [1]. Bis(1-pyrazolyl)methane [8], tris(1-pyrazolyl)methane [8], bis(3,5-dimethyl-1-pyrazolyl)methane [8], bis(2-pyridyl)methane [11], 1-(2-pyridyl)pyrazole [12, 13] and 1-(2-pyridyl)3,5-dimethylpyrazole [14] were prepared by the literature methods. Analytical grade solvents were dried and distilled prior to use under nitrogen atmosphere.

Infrared spectra were recorded in nujol mulls between CsI plates in the range 2000–200 cm^{-1} with a Perkin-Elmer 180 spectrophotometer. The ^1H, ^{13}C and ^{119}Sn NMR Spectra were recorded on Varian FT-80A spectrometer in $CDCl_3$ operating at 79.5, 20 and 29.6 MHz, respectively. Chemical shifts are reported in ppm downfield from TMS (for ^1H and ^{13}C) and Me_4Sn (for ^{119}Sn). The ^{119}Sn Mössbauer spectra were recorded at 78 K using a constant acceleration drive coupled with a multichannel analyser. The source used was $Ba^{119}SnO_3$ which was maintained at room temperature, and isomer shifts are reported with respect to this source. Observed spectra were least square fitted using a

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TABLE I. Physical and Analytical Data for $[R_2SnCl_2(\widehat{NN})]$ Complexes

Complex	Recrystallisation solvent (yield %)	Melting point (°C)	Analyses: found (calculated) (%)			
			C	H	N	Cl[b]
$[Me_2SnCl_2pz_2CH_2]$	Hexane (89)	125	29.20(29.39)	3.97(3.84)	15.12(15.23)	18.92(19.28)
$[Et_2SnCl_2pz_2CH_2]$	Hexane (85)	89	33.70(33.37)	4.75(4.58)	13.55(14.15)	17.56(17.91)
$[Pr_2SnCl_2pz_2CH_2]$	Hexane (80)	77	37.08(36.83)	5.35(5.23)	13.88(13.21)	16.99(16.72)
$[Me_2SnCl_2pz_3CH]$[a]	Hexane (78)	61	31.98(33.06)	4.05(3.70)	19.63(19.74)	14.80(16.27)
$[Et_2SnCl_2pz_3CH]$[a]	Hexane (70)	129	–	–	–	15.52(15.28)
$[Me_2SnCl_2(Me_2pz)_2CH_2]$	Hexane (65)	81	34.34(36.83)	5.16(5.23)	11.46(13.21)	16.76(16.72)
$[Et_2SnCl_2(Me_2pz)_2CH_2]$	Hexane (67)	79	38.32(39.86)	5.71(5.80)	11.95(12.39)	16.36(15.69)
$[Me_2SnCl_2pzpy]$	C_6H_6/Hexane (96)	139	33.31(32.92)	3.66(3.59)	11.60(11.52)	19.08(19.43)
$[Et_2SnCl_2pzpy]$	C_6H_6/Hexane (91)	123	38.89(36.68)	4.54(4.36)	11.20(10.69)	18.09(18.05)
$[Me_2SnCl_2(Me_2pz)py]$	C_6H_6/Hexane (70)	117	36.24(36.60)	4.42(4.36)	10.88(10.69)	17.85(18.05)
$[Et_2SnCl_2(Me_2pz)py]$	C_6H_6/Hexane (86)	68	39.19(39.95)	4.98(5.03)	9.83(9.98)	16.81(16.84)
$[Pr_2SnCl_2(Me_2pz)py]$	C_6H_6/Hexane (83)	68	44.27(42.80)	5.84(5.61)	9.40(9.36)	16.36(15.79)
$[Me_2SnCl_2py_2CH_2]$	$CHCl_3$/Hexane (90)	195	39.48(40.05)	3.98(4.14)	7.43(7.18)	18.14(18.19)
$[Et_2SnCl_2py_2CH_2]$	$CHCl_3$/Hexane (96)	138	42.91(43.11)	5.53(4.82)	7.54(6.70)	16.92(16.96)

[a] Turns to an oil on exposure to air. [b] Estimated by Volhard's method.

Lorenzian line shape. All complexes were prepared in the same manner, and a typical method of preparation is given below.

Preparation of $[Me_2SnCl_2(py_2CH_2)]$

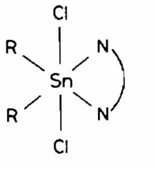
A hexane solution (~20 ml) of bis(2-pyridyl)-methane (1.02 g, 6.00 mmol) was added to a stirred hexane (~35 ml) solution of dimethyltin dichloride (1.32 g, 6.01 mmol). The reaction mixture was heated under reflux with stirring for 30 min during which white precipitate was formed. After cooling the precipitate was filtered out, washed with three aliquots of 5 ml hexane and dried under vacuum. Although the product thus obtained was pure enough, it may be recrystallised from chloroform. Yield 2.1 g (89%).

