

Synthesis and spectroscopic investigations (IR, NMR and Mössbauer) of tin(IV) and organotin(IV) derivatives of bis(pyrazol-1-yl) alkanes: X-ray crystal structures of bis(4-methylpyrazol-1-yl) methane and its dimethyltin(IV) dichloride adduct

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Abstract

A series of 1:1 adducts of the type $[(L)R_nSnX_{4-n}] \cdot zH_2O$ ($L \equiv$ bis(4-methylpyrazol-1-yl)methane (L^4), bis(3,4,5-trimethylpyrazol-1-yl)methane (L^T), 1,2-bis(pyrazol-1-yl)ethane (L^A) or 1,2-bis(3,5-dimethylpyrazol-1-yl)ethane (L^B); $R \equiv$ Me, Et, Bu or Ph; $X \equiv$ I, Br or Cl; $n = 0, 1$ or 2 ; $z = 1, 1.5$ or 2), and the likely polynuclear $[(L^A)_5(SnCl_4)_4] \cdot (H_2O)_5$ and $[(L^B)_2(SnCl_4)_3] \cdot \frac{1}{2}[Et_2O]$ have been characterized in the solid state and in solution by analyses, spectral (IR, Mössbauer, and 1H , ^{13}C and ^{119}Sn NMR) data and conductivity measurements. When L^T reacts with $SnCl_4$, cleavage of a carbon (sp^3)–nitrogen bond was observed and the adduct $[(3,4,5-trimethylpyrazole)_2SnCl_4]$ was obtained. The diorganotin(IV) complexes generally dissociate in chloroform or in acetone solution, while the trichlorotin(IV) and tetrachlorotin(IV) adducts probably retain the hexacoordinate configuration. The crystal structures of L^4 and of the adduct $[(L^4)(CH_3)_2SnCl_2]$ have been determined by X-ray analysis. In the adduct the tin atom is coordinated to two halide atoms, two methyl groups and two N atoms, with *trans*-(CH_3)₂Sn in a slightly distorted octahedral configuration. The long Sn–N bond distance (2.436(6)Å) indicates weak donor ability of the N_2 donor L^4 . Comparison is made with the X-ray crystal structures of several $R_2SnX_2N_2$ -type compounds.

Keywords: Tin; X-ray structure; Infrared spectroscopy; Group 14; Pyrazole; NMR

1. Introduction

Poly(pyrazol-1-yl)alkanes (Fig. 1) constitute a family of stable and flexible bidentate ligands, isoelectronic and isosteric with the well-known poly(pyrazol-1-yl)borate donors discovered by Trofimenko [1]. The coordinating behaviour of $(pz)_n(CR_{4-n})_m$ ($n = 2$ or 3 ; $m = 1$ or 2) towards transition and main group metal ions has been extensively investigated [2,3], but much less work has been done on the donor ability of such ligands towards organometallic derivatives of main group elements [1,4,5], although tin(IV) and organo-

tin(IV) adducts containing nitrogen ligands are becoming increasingly important because a number of compounds of this type show antitumour activity towards P388 lymphocytic leukaemia in mice [6].

In our previous papers we have described the interaction between the N_2 donors bis(pyrazol-1-yl)methane (L^1) [7], bis(3,5-dimethylpyrazol-1-yl)methane (L^2) [8] and 2,2'-bis(pyrazol-1-yl)propane (L^3) [8] and several tin(IV) and organotin(IV) acceptors, and we have shown that different reactions take place depending on the nature of the donor and of the tin(IV) derivative.

Extending our interest in the chemistry of tin(IV) [9] and azoles [10], we decided to research the synthesis, analytical and spectroscopic characterization (1H , ^{13}C and ^{119}Sn NMR, IR, and ^{119}Sn Mössbauer spectra) of

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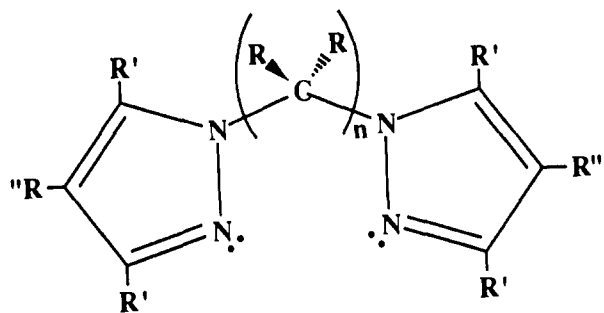


Fig. 1. L^1 : $n=1$; $R=R'=R''=H$. L^2 : $n=1$; $R=R''=H$; $R'=CH_3$. L^3 : $n=1$; $R=CH_3$; $R'=R''=H$. L^4 : $n=1$; $R=R'=H$; $R''=CH_3$. L^T : $n=1$, $R=R'=R''=CH_3$. L^A : $n=2$; $R=R'=R''=H$. L^B : $n=2$; $R=R''=H$; $R'=CH_3$.

new derivatives containing the bidentate nitrogen ligands 1,2-bis(pyrazol-1-yl)ethane (L^A), 1,2-bis(3,5-dimethylpyrazol-1-yl)ethane (L^B), bis(4-methylpyrazol-1-yl)methane (L^4) and bis(3,4,5-trimethylpyrazol-1-yl)methane (L^T).

In order to gain insight into the factors controlling the structure and bonding in complexes of the type $[(L)R_2SnX_2]$ (L = bidentate nitrogen donor), the X-ray crystal structure of $[(L^4)(CH_3)_2SnCl_2]$ was also determined and the results compared with those of L^4 and of several $R_2SnX_2N_2$ model compounds.

Comparison is made with the results obtained with tin(IV) and organotin(IV) derivatives of other poly(azol-1-yl)alkanes [4,5,7,8].

2. Experimental section

2.1. Material and methods

The tin(IV) and organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The donors 1,2-bis(pyrazol-1-yl)ethane (L^A), 1,2-bis(3,5-dimethylpyrazol-1-yl)ethane (L^B), bis(4-methylpyrazol-1-yl)methane (L^4) and bis(3,4,5-trimethylpyrazol-1-yl)methane (L^T) were prepared according to literature methods [11–14].

The samples for microanalysis were dried in vacuo to constant weight (20 °C; about 0.1 Torr). Elemental analyses (C, H and N) were performed in house with a Carlo-Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 Fourier transform IR instrument. 1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for 1H , 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Melting points were obtained on an IA 8100 Electrothermal instrument. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The molecular

weight determinations were performed by the Pascher Mikroanalytisches Laboratorium, Remagen, Germany.

^{119}Sn Mössbauer spectra were recorded at liquid-nitrogen temperature with an Elscint-Laben spectrometer equipped with an AERE cryostat. A $Ca^{119}SnO_3$ Mössbauer source of 10 mCi (from the Radiochemical Centre, Amersham, England) moved with constant acceleration and triangular waveform was used.

2.2. Synthesis of the complexes

2.2.1. [Bis(4-methylpyrazol-1-yl)methane]dimethyldichlorotin(IV) (1)

To a stirred diethyl ether solution (25 ml) of $(CH_3)_2SnCl_2$ (440 mg, 2.0 mmol) at room temperature a diethyl ether solution (25 ml) of bis(4-methylpyrazol-1-yl)methane (L^4) (704 mg, 4.0 mmol) was added. A colourless precipitate was formed immediately; it was filtered off, washed with diethyl ether and shown to be **1**. Adducts **2–21** and **23–31** were obtained similarly.

2.2.2. [1,2-Bis(pyrazol-1-yl)ethane]tetrachlorotin(IV) (22)

Anhydrous $SnCl_4$ (521 mg, 2.0 mmol) was added to a stirred diethyl ether solution (50 ml) of L^A (324 mg, 2.0 mmol) under N_2 . A colourless precipitate was obtained immediately. This was filtered off and washed with Et_2O under N_2 and shown to be **22**.

2.2.3. Bis(3,4,5-trimethylpyrazole)tetrachlorotin(IV) (32)

To a stirred diethyl ether solution of L^T (437 mg, 2.0 mmol) a 1 M dichloromethane solution of $SnCl_4$ (2.0 ml, 2.0 mmol) was added. A colourless precipitate was formed, which was filtered off after 1 day and washed with Et_2O ; it was shown to be **32**.

2.3. Crystallographic study

2.3.1. L^4

A summary of the experimental conditions are reported in Table 1.

Colourless crystals of L^4 were obtained by slow evaporation from an ether solution. Preliminary investigations were by inspection of oscillation and Weissenberg photographs. The space group was found to be either Cc or $C2/c$ ($C2/c$ after refinement).

A colourless crystal with approximate dimensions 0.2 × 0.3 × 0.4 mm was mounted on a Nicolet R_3 four circle diffractometer, and accurate lattice parameters were obtained by least-squares refinement of 15 reflections collected in the range $21^\circ \leq 2\theta \leq 34^\circ$. 1118 unique reflections were collected in the range $1.5^\circ \leq 2\theta \leq 55^\circ$ by ω - 2θ scan data collection, but only 650, with I greater than $3\sigma(I)$, were used in the successive refinement.

A continuous decay (of 10%) of the intensity of standard reflections was observed and a correction was made. The data were also corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods, using the SIR92 computer program [15], and then refined by the full-matrix least squares method using the CRYSTALS package [16].