Ccomplexes derived from bis(1-pyrazolyl)-methane bis(3,5-dimethyl-1-pyrazolyl)methane, tris-(1-pyrazolyl)methane were soluble in hexane: thus they could not be precipitated out from the reaction mixture. In such cases hexane was reduced to 15–20 ml under vacuum and the solution was kept in an air tight stoppered flask at ~0 °C for 18–24 h. Crystals were separated out by decanting the supernatant liquid and dried under vacuum. Physical and analytical data for these complexes are given in Table I.

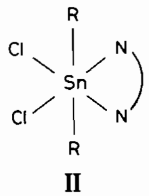
Results and Discussion

Addition of equimolar amounts of a bi- or tridentate nitrogen donor ligand to a hexane solution of diorganotin dichlorides affords the complexes of the type $[SnR_2Cl_2(\widehat{NN})]$ (R = Me, Et or Pr^n and $\widehat{NN} = pz_2CH_2$ pz_3CH, $[(Me_2pz)_2CH_2]$, pzpy, $(Me_2pz)py$ and py_2CH_2). They were either precipitated or recrystallised from the reaction mixture. The molar conductances of these complexes were found to be in the range 2–20 ohm^{-1} cm^2 mol^{-1} indicating their non-electrolytic behaviour [15].

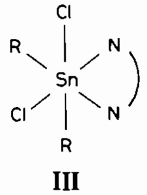
Three geometrical isomers (I–III) of $[SnR_2Cl_2(\widehat{NN})]$ are possible in which $\widehat{NN}$ behaves as a bidentate ligand.



I



II



III

The low frequency (600–200 cm^{-1}) IR region, where Sn–C, Sn–Cl and Sn–N vibrations are expected, gives information regarding the stereochemistry of organotin complexes [16, 17]. For the complexes of the type $[SnR_2Cl_2L_2]$ (L = nitrogen donor ligand and R = Me) only a single νSn–C band appears for the linear *trans*-alkyl group (configuration **II**), whereas two bands appear for *trans* chloride (**I**), non-linear *trans*-R (**II**) and configuration **III**. Our complexes generally showed two Sn–C stretching bands assignable to asymmetric and symmetric stretchings of medium to weak intensity (Table II) indicating a nonlinear configuration of the C–Sn–C moiety. On coordination the tin–chlorine bond lengthens due to electron donation from the ligand to the vacant d orbitals of the tin atom and consequently lowers the tin–chlorine stretching frequencies. Thus bands appearing below 310 cm^{-1} (~335 cm^{-1}) in uncomplexed SnR_2Cl_2 (R = Me, Et,

TABLE II. IR Frequencies in the Region 600–250 cm^{-1} for the Ligands and their Diorganotin Dichloride Adducts

Ligand/complex	IR bands[a]
pz_2CH_2	395vs, 355vs, 270w
$[Me_2SnCl_2pz_2CH_2]$	600s, 595w, 570s, 400s, 350m, 310m
$[Et_2SnCl_2pz_2CH_2]$	605s, 600s, 533m, 483m, 405m, 355w, 315w, 290w, 275w
$[Pr_2SnCl_2pz_2CH_2]$	630s, 610sh, 410m, 370w, 325w, 275vs, 270vs, 250vs
pz_3CH	600sh, 435vw, 370s, 290m
$[Me_2SnCl_2pz_3CH]$	600vs, 565s, 520m, 365m, 328s, 295sh, 270s
$[Et_2SnCl_2pz_3CH]$	600vs, 535s, 492m, 375m, 355vw, 280s, 252s
$(Me_2pz)_2CH_2$	470m, 300w, 270m
$[Me_2SnCl_2(Me_2pz)_2CH_2]$	590w, 570s, 511w, 480w, 460w, 355m, 310m, 275s
$[Et_2SnCl_2(Me_2pz)_2CH_2]$	585m, 525m, 520m, 478m, 465m, 405w, 355m, 325m, 250s
pzpy	570s, 465w, 405s, 370m, 270vw
$[Me_2SnCl_2pzpy]$	515m, 480m, 385w, 252vs
$[Et_2SnCl_2pzpy]$	595s, 532m, 505m, 485m, 405m, 382m, 345vw, 252vs
$(Me_2pz)py$[b]	585w, 535w, 405m, 370m, 325vw, 272w
$[Me_2SnCl_2(Me_2pz)py]$	575m, 545w, 520vw, 500vw, 445vw, 425w, 387w, 340vw, 275vs
$Et_2SnCl_2(Me_2pz)py]$	532w, 480w, 420w, 385w, 270sh, 260s
$[Pr_2SnCl_2(Me_2pz)py]$	585w, 545w, 418w, 385w, 352vw, 345vw, 305w, 275sh
py_2CH_2[b]	610vs, 575m, 470w, 400m, 275w
$[Me_2SnCl_2py_2CH_2]$	540s, 525s, 485m, 470m, 378w, 368vw, 320m, 290m
$[Et_2SnCl_2py_2CH_2]$	588vs, 529s, 478s, 422s, 385s, 275sh, 265m

[a] vw = very weak w = weak, m = medium, s = strong, vs = very strong [b] As neat liquid.

Pr^n) for our complexes can be assigned for νSn–Cl. In some cases two bands due to ν_{as}Sn–Cl and ν_sSn–Cl were observed while in others only a single band appeared, probably the other one appearing below 250 cm^{-1}. A band appearing in the region 350–400 cm^{-1} may tentatively be assigned for νSn–N modes [10, 16], although the assignment of such vibrations appearing at ~350 cm^{-1} in bipyridine or phenanthroline complexes have been questioned [18].

TABLE III. ^{119}Sn Mössbauer Data[a] for $[R_2SnCl_2\widehat{NN}]$ at 78 K

Complex	*IS* values (mm/s)	*QS* values (mm/s)	*QS*/*IS* values
$[Me_2SnCl_2]$	1.54	3.33	2.16
$[Me_2SnCl_2pz_2CH_2]$	1.44	4.12	2.86
$[Me_2SnCl_2(Me_2pz)_2CH_2]$	1.43	3.95	2.76
$[Me_2SnCl_2pz_3CH]$	1.51	3.75	2.48
$[Me_2SnCl_2(Me_2pz)py]$	1.46	4.02	2.75
$[Me_2SnCl_2py_2CH_2]$	1.40	3.99	2.85

[a] Errors in the estimation of *IS* and *QS* are 0.05 mm/s.

^{119}Sn Mössbauer effect parameters for some of the representative complexes are listed in Table III. All of our samples gave two line spectra originating from tin atoms in an asymmetric environment. The observed *IS* and *QS* values of ~1.4 and ~4 mm/s, respectively, clearly indicate a *trans* R_2Sn octahedral geometry. It has been shown previously that hexacoordinate tin complexes with two *trans*-R groups exhibit *QS* ~4 mm/s while complexes with *cis* configurations exhibit splitting only half as large [19, 20]. Similarly *IS* values have been shown to be dependent on the stereochemistry of organotin complexes. The *IS* values are generally greater than 1.2 mm/s for *trans*-SnR_2 complexes, whereas very few *cis*-SnR_2 complexes exhibit isomeric shifts greater than 1.0 mm/s [21]. Since we observed both ν_{as} and ν_s Sn–C in IR spectra, a distorted *octahedral* structure with *trans* R_2Sn moiety is proposed for these complexes.

To explore further the nature of these complexes in solution we have recorded the NMR spectra in $CDCl_3$ at room temperature, and the resulting data are given in Table IV. The ^1H and ^{13}C chemical shifts of the complexes are more or less the same as those of the corresponding free ligands and uncomplexed diorganotin dichlorides. The magnitude of $^2J(^{119}Sn-^1H)$ is a measure of the percentage s character in the Sn–C bond in dimethyltin(IV) complexes [22] and hence gives information about the coordination number of tin. The $^2J(^{119}Sn-^1H)$ for four-coordinate dimethyltin(IV) complexes has been reported in the range 60–71 Hz; it has generally been found to increase as the coordination number of tin increases from four to five, six or seven and has been observed in the range of 71–116 Hz depending upon the stereochemistry [16, 22, 23]. The $^2J(^{119}Sn-^1H)$ for our dimethyltin(IV) complexes, except the one derived from py_2CH_2, are comparable (~70 Hz) to the uncomplexed dimethyltin(IV) dichloride. This reflects that the complexes of the type $[R_2SnCl_2\widehat{NN}]$ may either have

TABLE IV. ^{1}H and ^{13}C NMR Data for $\widehat{NN}$ Ligands and [R$_2$SnCl$_2$($\widehat{NN}$)] Complexes in CDCl$_3$ at Room Temperature