The structure was first refined isotropically, and then anisotropically with unitary weight. Hydrogen atoms were introduced (and then refined as riding), at positions determined by a Fourier difference map, except for the disordered methyl hydrogen atoms which were introduced at calculated positions by imposing a distance from the bonded atom equal to 0.95 Å. A final refinement was performed with an optimized weighting scheme [17–19], as available in CRYSTALS: $w^{-1} = P(F_c/F_c^{\max})\{1 - (|F_o - F_c|/[6|F_o - F_c|_{\text{est}}])^2\}^2$ where $P(F_c/F_c^{\max})$ is a third-order optimized truncated Chebyshev polynomial with coefficients $a_1 = 0.820$, $a_2 =$

Table 1
Crystal data: data collection and refinement of the structure for L^4

Formula	$C_9H_{12}N_4$
Formula weight	176.223
Space group	$C2/c$
Colour	Colourless
a (Å)	10.845(4)
b (Å)	4.240(4)
c (Å)	21.062(8)
β (°)	96.06(3)
V_c (Å ³)	963(1)
Z	4
D_c (g cm ⁻³)	1.216
Crystal size (mm)	0.2 × 0.3 × 0.4
μ (Cu K α) (cm ⁻¹)	0.852
Data collection instrument	Nicolet R_3
Radiation (monochromated)	Mo K α ($\lambda = 0.7107$ Å)
T of data collection (K)	293
Scan mode	$\omega - 2\theta$
Scan width (°)	1.1 below K α_1 , 1.3 above K α_2
Scan speed (° min ⁻¹)	Minimum, 1.002; Maximum, 14.648
Background/scan ratio	0.5
Data collection range, (°)	$1.5 \leq 2\theta \leq 55$
Standards (measured every 100 reflections)	6 0 4, 0 2 7, 2 2 7
Number of unique reflections measured	1118
Number of data with $I \geq 3\sigma(I)$	650
Refinement	Full-matrix least-squares method on F
Number of parameters refined	60
R^a	0.056
R_w^b	0.063
S^c (goodness of fit)	1.18

$$^a R = (\sum \|F_o - k|F_c|\|) / \sum |F_o|$$

$$^b R_w = [\sum w(|F_o - k|F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

$$^c S = [\sum w(|F_o - k|F_c|)^2 / (N_{\text{obs}} - N_{\text{par}})]^{1/2}$$

Table 2

Crystal data: data collection and refinement of the structure for $(L^4)Sn(CH_3)_2Cl_2$

Formula	$SnCl_2C_{11}H_{18}N_4$
Formula weight	395.89
Space group	$P2_1/m$
Colour	Colourless
a (Å)	6.703(9)
b (Å)	15.674(9)
c (Å)	8.467(8)
β (°)	118.2(3)
V_c (Å ³)	784(2)
Z	2
D_c (g cm ⁻³)	1.678
Crystal size (mm)	0.1 × 0.3 × 0.3
μ (Mo K α) (cm ⁻¹)	19.67
$F(000)$	392
Data collection instrument	Huber CS
Radiation (monochromated)	Mo K α ($\lambda = 0.7107$ Å)
T of data collection (K)	293
Scan mode	ω
Scan width (°)	1.2
Scan speed (° min ⁻¹)	min = 1.0, max = 30.0
Background to scan ratio	0.5
Data collection range (°)	$4.0 \leq 2\theta \leq 80$
Standards (measured every 100 reflections)	2 5 - 2, 0 3 3, - 2 5 3
Number of unique reflections measured	1920
Number of data with $I \geq 3\sigma(I)$	1441
Refinement	Full-matrix least-squares method on F
Number of parameters refined	92
R^a	0.057
R_w^b	0.059
S^c (goodness of fit)	0.94

^{a,b,c} See footnotes to Table 1.

0.839 and $a_3 = 0.447$, and $|F_o - F_c|_{\text{est}}$ is estimated by using the polynomial to fit $|F_o - F_c|$ against F_c .

The final $R = 0.056$ and $R_w = 0.063$. The r.m.s. shift for the last cycle of refinement was 0.04. The largest peaks on a final Fourier difference map were 0.23 and -0.26 electrons Å⁻³.

2.3.2. $[(L^4)(CH_3)_2SnCl_2]$

A summary of the experimental conditions is reported in Table 2.

Crystals of $[(L^4)(CH_3)_2SnCl_2]$ were obtained by slow evaporation from an ether solution. Preliminary investigations were by inspection of oscillation and Weissenberg photographs, revealing the space group to be either $P2_1$ or $P2_1/m$ ($P2_1/m$ after structure solution).

A colourless crystal (approximate dimensions, 0.2 × 0.3 × 0.4 mm) was mounted on a Huber four-circle diffractometer operating under the control of the CS software [20]. Lattice parameters were obtained by least-squares refinement of 15 reflections in the range $10^\circ \leq 2\theta \leq 20^\circ$. Unique reflections were collected by ω

Table 3
Physical, analytical and conductivity data of derivatives 1–32

Compound and formula ^a	Yield (%)	Melting point (°C)	Elemental analysis: Found (calculated) (%)			Conductivity ^b		
			C	H	N	Solvent	Concentration	Λ
$[(L^d)(CH_3)_2SnCl_2]^c$ (1) C ₁₁ H ₁₈ Cl ₂ N ₄ Sn	40	143–145	33.49 (33.37)	4.60 (4.58)	13.94 (14.15)	Acetone	2.0	2.8
$[(L^d)(CH_3)_2SnBr_2]^d$ (2) C ₁₁ H ₁₈ Br ₂ N ₄ Sn	51	134–137	27.45 (27.25)	3.96 (3.74)	11.23 (11.56)	Acetone	1.0	6.8
$[(L^d)(C_2H_5)_2SnCl_2]$ (3) C ₁₃ H ₂₂ Cl ₂ N ₄ Sn	60	150–153	36.98 (36.83)	5.72 (5.83)	13.00 (13.22)	Acetone	1.0	1.0
$[(L^d)(C_2H_5)_2SnBr_2]$ (4) C ₁₃ H ₂₂ Br ₂ N ₄ Sn	30	137–140	30.48 (30.45)	4.69 (4.32)	9.96 (10.92)	DMSO	1.1	7.8
$[(L^d)(CH_3)SnCl_3]$ (5) C ₁₀ H ₁₅ Cl ₃ N ₄ Sn	72	318–319	29.12 (28.85)	3.92 (3.63)	12.87 (13.46)	Acetone	1.5	6.2
$[(L^d)(C_6H_5)_2SnCl_2]^e$ (6) C ₂₁ H ₂₂ Cl ₂ N ₄ Sn	75	170–172	46.83 (46.88)	4.43 (4.50)	10.27 (10.41)	DMSO	1.1	10.2
$[(L^d)(C_4H_9)SnCl_3]$ (7) C ₁₃ H ₂₁ Cl ₂ N ₄ Sn	71	176–177	34.56 (34.06)	4.97 (4.62)	11.72 (12.22)	Acetone	1.0	3.0
$[(L^d)(C_6H_5)SnCl_3]$ (8) C ₁₅ H ₁₇ Cl ₃ N ₄ Sn	63	325–329	37.40 (37.66)	3.68 (3.58)	11.60 (11.71)	DMSO	1.1	7.4
$[(L^d)SnCl_4]$ (9) C ₉ H ₁₂ Cl ₄ N ₄ Sn	82	314–315	24.98 (24.75)	3.04 (2.77)	12.95 (12.83)	Acetone	4.0	2.5
$[(L^d)SnBr_4]$ (10) C ₉ H ₁₂ Br ₄ N ₄ Sn	90	276–277	17.89 (17.59)	2.09 (1.97)	8.91 (9.12)	DMSO	1.2	4.6
$[(L^T)(C_6H_5)_2SnCl_2 \cdot H_2O]^f$ (11) C ₂₅ H ₃₂ Cl ₂ N ₄ OSn	35	170–171	50.17 (50.54)	5.40 (5.43)	9.23 (9.43)	Acetone	3.2	3.8
$[(L^T)(CH_3)SnCl_3]$ (12) C ₁₄ H ₂₃ Cl ₃ N ₄ Sn	64	180 decomposition	35.41 (35.59)	5.17 (4.91)	11.46 (11.86)	DMSO	0.9	38.1
$[(L^T)(C_4H_9)SnCl_3]$ (13) C ₁₇ H ₂₉ Cl ₃ N ₄ Sn	63	166–168	39.74 (39.69)	5.82 (5.68)	10.90 (10.89)	Acetone	1.1	7.5
$[(L^T)(C_6H_5)SnCl_3] \cdot H_2O$ (14) C ₁₉ H ₂₇ Cl ₃ N ₄ OSn	58	80–130	40.98 (41.31)	5.12 (4.93)	10.44 (10.14)	Acetone	1.0	20.6
$[(L^T)SnBr_3OH]$ (15) C ₁₃ H ₂₁ Br ₃ ON ₄ Sn	31	166–168	26.13 (25.69)	3.60 (3.48)	9.22 (9.22)	DMSO	1.0	73.6
$[(L^T)SnI_4]$ (16) C ₁₃ H ₂₀ I ₄ N ₄ Sn	34	140–180	18.35 (18.19)	2.47 (2.35)	5.99 (6.53)	Acetone	1.0	109.6
$[(L^A)(CH_3)_2SnCl_2] \cdot 2H_2O$ (17) C ₁₀ H ₂₀ Cl ₂ O ₂ N ₄ Sn	30	113 decomposition	29.17 (28.73)	4.66 (4.78)	13.05 (13.40)	Acetone	1.3	19.0
$[(L^A)(CH_3)SnCl_3]$ (18) C ₉ H ₁₃ Cl ₃ N ₄ Sn	60	167–168	27.04 (26.86)	3.40 (3.23)	13.70 (13.93)	Acetone	1.0	15.5
$[(L^A)(C_6H_5)_2SnCl_2]$ (19) C ₂₀ H ₂₀ Cl ₂ N ₄ Sn	28	70 decomposition	47.30 (47.45)	4.05 (3.95)	11.21 (11.07)	DMSO	1.2	20.6
$[(L^A)(C_6H_5)SnCl_3]$ (20) C ₁₄ H ₁₅ Cl ₃ N ₄ Sn	52	121 decomposition	36.04 (36.19)	3.47 (3.23)	12.36 (12.06)	Acetone	1.0	6.7
$[(L^A)(C_4H_9)SnCl_3]$ (21) C ₁₂ H ₁₉ Cl ₃ N ₄ Sn	63	86 decomposition	32.87 (32.42)	4.41 (4.28)	13.76 (12.61)	Acetone	1.3	10.8
$[(L^A)SnCl_4]$ (22) C ₈ H ₁₀ Cl ₄ N ₄ Sn	70	267–271	23.16 (22.73)	2.44 (2.38)	13.58 (13.25)	Acetone	1.0	25.0
$[(L^A)_5(SnCl_4)_4] \cdot 5H_2O$ ^g (23) C ₄₀ H ₆₀ Cl ₁₆ N ₂₀ O ₅ Sn ₄	78	120 decomposition	24.82 (24.73)	3.27 (3.11)	14.18 (14.42)	Acetone	0.2	11.0
$[(L^A)(SnBr_4)]^h$ (24) C ₈ H ₁₀ Br ₄ N ₄ Sn	65	163–164	15.78 (16.00)	1.99 (1.68)	9.63 (9.33)	DMSO	1.0	62.0
$[(L^A)SnI_2(OH)_2]^i$ (25) C ₈ H ₁₂ I ₂ N ₄ O ₂ Sn	71	100–102	17.23 (16.90)	2.07 (2.13)	9.73 (9.85)	Acetone	1.1	47.6
$[(L^B)(CH_3)SnCl_3] \cdot 2H_2O$ (26) C ₁₃ H ₂₅ Cl ₃ N ₄ O ₂ Sn	25	130–131	31.70 (31.48)	5.04 (5.06)	11.39 (11.33)	DMSO	1.0	76.7
$[(L^B)(C_6H_5)SnCl_3] \cdot H_2O$ (27) C ₁₈ H ₂₅ Cl ₃ N ₄ OSn	60	135–136	39.52 (40.14)	4.75 (4.64)	10.22 (10.41)	Acetone	1.0	30.5
$[(L^B)(C_4H_9)SnCl_3] \cdot 1.5H_2O$ (28) C ₁₆ H ₃₀ Cl ₃ N ₄ O _{1.5} Sn	57	132–133	36.72 (36.42)	5.73 (5.41)	10.60 (10.62)	DMSO	0.9	25.4
$[(L^B)_2(SnCl_4)_3] \cdot \frac{1}{2}[Et_2O]^l$ (29) C ₂₆ H ₄₁ Cl ₁₂ N ₈ Sn ₃ O _{0.5}	70	245 decomposition	24.86 (24.88)	3.76 (3.29)	8.57 (8.93)	Acetone	1.0	10.2
$[(L^B)SnBr_4]$ (30)	83	200 decomposition	21.82	3.22	8.10	DMSO	0.5	51.2
						Acetone	1.0	46.0