Ligand/complexes	^{1}H NMR Data[a]		^{13}C NMR Data	
	δSn–R (ppm) $^2J(^{119}$Sn–^{1}H) (Hz)	Ligand protons	δSn–C (ppm)	Ligand carbons
pz$_2$CH$_2$		6.29(CH$_2$ + 4H), 7.55(3-H) 7.65(5H)		65.1,107.0, 129.6, 140.7
[Me$_2$SnCl$_2$pz$_2$CH$_2$]	1.15(69)	6.22(CH$_2$ + 4H) 7.64(d, 3-H), 7.75(d, 5H)	6.72	65.2, 107.1, 129.6, 140.7
[Et$_2$SnCl$_2$pz$_2$CH$_2$]	1.36–1.93(m)	6.40(CH$_2$ + 4H), 7.64(d, 3H), 7.75(d, 5H)	9.1, 18.5	65.2, 107.1, 129.6, 140.7
[Pr$_2$SnCl$_2$pz$_2$CH$_2$]	0.99 m 1.73m	6.19(CH$_2$ + 4H), 7.43(d, 3-H), 7.53(d, 5-H)	17.4, 18.4, 29.3	65.1, 107.0, 129.5, 140.6
pz$_3$CH		8.34(CH),7.60d(1.3 Hz, 5-H), 7.50d(2.4 Hz, 3-H), 6.30d, d(2.3 Hz, 4-H)		
[Me$_2$SnCl$_2$pz$_3$CH]	1.24(69.3)	6.33d,d (1.9 Hz, 4-H), 7.53d(2.5 Hz, 3-H), 7.62d(1.5 Hz, 5-H),8.37s(CH–N)	8.2	83.2, 107.2, 129.5 141.7
[Et$_2$SnCl$_2$pz$_3$CH]	1.33-1.80 m	6.31d,d(~2 Hz, 4-H), 7.52d(2.4 Hz, 3-H), 7.60d (1.2 Hz, 5-H), 8.35s(CH–N)		
(Me$_2$pz)$_2$CH$_2$		2.11s(Me), 2.33s(Me) 5.71(CH$_2$), 5.98s(4-H)		
[Me$_2$SnCl$_2$(Me$_2$pz)$_2$CH$_2$]	1.19(70)	2.16(Me), 2.39s(Me) 5.77s(CH$_2$), 6.04s(4-H)		
[Et$_2$SnCl$_2$(Me$_2$pz)$_2$CH$_2$]	1.34–1.88m	2.22(Me), 2.45s(Me), 5.82(CH$_2$), 6.10s(4-H)		
pzpy		6.45s(4-Hpz), 7.16m, 7.75m, 7.95m, 8.47m		
[Me$_2$SnCl$_2$pzpy]	1.18(71.5)	6.49d,d(4-Hpz), 7.17m, 7.83m, 8.50m		
[Et$_2$SnCl$_2$pzpy]	1.25–1.91m	6.46d,d(4-Hpz); 7.17m; 7.83(m); 8.28m		
(Me$_2$pz)py		2.28s(Me); 2.61s(Me) 5.96s(4-Hpz); 7.08 m(5-Hpy); 7.68 m(3 + 4-H py); 8.38d(6-H py)		14.7, 15.6, 110.2, 116.7, 121.5, 139.1, 142.5, 148.4, 150.7, 155.0
[Me$_2$SnCl$_2$(Me$_2$pz)py]	1.16(74.7)	2.31s(Me); 2.59s(Me); 5.97s(4-H pz); 7.15m(5-H py); 7.73 d,d (3,4-H py); 8.45 d,d (6-H py)	9.41	13.5, 14.2, 110.9, 115.7, 121.1, 138.7, 141.5, 147.6, 150.3, 152.4
[Et$_2$SnCl$_2$(Me$_2$pz)py]	1.20–1.92m	2.32s(Me); 2.62s(Me); 6.00(4-H pz); 7.19m(5-Hpy); 7.80d,d(3,4-H py); 8.49d,d(6-H py)	9.7, 26.2	13.6, 14.4, 110.3, 115.4, 121.6, 139.5, 141.5, 147.9, 150.9
[Pr$_2$SnCl$_2$(Me$_2$pz)py]	1.09m, 1.81m	2.30s(Me); 2.62s(Me); 5.99s(4-Hpz); 7.19m(5-Hpy); 7.78m(3,4-H py); 8.43(6-H py)	17.4, 18.5, 31.8	13.4, 14.2, 109.4, 115.5, 120.9, 138.5, 141.4, 147.5, 150.0, 152.5
py$_2$CH$_2$		4.37s(CH$_2$); 7.07–7.4m (4,5-H); 7.65m(3-H); 8.58d(6-H J = 5)		
[Me$_2$SnCl$_2$py$_2$CH$_2$]	1.26(78)	4.45s(CH$_2$); 7.31m(4,5-H); 7.69m(3-H); 8.67m(6-H)		
[Et$_2$SnCl$_2$py$_2$CH$_2$]	1.29–1.84m	4.43s(CH$_2$); 7.32m(4,5-H); 7.67m(3-H); 8.58m(6-H)		