Table 3 (continued)

Compound and formula ^a	Yield (%)	Melting point (°C)	Elemental analysis: Found (calculated) (%)			Conductivity ^b		
			C	H	N	Solvent	Concentration	A
C ₁₂ H ₁₈ Br ₄ N ₄ Sn [(L ^B)SnI ₄] (31)	85	137–138	(21.94)	(2.74)	(8.53)	DMSO	0.9	30.2
C ₁₂ H ₁₈ I ₄ N ₄ Sn [(L ^B)SnI ₄] (31)			16.78	2.39	6.71	Acetone	0.3	96.0
C ₁₂ H ₁₈ I ₄ N ₄ Sn [(pzH) ₂ SnCl ₄] ^m (32)	48	289–292	(17.07)	(2.15)	(6.63)	DMSO	1.0	41.3
C ₁₂ H ₂₀ Cl ₄ N ₄ Sn			29.91	4.34	11.40	Acetone	1.1	50.9
C ₁₂ H ₂₀ Cl ₄ N ₄ Sn			(29.98)	(4.19)	(11.65)			

^a L^A ≡ bis(4-methylpyrazol-1-yl)methane; L^T ≡ bis(3,4,5-trimethylpyrazol-1-yl)methane; L^B ≡ 1,2-bis(pyrazol-1-yl)ethane;

L^B ≡ 1,2-bis(3,5-dimethylpyrazol-1-yl)ethane.

^b At room temperature and at molar concentration × 10⁻³ indicated in parentheses.

^c Molecular weight: in CHCl₃, 222; in acetone, 277; calculated, 395.89.

^d Molecular weight: in CHCl₃, 224; in acetone, 315; calculated, 484.79.

^e Molecular weight: in CHCl₃, 260; in acetone, 354; calculated, 520.03.

^f Molecular weight: in CHCl₃, 270; in acetone, 368; calculated, 594.16.

^g Cl%: found, 28.9; calculated, 29.19.

^h Br%: found, 54.8; calculated, 53.22.

ⁱ I%: found, 43.5; calculated, 44.6.

^l Cl%: found, 32.9; calculated, 33.89.

^m pzH ≡ 3,4,5-trimethylpyrazole.

scan mode, but only 1441 with *I* greater than 3σ(*I*) were used during the refinement.

The analysis of the standard reflections showed no decay, and the data reduction was performed as for L^A, by using DARX software [21].

The structure was solved by direct methods and then refined, first isotropically (same software as used for L^A) and then anisotropically but with weight $w^{-1} = [\sigma(F_o)]^2$. The hydrogen atoms were then introduced at calculated positions, using the same parameter as for L^A, and then refined as riding. Extinction [22] and anomalous scattering corrections were included in the calculations. A final refinement with optimized weights was performed as for L^A (with coefficients $a_1 = 13.420$, $a_2 = 3.717$ and $a_3 = 10.669$), giving a final $R = 0.057$ and $R_w = 0.059$. The r.m.s. shift for the last cycle was 0.06.

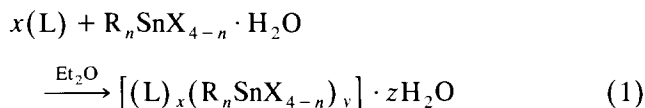
A final Fourier difference map gave the largest peak (2.6 electrons Å³) at 0.5 Å from the Sn atom.

All the calculations were performed on a personal computer. The PARST program [23] was used for some geometrical calculations. Scattering factors were used from [24].

3. Results and discussion

Interaction between various tin(IV) and organotin(IV) compounds and an excess of donor in organic solvent (diethyl ether and/or petroleum ether) produces the

compounds **1–14**, **16–24** and **26–31** listed in Table 3, according to the reaction



With the exception of **23** and **29** (for which the ligand-to-metal ratios of 5 to 4 and of 2 to 3 respectively suggest the presence of an organic ligand bridging between metal centres), 1:1 adducts were always isolated, even in the presence of a great excess of donor.

It has been previously noted [8] that the reaction of tin(IV) compounds with potentially bidentate N donors may give different products depending on the ligands and/or the stoichiometric ratios employed; the 1:1 adduct **22** was obtained only when 1 mol of L^A was treated with equimolar quantities of anhydrous SnCl₄ under reflux in diethyl ether under N₂.

When L^T reacts with SnBr₄ and L^A reacts with SnI₄ in diethyl ether, the compounds [(L^T)SnBr₃OH] (**15**) and [(L^A)SnI₂(OH)₂] (**25**) respectively are isolated; these contain one and two OH groups in place of the halide, probably because of the presence of traces of moisture.

Various amounts of water from 1 in [(L^T)(C₆H₅)₂SnCl₂] · H₂O to 1.5 in [(L^B)(C₄H₉)SnCl₃] · 1.5H₂O, to 2 in [(L^A)(CH₃)₂SnCl₂] · 2H₂O and finally to 5 in [(L^A)₅(SnCl₄)₄] · 5H₂O are also probably due to traces of moisture in the starting reagents.

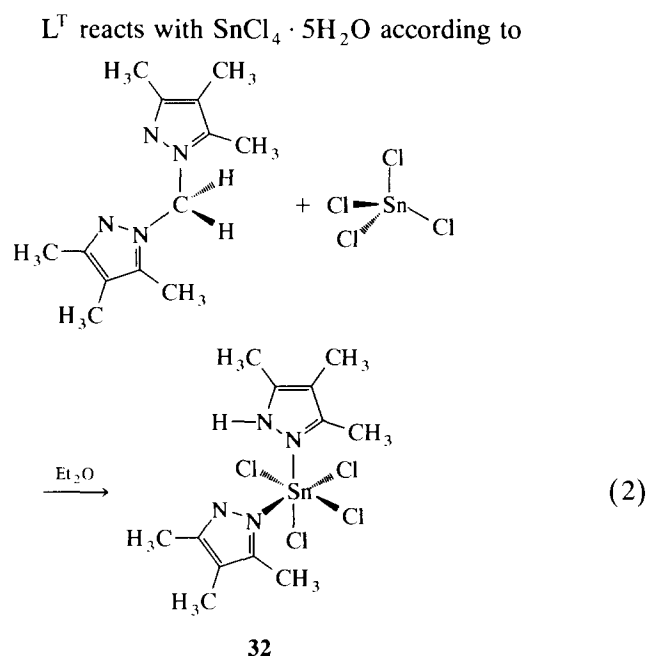
Table 4
Selected IR data of bases and of 1–32

Compound	ν (cm ⁻¹)			Other data
	> 3000 cm ⁻¹	1600–1500 cm ⁻¹	< 600 cm ⁻¹	
L ^d	3150m, 3085w	1575m	422m, 398w, 346w, 288m, 249m	
1	3157w, 3110m, 3098m, 3007m	1577w, 1540w	599m, 425w, 289w, 186br	ν (Sn–Cl), 259s br; ν (Sn–C), 576w; δ (Sn–Cl), 159br, 141br
2	3160w, 3107m, 3095sh, 3001sh	1570vw	598w, 422w, 289m, 226w	ν (Sn–C), 568m; ν (Sn–Br), 180s br
3	3157w, 3121w, 3105m, 3091m, 3015m	1576w	600m, 485w, 425w	ν (Sn–C), 532w; ν (Sn–Cl), 259s br; δ (Sn–Cl), 151w, 139vw
4	3156w, 3113m, 3091m, 3004m	1576w	598m, 476m, 418w, 226w	ν (Sn–C), 525w; ν (Sn–Br), 176br δ (Sn–Cl), 151w, 139vw
5	3158vw, 3117m, 3101m, 3032w	1577w	597m, 424m, 356m, 227w	ν (Sn–C), 543w; ν (Sn–Cl); 311s, 289s δ (Sn–Cl), 165br, 152m
6	3145w, 3111m, 3091w, 3068w, 3051w, 3014w	1574w	605w, 599w, 560w, 420w, 288m, 460m,	ν (Sn–C), 277m; ν (Sn–Cl), 277m, 248m, 226m; δ (Sn–Cl), 169br, 151w, 139vw
7	3127w, 3103w, 3032w	1581w, 1548w	431m, 405w, 367w, 453m	ν (Sn–C), 600m; ν (Sn–Cl), 301br, 277br; δ (Sn–Cl), 152br, 141w
8	3125m, 3113w, 3094w, 3068w, 3036w	1577w	601m, 433m, 280s, 201m, 255m, 229m	ν (Sn–C), 279s; ν (Sn–Cl); 304s; δ (Sn–Cl), 179m, 159m, 152m, 139m
9	3126m, 3110w, 3030m	1578w, 1551vw	596m, 433m, 287m, 202m	ν (Sn–Cl), 344sbr, 328s, 315w; δ (Sn–Cl), 153m, 141w
10	3118m, 3102w, 3106w	1577w	594m, 430m, 360w, 305m, 280w	ν (Sn–Br), 246m, 221m; δ (Sn–Br), 169br, 151w, 121w, 101m
L ^T		1585m, 1575sh	565w, 528w, 516w, 390w, 367w, 282m br, 230m	
11	3068vw, 3043vw	1576m, 1540m, 1508m	542m, 465m, 458s, 419w, 393w, 369w	ν (Sn–C), 272s; ν (Sn–Cl), 288s, 255vs, 232vs; δ (Sn–Cl): 204m, 151m
12		1575m, 1558m, 1539w, 1508m	570w, 419w, 373m, 142br	ν (Sn–Cl), 325m, 270br, 250br; δ (Sn–Cl), 206m, 142br; ν (Sn–C), 541m
13		1575w	561vw, 537vw, 456m, 230w, 152vw	ν (Sn–C), 285br; ν (Sn–Cl), 329s; δ (Sn–Cl), 200m, 152s br
14		1580w, 1540m	536m, 417vw, 376w,	ν (Sn–C), 615m, 589m; ν (Sn–Cl), 366s, 273s br; δ (Sn–Cl), 206w, 142s
15		1586w	517br, 296w	ν (Sn–Br), 210m; δ (Sn–Br), 135br; ν (OH), 3200br
16		1559m	514br, 296br, 225s br, 200s br	ν (Sn–I), 144m, 137m
L ^A	3115m	1515s	490m, 470w, 358w	ν (CH ₂), 2955m
17	3140m, 3120m	1520m, 1510m	522w, 417s, 341s	ν (Sn–C), 572s; ν (OH), 3380br; ν (Sn–Cl): 270–240br
18	3150w, 3140w, 3120m	1559w, 1542m,	480m, 360m, 340m 1508w	ν (Sn–C), 551s, 541s; ν (Sn–Cl), 320s, 305s, 280s, 247s
19	3140w, 3120w	1570m, 1510m	550w, 460s, 431w, 398w, 351m	ν (Sn–C): 279s; ν (Sn–Cl), 270s br
20	3120m	1560w, 1510sh, 1500m	550w, 470s, 419w, 398w, 352m, 225m	ν (Sn–C), 280m; ν (Sn–Cl), 325s, 302s; δ (Sn–Cl), 203m, 177m, 151m
21	3140m	1520sh, 1510m	400s br, 280m, 247m, 225m	ν (Sn–C), 618s; δ (Sn–Cl), 203m, 177m 156m; ν (Sn–Cl), 352m, 330s, 302m
22	3123m	1558m, 1515w	552w, 445w, 419w, 281m, 245m	ν (Sn–Cl), 340br, 324s, 300s; δ (Sn–Cl), 200–150s br
23	3119w	1560w, 1515w	552w, 419w, 281w	ν (Sn–Cl), 318s br; ν (OH): 3300br
24	3120sh, 3100w	1510m	600m, 576m, 351w, 300m, 283m	ν (Sn–Br), 230s, 215s br; ν (OH), 3300–3200br; δ (OH): 1580br
25	3127w, 3071w	1525m	397m, 352m, 333m, 295m, 280m, 247m, 225w	ν (Sn–I), 150s, 140s, 124s
L ^B	3120w	1515s	460w, 375w, 340w, 295m, 280m	
26	3180w, 3130m	1580w, 1549m	280m, 254m	ν (Sn–C), 553m, 543m; ν (Sn–Cl), 300m; ν (OH), 3319br; δ (Sn–Cl), 177m, 156m
27	3131m, 3053m	1590m, 1563m, 1516m	585m, 430, 456m, 232m, 181m	ν (Sn–C), 268m; ν (Sn–Cl): 300m, 291m; ν (OH), 3349s br; δ (Sn–Cl), 181m, 156br

Table 4 (continued)

Compound	ν (cm ⁻¹)			Other data
	> 3000 cm ⁻¹	1600–1500 cm ⁻¹	< 600 cm ⁻¹	
28	3134w	1598m, 1560m, 1515m	550m, 330w, 320w, 280w, 250m, 240m	ν (Sn–C), 620br; ν (OH): 3320br; ν (Sn–Cl), 300m, 290m
29	3133m	1591m, 1558w	490s br, 227w, 212w, 161s	ν (Sn–Cl), 320–280br
30	3140m, 3129m	1590m, 1552m	528m, 503m, 482m, 469m, 444m, 326m, 280m,	ν (Sn–Br), 240s, 220s, 211s, 194s
31	3123w	1559w, 1542w, 1508w	550w, 524m, 398w, 352m, 280m, 247w, 203w, 195w	ν (Sn–I), 152m, 138s, 134s
32	3029sh	1578m, 1515m	539m, 400m, 373m, 280s, 247m	ν (Sn–Cl), 337s, 310s; ν (N–H), 3200br δ (Sn–Cl), 170s, 150vs

^a Nujol mull.



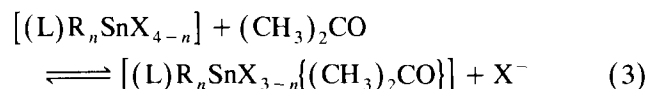
32 being formed. Reaction (2) is unusual, but recently, cleavage of a carbon (sp³)–nitrogen bond in L³ has been reported in platinum(II) [25], vanadium(IV) and tin(IV) [26] chemistry and it has been hypothesized, in the case of platinum compounds, that an agostic M ··· H–C “interaction” between the metal and one of the protons of the methyl groups, analogous to that observed in the structure of [(L³)PdCl₂] [27], takes place. In our case such an agostic “interaction” is not possible. However, the bond cleavage observed could be explained by the greater stability of the adduct **32** than the adduct between SnCl₄ and L^T, perhaps owing to the greater steric bulk of the donor bis(3,4,5-trimethylpyrazol-1-yl)methane.

All the compounds, colourless precipitates (with the exception of **16**, **25** and **31**, which are red, a colour which arises because of charge transfer) were characterized by the analytical data listed in Table 3, together with their melting points, yields and specific conductivities. They are generally soluble in acetone, ethanol, dimethylsulphoxide (DMSO) and acetonitrile, but insol-

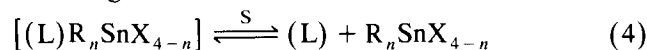
uble in water, whereas the diorganotin(IV) derivatives are also soluble in chlorinated solvents. As previously found for tris(pyrazolyl)borates and tetrakis(pyrazolyl)borates [28] no adducts could be isolated under our conditions when trimethyl-, tri-*n*-butyl- or triphenylchlorotin(IV) was employed, consistent with the low acidity of this organotin(IV) acceptor [29].

3.1. Conductivity data

The complexes **1–11**, **13**, **17–23** and **26–29** are not electrolytes in acetone, ruling out ionic structures in this solvent or equilibria such as



However, according to the molecular weights determined by vapour pressure osometry, the diorganotin complexes **1**, **2**, **6** and **11** are extensively dissociated into the starting reagents (the ratio *n* of the determined molecular weight to the formula weight, being 0.56, 0.46, 0.50 and 0.46 respectively in chloroform and 0.70, 0.65, 0.68 and 0.62 respectively in acetone solution) according to



In acetone solution the remaining compounds **12**, **14–16**, **24,25** and **30–32** are partly ionized (the typical 1:1 electrolyte tetra-*n*-butylammonium bromide has a specific conductivity of 137 Ω⁻¹ cm² mol⁻¹), and in this case an ionization such as that indicated in Eq. (3) is suggested.

The complexes **3**, **5–9**, **18**, **27** and **28** are not electrolytes even in DMSO solution, whereas **2**, **10**, **23**, **24**, **29** and **30**, non-electrolytes in acetone, become conducting in DMSO, but the solvation in this case is due to the strongly complexing nature of DMSO.

3.2. IR data

The IR spectra (Table 4) of **1–31** show several bands which may be taken as diagnostic of bis(pyrazol-1-yl)al-