[a] m = multiplet, s = singlet, d = doublet, d,d = doublet–doublet.

a six-coordinate geometry or have dissociated into reactant molecules in chloroform solution. However, the magnitude of $^2J(^{119}Sn-^1H)$ (78 Hz), for $[Me_2SnCl_2py_2CH_2]$ clearly indicates that $(R_2SnCl_2py_2CH_2]$ (R = Me or Et) retain their six-coordinate geometry in chloroform solution.

TABLE V. Tin-119 NMR Chemical Shifts of some Diorganotin Compounds in Chloroform

Compound	$\delta\,^{119}Sn$ (ppm)
Me_2SnCl_2[a]	~140
Et_2SnCl_2[a]	122
$[Me_2SnCl_2pz_2CH_2]$	119
$[Et_2SnCl_2pz_3CH]$	107
$[Me_2SnCl_2(Me_2pz)_2CH_2]$	117
$[Me_2SnCl_2pzpy]$	33
$[Et_2SnCl_2(Me_2pz)py]$	−73

[a] From ref. 42.

It has generally been observed that as the coordination number of tin increases from four to five, six or seven the ^{119}Sn NMR signal gradually moves to lower fields [23–26]. ^{119}Sn NMR spectral data for some of the representative compounds are given in Table V. The ^{119}Sn NMR chemical shift for Me_2SnCl_2 occurs at ~140 ppm in $CDCl_3$ which moves downfield in coordinating solvents such as acetone (~36 ppm) or dimethylsulphide (~50 ppm) [26]. The ^{119}Sn chemical shifts for $[Me_2SnCl_2pz_2CH_2]$, $[Me_2SnCl_2(Me_2pz)_2CH_2]$ and $[Et_2SnCl_2pz_3CH]$ (Table V) clearly indicate that the complexes derived from pz_2CH_2, $[(Me_2pz)_2CH_2]$ or pz_3CH ligands are dissociated in chloroform solution. However, the complexes containing pyridyl pyrazolyl ligands are coordinated in chloroform solution as the chemical shifts for $[Et_2SnCl_2((Me_2pz)py)]$ and $[Me_2SnCl_2(pzpy)]$ moved considerably downfield from corresponding dichlorides. The low solubilities of bis(2-pyridyl)methane complexes prevented us from recording their ^{119}Sn NMR spectra.

The diorganotin(IV) complexes containing pyrazolyl methane ligands appear to dissociate in solution presumably due to a weak metal–ligand back bonding effect, as the pyrazolyl ligands are reported [27] to be weaker π acceptors than the pyridine type ligands. Since the ^{119}Sn NMR chemical shifts for pyrazolyl methane complexes are slightly lower than those of the corresponding dichlorides, an equilibrium of the type

$$R_2SnCl_2\overset{\frown}{NN} \rightleftharpoons R_2SnCl_2 + \overset{\frown}{NN}$$

appears to be established. Further, the ^{119}Sn NMR chemical shift moved to 71 ppm on addition of one equivalent of $(Me_2pz)_2CH_2$ to the solution of $[Me_2SnCl_2(Me_2pz)_2CH_2]$.

The complexes derived from tris(1-pyrazolyl)methane are non-ionic and their *IS* and *QS* values are comparable to those of other complexes of the series. A six-coordinate geometry in which only two out of the three pyrazolyl rings are coordinated can also be proposed for these complexes. Since *IS* and *QS* values are sensitive to the coordination geometry around tin, a change in coordination number from six to seven (when all pz rings are coordinated) would affect these parameters. It is noteworthy that the behaviour of tris(1-pyrazolyl)methane is quite different from that of 2,2′,2″-terpyridyl, as the latter forms an ionic complex with dimethyl tin dichloride [28].

In conclusion, diorganotin complexes containing pz_2CH_2, pz_3CH, $(Me_2pz)_2CH_2$, pzpy, $(Me_2pz)py$ and py_2CH_2 are six-coordinated in the solid state as shown by IR and Mössbauer effect studies. However, the complexes containing pz_2CH_2, pz_3CH and $(Me_2pz)_2CH_2$ ligands appear to exist in a dissociated state in chloroform solution as evidenced by ^{119}Sn NMR spectral data.

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