Table 5
¹H NMR data

Compound	Solvent	δ (ppm)					Other data
		CH ₂	4-CH	3-CH	5-CH	CH ₃	
L ⁴	Acetone	6.20s		7.55s	7.26s	2.00s	
	DMSO	6.22s		7.67s	7.30s	2.00s	
	CDCl ₃	6.23s		7.37s	7.33s	2.00s	
1	CDCl ₃	6.14s		7.39s	7.35s	2.03s	CH ₃ -Sn, 1.21s (² J(¹¹⁹ Sn- ¹ H) = 71.0 Hz) (² J(¹¹⁷ Sn- ¹ H) = 67.9 Hz)
2	CDCl ₃	6.13s		7.38s	7.34s	2.04s	CH ₃ -Sn, 1.40s (² J(¹¹⁹ Sn- ¹ H) = 85 Hz)
3	CDCl ₃	6.14s		7.40s	7.35s	2.03s	R-Sn, 1.45t, 1.79q (³ J(¹¹⁹ Sn- ¹ H) = 66 Hz)
4	CDCl ₃	6.20s		7.40s	7.37s	2.02s	R-Sn, 1.40t, 1.83q (³ J(¹¹⁹ Sn- ¹ H) = 79 Hz)
5	CDCl ₃	6.75s br		7.96s br	7.60s br	2.08s	CH ₃ -Sn, 1.60br
6	CDCl ₃	6.10s br		7.40br	7.40br	2.02s	Ph-Sn, 7.60–7.50m, 7.65–7.85m
7	CDCl ₃	6.55br		7.70br	7.42br	2.05s br	Ph-Sn, 7.55br, 7.70br
	Acetone	7.05br		8.00br	7.40m br	2.15s br	Ph-Sn, 7.40m br
8	CDCl ₃	6.80s br		7.96s br	7.63s	2.04s	ⁿ Bu-Sn, 0.96t, 1.42p s, 1.83m, 2.05t
9	Acetone	7.20br		8.33br	8.20br	2.25br	
10	Acetone	7.30s		8.45s	8.13s	2.20s	
L ^T	Acetone	6.00s				1.81s, 2.01s, 2.34s	
	DMSO	6.04s				1.81s, 2.02s, 2.32s	
	CDCl ₃	6.03s				1.83s, 2.10s, 2.31s	
	CD ₂ Cl ₂	5.96s				1.84s, 2.07s, 2.34s	
11	CDCl ₃	6.02				1.85s, 2.10s, 2.30s	Ph-Sn, 7.50m, 7.70m, 7.95m
12	Acetone	6.30				1.88s, 2.15s, 2.43s	CH ₃ -Sn, 1.63s H ₂ O, 4.24s br
13	Acetone	6.11				1.86s, 2.03s, 2.40s	Ph-Sn, 7.14–7.58m, 7.80–7.92m, 8.06–8.12m
14	CDCl ₃	6.40s				1.90s, 2.25s, 2.43s	ⁿ Bu-Sn, 0.95t, 1.40p s, 1.78–2.06m br, 2.26p t
15	CDCl ₃	6.56s				1.90s, 2.25s, 2.43s	O-H, 6.25s
16	Acetone	6.53s				1.98s, 2.25s, 2.50s	
L ^A	Acetone	4.68s	6.11t	7.46d (<i>J</i> _{3,4} = 2.0 Hz)	7.21 (<i>J</i> _{4,5} = 2.4 Hz)		
	DMSO	4.55s	6.18t	7.49d (<i>J</i> _{3,4} = 1.8 Hz)	7.39d (<i>J</i> _{4,5} = 2.1 Hz)		
	CDCl ₃	4.52s	6.07t	7.50d (<i>J</i> _{3,4} = 1.9 Hz)	6.89d (<i>J</i> _{4,5} = 2.3 Hz)		
17	CDCl ₃	4.54s	6.10t	7.50d (<i>J</i> _{3,4} = 1.4 Hz)	6.90d (<i>J</i> _{4,5} = 2.1 Hz)		CH ₃ -Sn, 1.30s (² J(¹¹⁹ Sn- ¹ H) = 72.5 Hz) (² J(¹¹⁷ Sn- ¹ H) = 69.3 Hz)
18	CDCl ₃	4.68s	6.20t	7.61d (<i>J</i> _{3,4} = 2.0 Hz)	7.50d (<i>J</i> _{4,5} = 2.4 Hz)		CH ₃ -Sn, 1.65s (² J(¹¹⁹ Sn- ¹ H) = 106.5 Hz) (² J(¹¹⁷ Sn- ¹ H) = 101.8 Hz)
19	CDCl ₃	4.52s	6.10t	7.50d (<i>J</i> _{3,4} = 1.7 Hz)	6.90d (<i>J</i> _{4,5} = 2.1 Hz)		Ph-Sn, 7.55–7.60m, 7.68–7.72m
20	Acetone	4.70s	6.20t	7.60d (<i>J</i> _{3,4} = 1.9 Hz)	7.40d (<i>J</i> _{4,5} = 2.4 Hz)		Ph-Sn, 7.45–7.48m, 7.84–7.87m
21	CDCl ₃	4.60s	6.18t	7.60d (<i>J</i> _{3,4} = 2.1 Hz)	7.40d (<i>J</i> _{4,5} = 2.4 Hz)		ⁿ Bu-Sn, 0.89t, 1.40ps, 1.72–1.86m, 2.08–2.14m
22	Acetone	4.90s	6.30t	7.79d (<i>J</i> _{3,4} = 1.7 Hz)	7.60 (<i>J</i> _{4,5} = 2.1 Hz)		H ₂ O, 8.95br
24	Acetone	4.95s	6.43t	7.85d (<i>J</i> _{3,4} = 2.4 Hz)	7.72d (<i>J</i> _{4,5} = 2.4 Hz)		
25	Acetone	4.85s	6.38t	7.74d (<i>J</i> _{3,4} = 2.1 Hz)	7.59d (<i>J</i> _{4,5} = 2.4 Hz)		H ₂ O, 5.60s br
L ^B	Acetone	4.25s	5.64s			1.67s, 2.11s	
	DMSO	4.20s	5.70s			1.66s, 2.10s	
	CDCl ₃	4.30s	5.65s			1.62s, 2.20s	
	CD ₃ OD	4.28s	5.73s			1.62s, 2.16s	

Table 5 (continued)

Compound	Solvent	δ (ppm)					Other data
		CH ₂	4-CH	3-CH	5-CH	CH ₃	
26	CD ₃ OD	4.40s	5.95s			1.80s, 2.25s	CH ₃ -Sn, not observed
	Acetone	4.50s	5.95s			1.90s, 2.25s	CH ₃ -Sn, 1.45s (² J(¹¹⁹ Sn- ¹ H): 58.5 Hz)
27	Acetone	4.51s	5.95s			1.98s, 2.25s	H ₂ O, 4.20s br Ph-Sn, 7.20–8.20m
28	CDCl ₃	4.60s	5.90s			1.95s, 2.30s	ⁿ Bu-Sn: 0.92t, 1.44ps, 1.75–1.95m, 2.14–2.28m H ₂ O, 5.3s
29	CD ₃ OD	4.50s	6.10s			1.92s, 2.25s	H ₂ O, 4.96s br
30	Acetone	4.65s	6.03s			2.00s, 2.25s	
31	Acetone	4.78s	6.23s			2.24s, 2.38s	
32	Acetone					2.00s, 2.57s, 2.73s	N-H, 7.32s br

^a Chemical shifts measured from internal standard tetramethylsilane (TMS): s, singlet; m, multiplet; t, triplet; q, quartet; ps, pseudo-sixtet; br, broad.

kane ligands, weak and medium vibrations at about 3100 cm⁻¹ due to C–H stretching of the heterocyclic ring, and other more intense vibrations between 1600 and 1500 cm⁻¹ typical of ring breathing [30].

In the far-IR spectra of the dimethyltin(IV) complexes, we assign the strong band at about 570 cm⁻¹ to $\nu_{\text{asym}}(\text{Sn}-\text{C})$, whereas we find no evidence for $\nu_{\text{sym}}(\text{Sn}-\text{C})$, consistent with an approximately linear *trans*-(R)₂ configuration [31].

The RSnX₃ adducts show, as expected [32], a single Sn–C stretching vibration at around 270 cm⁻¹ (R ≡ phenyl), 540 cm⁻¹ (R ≡ methyl) and 600 cm⁻¹ (R ≡ *n*-butyl).

In addition, in the phenyltin(IV) derivatives two weak bands in the 170–300 cm⁻¹ region and other more intense band at about 450 cm⁻¹ can always be detected, which are assigned to “in-plane phenyl ring rotation” (Whiffen’s *u* notation), “out-of-plane phenyl ring bending” (*x*) and “out-of-plane bending” (*y*) [33].

The tin–halogen stretching frequencies may be assigned with more certainty. A single broad band at about 260 cm⁻¹ assignable as $\nu(\text{Sn}-\text{Cl})$ is observed for the diorganotin(IV) complexes [34], whereas these are two or three bands between 270 and 300 cm⁻¹ for the trihalide and more than three bands between 350 and 300 cm⁻¹ for the tetrahalidotin(IV) derivatives consistent for the last with a *cis* structure, analogous to that described [35] for analogous complexes of 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen).

The (Sn–Cl) stretching absorptions described in the literature [35,36] for compounds of formula *cis*-[Cl₄Sn(L)₂] and [Cl₄Sn(L–L)] imply that our ligands are poorer donors than pyridine, bipy and phen. The Sn–Cl bond becomes stronger and the Sn–Cl stretching frequencies increase as the Sn–L bond becomes weaker [37], and in our compounds the $\nu(\text{Sn}-\text{Cl})$ are higher than those detected for SnCl₄ adducts of other borderline *N*-donors.

Finally, in the spectra of **10**, **15**, **24** and **30**, we assign the broad bands at about 240 cm⁻¹ to $\nu(\text{Sn}-\text{Br})$, while in the spectra of **16**, **25** and **31** the broad bands at about 150 cm⁻¹ are likely to be due to $\nu(\text{Sn}-\text{I})$. These assignments are consistent with those previously reported for other octahedral or pseudo-octahedral tin(IV) halide complexes of nitrogen donors [34–37].

In none of the compounds can the Sn–N stretching bands be assigned.

In the IR spectrum of **32**, consistent with the structure proposed, the N–H stretching vibration, which shifted to lower frequencies compared with the broad $\nu(\text{N}-\text{H})$ absorption observed (about 3300 cm⁻¹) for 3,4,5-trimethylpyrazole, is also detected.

3.3. NMR data

The ¹H (Table 5) and ¹³C NMR spectra (Table 6) of **1–31** in chloroform solution or, when not possible, in acetone or methanol, support the formulae proposed and show that ligand L has not undergone any structural change upon coordination.

On comparison between the chemical shifts related to the same type of proton in the free bases and in their diorganotin(IV) complexes, and when the molecular weight determinations mentioned above are considered, here is extensive dissociation of this type of adduct in acetone and in chloroform solution. For mono-organotin(IV) halide compounds, when complexation occurs, a downfield displacement of all the signals was observed. Additional support for our hypotheses are by the magnitudes of ²J(¹¹⁹Sn-¹H); for example, the ²J(¹¹⁹Sn-¹H) values for **1**, **2** and **17** are in the range 68–73 Hz comparable with the values 67–68 Hz reported for the uncomplexed four-coordinated dimethyltin(IV) chloride or bromide [38], whereas the value for **18** (106.5 Hz) is comparable with those previously reported for six-coordinated pseudo-octahedral tin(IV) adducts [39].

The ^{119}Sn NMR data (Table 7) are reported for only some compounds, because the quality of the spectra is sometimes poor owing to the low solubility. The ^{119}Sn NMR chemical shifts of the dimethyltin(IV) and diethyltin(IV) halide derivatives are comparable with that of the corresponding Lewis acid in the same solvent [40] and clearly indicate that this type of complex is extensively dissociated in chloroform solution. Acetone solutions of **7**, **14**, **22** and **29** show more than one signal (the same multiplicity is often observed in the ^{13}C spectra), but none of the signals corresponds to the starting tin(IV) derivative. Isomers are possible for the organ-

otin(IV) trihalide derivatives in general, but not for adducts of SnCl_4 , for which an octahedral solid state structure is likely. These complexes may undergo different equilibria in acetone solution, as indicated by conductivity data. For example, both ionized and non-ionized species, as in equilibrium (3) are likely to be present.

3.4. ^{119}Sn Mössbauer data

The isomer shift (ISs), quadrupole splittings (QSs), average linewidths Γ^\pm at half-maximum and calculated C–Sn–C bond angles are reported in Table 8.

Table 6
 ^{13}C NMR data of the ligands and of their complexes

Compound	Solvent	δ (ppm) (J (Hz))					
		CH_2	C(3)	C(4)	C(5)	CH_3	Sn–C
L^{D}	CDCl_3	65.8	141.8	118.1	128.5	9.3	
	Acetone	66.1	141.7	117.9	129.4	9.1	
1	CDCl_3	65.6	141.9	118.2	128.7	9.3	8.1
2	CDCl_3	65.2	141.3	117.6	128.1	8.4	8.8
3	CDCl_3	65.8	141.8	118.2	128.6	9.3	9.7 (CH_3); 19.1 (CH_2)
4	CDCl_3	65.0	141.4	117.6	128.3	8.8	10.1 (44) (CH_3); 19.8 (CH_2)
5	CDCl_3	59.1, 62.6	141.9	117.6	130.2	8.8	NO
6	CDCl_3	64.9	141.5	117.6	128.4	8.8	129.6 (88), 131.6 (18), 135.0 (65)
7	CDCl_3	61.8	142.1	117.4	131.2	8.7	13.6, 25.4, 27.9, 43.7
8	Acetone	62.9	143.2	118.0	131.8	8.9	129.2, 130.7, 135.0, 136.4
		62.4	142.9	114.4	133.0		
9	Acetone	61.1	142.0	117.3	133.7	7.6	
10	Acetone	60.5	141.2	116.7	134.0	7.6	
L^{T}	CDCl_3	61.4	147.6	113.1	137.3	8.5, 10.2, 12.4	
	Acetone	60.9	147.5	112.8	137.5	8.3, 10.0, 12.3	
11	CDCl_3	61.1	147.9	113.2	137.4	8.5, 10.3, 12.4	130.0 (88), 132.0 (17), 135.6 (64), 139.0
12	Acetone	58.8	NO	NO	NO	6.9, 8.8, 11.0	NO
13	CDCl_3	59.8	148.4	114.5	138.5	8.3, 10.5, 12.1	14.1 (CH_3), 25.9, 27.9, 30.2 (CH_2)
14	Acetone	59.5	146.4	111.9	135.7	7.0, 8.8, 10.9	127.2, 128.1, 133.7 (81), 137.0
15	Acetone	60.4	148.3	114.9	140.8	8.1, 10.2, 11.7	
L^{A}	Acetone	51.9	139.7	105.4	130.4		
	CDCl_3	51.8	140.2	105.4	130.2		
17	CDCl_3	52.3	140.7	106.0	130.9		9.2 (CH_3)
18	Acetone	52.6	140.2	106.7	132.4		20.8s br
	CDCl_3	51.8	140.1	105.7	130.8		NO
19	CDCl_3	51.8	140.3	105.4	130.3		129.7 (86), 131.8 (18), 135.0 (66), 137.2
20	Acetone	52.6	140.2	106.7	132.4		130.2 (93), 131.8 (19), 136.4 (65), 138.0
21	CDCl_3	51.7	139.9	105.8	131.0		13.5, 25.4, 27.3
22	Acetone	52.6	140.0	107.3	133.7		
23	Acetone	52.6	140.0	107.1	133.2		
24	Acetone	52.5	139.5	107.7	134.1		
25	Acetone	51.3	138.6	105.9	131.9		
	CDCl_3	48.7	148.1	104.8	140.4	9.5, 13.4	
	Acetone	49.6	148.2	105.5	140.9	10.1, 14.0	
	CD_3OD	^b	149.6	106.1	142.4	9.7, 13.2	
	CD_3OD	^b	149.5	107.5	144.3	10.2, 12.9	
27	Acetone	48.4	146.9	105.3	141.6	9.2, 12.1	128.7, 130.3, 135.3, 136.7
28	CDCl_3	48.3	147.5	105.9	142.3	10.2, 12.9	13.5, 25.5, 27.4, 29.7
29	CD_3OD	^b	149.3	108.1	145.3	10.5, 12.6	
30	Acetone	49.1	148.1	107.4	144.2	10.7, 13.0	
31	Acetone	47.6	146.8	106.9	144.2	9.8, 11.4	

NO, not observed.

^a Chemical shifts from internal TMS.

^c The singlet of the CH_2 could not be assigned owing to the presence of several overlapping bands of the solvents.

Table 7
¹¹⁹Sn NMR data

Compound	Solvent	δ (ppm) from tetramethyltin(IV) [relative intensity (%)]
Me ₂ SnCl ₂ ^a	30% CH ₂ Cl ₂	+137
[(L ^d)Me ₂ SnCl ₂] (1)	Acetone	+107.4
[(L ^A)Me ₂ SnCl ₂]-H ₂ O (17)	CDCl ₃	+101.5
Me ₂ SnBr ₂ ^a	3–20% CHCl ₃	+70
[(L ^d)Me ₂ SnBr ₂] (2)	CDCl ₃	+66
Et ₂ SnCl ₂ ^a	30% CCl ₄ /CH ₂ Cl ₂	+121
[(L ^d)Et ₂ SnCl ₂] (3)	CDCl ₃	+121.9
Et ₂ SnBr ₂ ^a	20% CCl ₄	+96
[(L ^d)Et ₂ SnBr ₂] (4)	CDCl ₃	+83
Ph ₂ SnCl ₂ ^a	CH ₂ Cl ₂	-32
[(L ^d)Ph ₂ SnCl ₂] (6)	CDCl ₃	-53.3
[(L ^T)Ph ₂ SnCl ₂]-H ₂ O (11)	Acetone	-188.7
[(L ^A)Ph ₂ SnCl ₂] (19)	CDCl ₃	-38.2
MeSnCl ₃ ^a	Acetone	-150.0
	3–20% CHCl ₃	+21
[(L ^A)MeSnCl ₃] (18)	Acetone	-227.5
	Acetone	-261.4
	CD ₃ OD	-400.0
PhSnCl ₃ ^a	Acetone	-256.9
	CH ₂ Cl ₂	-63
[(L ^T)PhSnCl ₃]-H ₂ O (14)	Acetone	-195.9, 197.0, -197.2 [\approx 30, 40 and 30 respectively]
[(L ^A)PhSnCl ₃] (20)	Acetone	-156.3
[(L ^B)PhSnCl ₃]-H ₂ O (27)	Acetone	-172.09 (1% P/V)
[(L ^B)PhSnCl ₃]-H ₂ O (28)	Acetone	-212.8 (2% P/V)
BuSnCl ₃ ^a	CDCl ₃	-3.3
[(L ^d)BuSnCl ₃] (7)	CDCl ₃	-450br
	Acetone	-253.0, -260br, -423.1, -429.6 [\approx 20, 20, 25 and 25 respectively]
SnCl ₄ ^a	Liquid	-150
[(L ^d)SnCl ₄] (9)	Acetone	-649.6
[(L ^A)SnCl ₄] (22)	Acetone	-609.2, -609.9, -636.6, -641.9, -678.4 [\approx 15, 20, 20, 20 and 15 respectively]
[(L ^B) ₂ (SnCl ₄) ₃] · $\frac{1}{3}$ Et ₂ O (29)	Acetone	-602.4, -656.5 [\approx 45 and 55% respectively]
[(pzH) ₂ SnCl ₄] (32)	Acetone	-677.9

^a Data from [38,40].Table 8
Mössbauer data

Compound	IS ^a (mm s ⁻¹)	QS (mm s ⁻¹)	I^{\pm} (mm s ⁻¹)	C-Sn-C (°)
[(L ^d)(CH ₃) ₂ SnCl ₂] (1)	1.40 ± 0.05	3.95 ± 0.05	0.91	166
[(L ^T)(C ₆ H ₅) ₂ SnCl ₂]-H ₂ O (11)	1.35	3.43	1.09	150
[(L ^A)(C ₆ H ₅) ₂ SnCl ₂] (19)	1.34	3.46	0.87	151
[(L ^A)(C ₆ H ₅)SnCl ₃] (21)	0.92	1.92	1.07	
[(L ^A)SnBr ₄] (24)	0.74	0	1.02	
[(LA)SnI ₂ (OH) ₂] (25)	0.23	0	1.35	
[(L ^B)(C ₆ H ₅)SnCl ₃]-H ₂ O (27)	0.74	1.91	1.12	
[(L ^B)(C ₄ H ₉)SnCl ₃] (28)	0.90	2.08	1.02	
[(L ^B) ₂ (SnCl ₄) ₃]- $\frac{1}{3}$ Et ₂ O (29)	0.36	0	1.20	
[(L ^B)SnBr ₄] (30)	0.57	0	1.12	

^a With respect to a room-temperature spectrum of CaSnO₃.

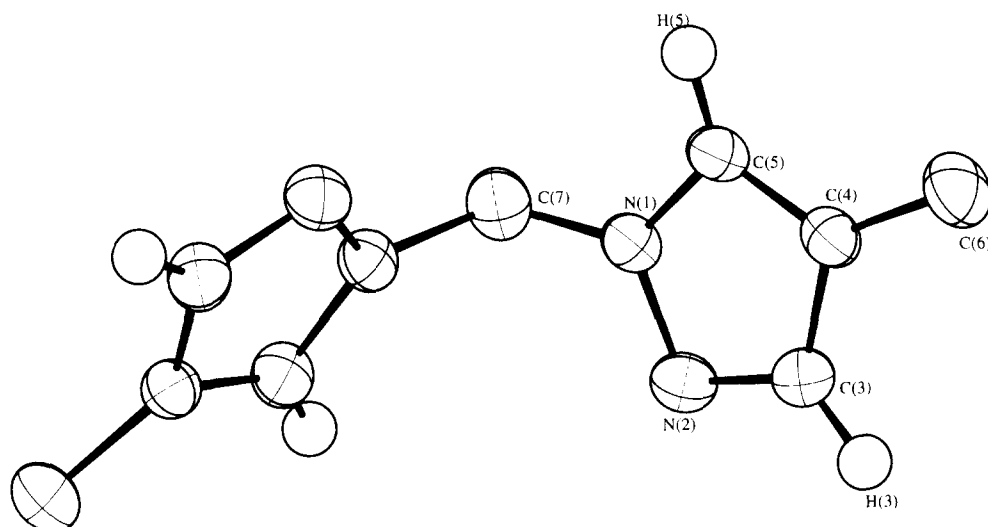


Fig. 2. The molecular structure of L^4 with atom numbering, as used in the crystallographic work.

The value of the IS decreases on going from four- to six-coordinated species and increases with the covalent character of the tin–ligand bonds. The shifts are typical of tin(IV) in inorganic and organometallic derivatives. The SnX_4 complexes **24**, **29** and **30** all show less positive IS values than the tetrahalides ($IS = 0.84 \text{ mm s}^{-1}$ and 1.05 mm s^{-1} for $SnCl_4$ and $SnBr_4$ respectively [41]), indicating a decrease in s-electron density and Sn–X bond covalency upon coordination. The low IS value of **25** is attributable to the higher electronegativity of the two OH groups. The same trend is observed in R_2SnCl_2 complexes, where the IS value of the phenyl derivative **27** is about 0.2 mm s^{-1} lower than those of the alkyl derivatives **21** and **28**.

Complexes **24**, **25**, **29** and **30** show a single resonance typical of a cubic symmetry around the tin. The

large values of Γ^\pm for **25**, **29** and **30** indicate unresolved QS, and the value was calculated for similar complexes [42]. This is due to a distortion from ideal octahedral symmetry, which can arise either on account of the different electron-withdrawing properties of the atoms bound to the tin, or on account of the steric demands of the ligands, which causes the N–Sn–N angle to deviate from 90° .

The R_2SnCl_2 and R_2SnCl_2 complexes have QS values consistent with six-coordinated structures. The QSs of the R_2SnCl_2 derivatives clearly indicate *trans*- R_2 configurations [42,43]. Using the Parish [43] relationship between QS and C–Sn–C angles, the latter have been estimated as 150° and 151° for the phenyl derivatives **11** and **19** respectively.

The calculated C–Sn–C angle (166°) in $[(L^4)(CH_3)_2-$

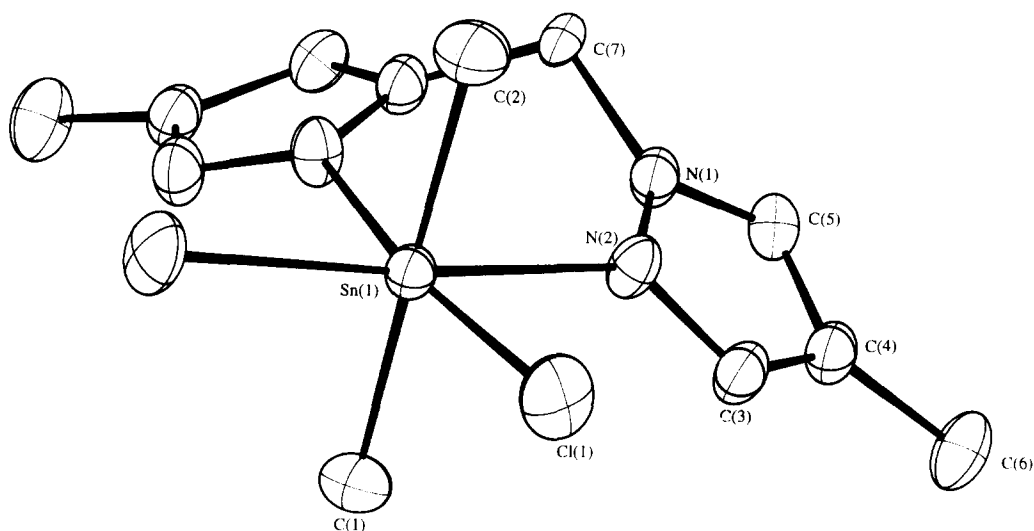


Fig. 3. The molecular structure of $(L^4)Sn(CH_3)_2Cl_2$ with atom numbering, as used in the crystallographic work.

Table 9

Interatomic distances (Å) and bond angles (deg) with e.s.d.'s in parentheses, for L⁴

Distances			
N(1)–N(2)	1.349(3)	C(3)–C(4)	1.398(3)
N(1)–C(5)	1.357(3)	C(4)–C(5)	1.355(3)
N(1)–C(7)	1.439(3)	C(4)–C(6)	1.497(3)
N(2)–C(3)	1.320(3)		
Angles			
N(2)–N(1)–C(5)	111.7(2)	C(3)–C(4)–C(5)	103.8(2)
N(2)–N(1)–C(7)	120.4(1)	C(3)–C(4)–C(6)	127.7(2)
C(5)–N(1)–C(7)	127.9(2)	C(5)–C(4)–C(6)	128.5(2)
N(1)–N(2)–C(3)	103.8(2)	N(1)–C(5)–C(4)	107.7(2)
N(2)–C(3)–C(4)	113.0(2)	N(1)–C(7)–N(1) ⁱ	112.7(3)

ⁱ Symmetry code: 2 – x, y, 1/2 – z.

SnCl₂] (**1**) is fairly near to the angle determined by X-ray analysis (174°).

3.5. Diffraction study of bis(4-methylpyrazol-1-yl)methane (L⁴) and of {[bis(4-methylpyrazol-1-yl)methane}dimethyldichlorotin(IV) [(L⁴)(CH₃)₂SnCl₂]

Fig. 2 shows the structure of the molecule of L⁴, which lies on a crystallographic two-fold axis passing through the C(7) atom.

The pyrazole ring is essentially planar (the least-squares planes of the two pyrazole rings and the displacements of atoms from it are available as supplementary material) with deviation from the best plane, passing through the non-hydrogen atoms in the range ±0.005 (3) Å. The angle between the symmetry-related pyrazole rings is 106.70 (7)°. The bond distances and angles are listed in Table 9. We compared the molecular parameters of L⁴ with those reported for similar derivatives and we found that the bond angles agree with the empirical rules of Bonati [44] concerning pyrazoles. The pyrazole ring geometry in L⁴ and in pyrazole [45] are very similar. There are small differences between L⁴ parameters and those of the analogous compound bis(4-nitropyrazol-1-yl)methane [46].

Fig. 3 shows the structure of the adduct **1** which consists of discrete molecules, with the tin atom surrounded by six donor atoms in a slightly distorted octahedral configuration, with a *cis* arrangement of the chloro ligands and a *trans* arrangement of the methyl groups. The adduct has a crystallographic mirror plane passing through Sn, C(1), C(2) and C(7) atoms. The bond distances and angles are listed in Table 10.

The effects of complex formation upon the distances and the angles of pyrazole rings are slight. Only small changes were observed in the molecular parameters of [(L⁴)(CH₃)₂SnCl₂] compared with free L⁴ (for instance N(1)–C(7)–N(1') in the complex is 2.5° smaller than in free L⁴).

The pyrazole ring still maintains its planarity (supplementary material), with maximum deviations of ±0.001(7) Å, and the angle between the two planes (that are still symmetry related) is 57.6(2)°.

The angle between the pyrazole ring and the (Sn, Cl, N) plane is 29.8(2)° and compares well with the values reported for other N ligands in similar complexes [47]. For instance, *trans*-[SnMe₂Cl₂(NC₃H₅)₂] [48] has an angle between the rings equal to 26° and, as for L⁴, non-bonding interactions determine the orientation of the ring about the Sn–N bond.

The six-membered chelate ring shows a very slightly distorted boat conformation. This is clear from the analysis of the puckering coordinate [49] with *Q* = 0.691 (8) Å, *φ* = 0.0(6)° and *θ* = 93.4(6)° and from the confrontation of *q*₂ and *q*₃ (which are 0.690(8) and –0.041(7) Å respectively) with *Q*. The displacements of the Sn and C(7) atoms from the plane passing through the four nitrogen atoms are –0.516(4) and –0.6451 (8) Å respectively, and the angle between this plane and the pyrazole ring is 29.6(2)°.

In Table 11, selected bond distances and angles of [(L⁴)(CH₃)₂SnCl₂] are compared with the values reported for other [R₂X₂N₂Sn] compounds [47,48,50–77]. Several general patterns emerge; for example, all the diorganotin(IV) dihalide derivatives with monodentate nitrogen-donor ligands (**I–XII**) have a perfect octahedral environment with all-*trans* coordination. The stereochemistry of the SnR₂ skeleton in complexes with bidentate N₂ donor is generally *trans* or distorted *trans*, with the exception of the derivatives **XXXVI–XXVIII**, where the presence of poor σ-donor aryl groups allows a distorted *cis* structure. Compounds with chem-

Table 10

Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses, for [(L⁴)Sn(CH₃)₂Cl₂]

Interatomic distances			
Sn(1)–Cl(1)	2.498(2)	N(1)–C(7)	1.471(4)
Sn(1)–N(2)	2.438(6)	N(2)–C(3)	1.340(5)
Sn(1)–C(1)	2.131(9)	C(3)–C(4)	1.39(1)
Sn(1)–C(2)	2.111(8)	C(4)–C(5)	1.371(7)
N(1)–N(2)	1.345(8)	C(4)–C(6)	1.512(9)
N(1)–C(5)	1.355(9)		
Interatomic angles			
Cl(1)–Sn(1)–Cl(1) ^a	100.2(1)	C(5)–N(1)–C(7)	125.8(6)
Cl(1)–Sn(1)–N(2)	91.7(2)	Sn(1)–N(2)–N(1)	126.8(3)
Cl(1)–Sn(1)–N(2) ^a	168.1(1)	Sn(1)–N(2)–C(3)	126.4(4)
N(2)–Sn(1)–N(2) ^a	76.4(3)	N(1)–N(2)–C(3)	105.1(6)
Cl(1)–Sn(1)–C(1)	93.0(3)	N(2)–C(3)–C(4)	111.3(5)
N(2)–Sn(1)–C(1)	86.3(4)	C(3)–C(4)–C(5)	105.1(5)
Cl(1)–Sn(1)–C(2)	91.0(3)	C(3)–C(4)–C(6)	127.3(6)
N(2)–Sn(1)–C(2)	88.9(4)	C(5)–C(4)–C(6)	127.6(8)
C(1)–Sn(1)–C(2)	173.8(6)	N(1)–C(5)–C(4)	107.2(7)
N(2)–N(1)–C(5)	111.4(4)	N(1)–C(7)–N(1) ^a	110.2(4)
N(2)–N(1)–C(7)	122.8(6)		

^a Symmetry code: x, 1/2 – y, z.

Table 11
Comparison of structural data for $[R_2X_2N_2Sn]$ compounds

Compound	Bond length (Å)			Bond angle (°)			Reference
	Sn–C	Sn–N	Sn–X	C–Sn–C	X–Sn–X	N–Sn–N	
[(Imidazole) ₂ (CH ₃) ₂ SnCl ₂] (I)	2.110(3)	2.312(2)	2.5955(7)	180	180	180	[50]
[(Pyrazole) ₂ (CH ₃) ₂ SnCl ₂] (II)	2.114(13)	2.338(6)	2.570(3)	180	180	180	[51]
[(3,5-Me ₂ pyrazole) ₂ (CH ₃) ₂ SnCl ₂] (III)	2.11(1), 2.12(1)	2.379(6)	2.581(2)	180	180	180	[47]
[(2-Chloroimidazole) ₂ (CH ₃) ₂ SnCl ₂] (IV)	2.134(4)	2.380(4)	2.591(2)	180	180	180	[52]
[Bis(N-methylimidazole)(CH ₃) ₂ SnCl ₂] (V)	2.118(5)	2.329(5)	2.571(3)	180	180	180	[53]
[(Pyridine) ₂ (CH ₃) ₂ SnCl ₂] (VI)	2.15(2)	2.39(2)	2.570(1)	180	180	180	[48]
[(Pyrazole) ₂ (C ₄ H ₉) ₂ SnCl ₂] (VII)	2.131(5) 2.149(5)	2.329(5) 2.388(5)	2.592(4) 2.587(4)	172.6(2)	176.02(9)	175.0(1)	[54]
[(Pyrazole) ₂ (vinyl) ₂ SnCl ₂] (VIII)	2.103(13)	2.322(5)	2.565(2)	180	180	180	[55]
[(Pyrazine)(CH ₃) ₂ SnBr ₂] (IX)	2.10(2)	2.40(1)	2.723(3)	180	180	180	[56]
[(Pyridine) ₂ (CH ₃) ₂ SnBr ₂] (X)	Not reported	2.34(3)	2.719(5)	180	180	180	[48]
[(Pyrazole) ₂ (CH ₃) ₂ SnBr ₂] (XI)	2.13(2) 2.13(2)	2.36(1) 2.34(1)	2.703(2) 2.766(2)	179.0(6)	178.78(7)	175.8(4)	[57]
[(Pyrazole) ₂ (C ₂ H ₅) ₂ SnBr ₂] (XII)	2.093(7)	2.356(4)	2.746(1)	180	180	180	[58]
[(2,2'-Bipyridyl)(C ₂ H ₅) ₂ SnCl ₂] (XIII)	2.127(6) 2.146(6)	2.368(4) 2.382(4)	2.529(1) 2.545(1)	175.8(2)	104.2(3)	69.0(1)	[59]
[(2,2'-Bipyridyl)(C ₆ H ₅) ₂ SnCl ₂] (XIV)	2.151(7) 2.153(8)	2.344(6) 2.375(6)	2.511(2) 2.508(2)	173.5(3)	103.5(1)	69.0(2)	[60]
[(4,4-dimethyl-2,2'-bipyridyl)(p-ClC ₆ H ₄) ₂ -SnCl ₂] (XV)	2.156(9)	2.402(8)	2.482(5)	177.4(7)	104.2(2)	68.3(4)	[61]
[(4,4'-dimethyl-2,2'-Bipyridyl)(cyclopentyl) ₂ -SnCl ₂] (XVI)	2.153(4) 2.157(4)	2.436(3) 2.435(3)	2.507(1)	174.5(1)	107.51(5)	66.49(9)	[62]
[1,10-Phenanthroline)(C ₄ H ₉) ₂ SnCl ₂] (XVII)	2.09(1) 2.22(1)	2.43(1) 2.35(2)	2.55(1) 2.55(1)	177(2)	105(1)	68(1)	[63]
[(4,7-Diphenylphenanthroline)(C ₄ H ₉) ₂ -SnCl ₂] (XVIII)	2.124(4) 2.173(5)	2.391(3) 2.395(3)	2.561(1) 2.546(1)	178.2(2)	109.12(5)	68.9(1)	[64]
[(2,2',6,6'-Bipyrimidine)(C ₆ H ₅) ₂ SnCl ₂] (XIX)	2.139(7) 2.141(7)	2.398(4) 2.413(4)	2.466(2) 2.451(2)	169.3(2)	103.81(5)	67.9(1)	[65]
[(2,2',6,6'-Bipyrimidine)(C ₄ H ₉) ₂ SnCl ₂] (XX)	2.14(1)	2.46(1) 2.472(9)	2.508(2) 2.525(2)	175.1(6)	106.0(1)	66.4(3)	[66]
[(2,2',6,6'-Bipyrimidine)(C ₂ H ₅) ₂ SnCl ₂] (XXI)	2.134(8) 2.148(9)	2.446(8)	2.508(2) 2.525(2)	171.7(5)	107.47(8)	66.4(2)	[67]
[(2,2',6,6'-Bipyrimidine)((C ₂ H ₅) ₂ SnCl ₂) ₂] (XXII)	2.15(1) 2.14(1)	2.496(8) 2.500(9)	2.502(4) 2.495(4)	174.6(4)	108.1(1)	66.0(3)	[67]
[Bis(4-methylpyrazol-1-yl)methane(CH ₃) ₂ -SnCl ₂] (XXIII)	2.125(9) 2.113(8)	2.436(6)	2.497(2)	174.1(6)	100.3(1)	76.4(3)	This work
[2-(2-Pyridyl)benzimidazole(CH ₃) ₂ SnCl ₂] (XXIV)	2.114(3)	2.447(2)	2.483(1)	171.9(1)	99.5	68.6(1)	[68]
[2-(2-Pyridyl)benzothiazole(C ₂ H ₅) ₂ SnCl ₂] (XXV)	2.156(8) 2.171(11)	2.494(4) 2.555(6)	2.505(2) 2.461(2)	161.2(4)	100.40(7)	66.6(2)	[69]
[2-(2-Pyridyl)benzothiazole(C ₂ H ₅) ₂ SnCl ₂] (XXVI)	2.120(7) 2.137(8)	2.472(4) 2.539(5)	2.509(2) 2.450(2)	164.3(3)	100.63(7)	66.1(2)	[69]
[(3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine)(C ₂ H ₅) ₂ SnCl ₂] (XXVII)	2.12(2) 2.15(2)	2.45(1) 2.55(1)	2.451(5) 2.506(5)	164.6(5)	103.2(5)	67.9(5)	[70]
[(3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine)(C ₂ H ₅) ₂ SnCl ₂] (XXVIII)	2.07(2) 2.11(2)	2.50(1) 2.56(1)	2.470(5) 2.482(5)	156.7(5) 167.0(5)	100.0(5)	66.1(5)	[70]
[2-(2'-Pyridyl)-6-methylbenzothiazole-(C ₂ H ₅) ₂ SnCl ₂] (XXIX)	2.171(4) 2.146(5)	2.472(3) 2.498(4)	2.500(0) 2.440(1)	162.8(2)	100.1(0)	65.2(1)	[71]

Table 11 (continued)

Compound	Bond length (Å)			Bond angle (°)			Reference
	Sn–C	Sn–N	Sn–X	C–Sn–C	X–Sn–X	N–Sn–N	
[2-MeOC ₆ H ₄ N=CHC ₅ H ₄ N-2-(CH ₃) ₂ -SnCl ₂] (XXX)	2.103(9) 2.108(9)	2.456(5) 2.459(5)	2.496(2) 2.519(2)	172.8(4)	100.17(6)	68.1(2)	[72]
[(CH ₃)Cl ₂ (2-2'-bipyridil)Sn(CH ₂)-SnCl ₂ (CH ₃)] (XXXI)	2.047(32) 2.160(32)	2.270(26) 2.372(34)	2.609(10) 2.577(11)	171.1(13)	100.2(3)	71.5(11)	[73]
[(CH ₃)Cl ₂ sSn(CH ₂)(N ₂ C ₄ H ₄) ₂ SnCl ₂ (CH ₃)] (XXXII)	2.124(10), 2.111(7) 2.106(13), 2.121(8)	2.608(5) 2.599(6)	2.434(1) 2.457(2)	153.7(3) 158.6(4)	95.3(1) 96.9(1)	96.3(2) 94.8(3)	[73]
[Bis{2-phenylazo}phenyl-C ¹ N ² }SnCl ₂] (XXXIII)	2.12(2) 2.15(1)	2.51(2) 2.58(2)	2.445(6) 2.368(6)	149.7(7)	97.4(2)	74.2(4)	[74]
[(N,N-Dimethyl-2,2'-bimidazole)(CH ₃) ₂ -SnBr ₂] (XXXIV)	2.11(2) 2.13(2)	2.32(1) 2.29(1)	2.767(2) 2.719(2)	177.7(6)	108.2(1)	69.8(4)	[75]
[2,2'-Azopyridine(CH ₃) ₂ SnBr ₂] (XXXV)	2.12(2) 2.19(3)	2.585(17) 2.793(18)	2.643(3) 2.650(3)	162.1(9)	95.50(9)	49.4(6)	[76]
[(2,2'-Bipyridyl)(<i>p</i> -tolyl) ₂ SnCl ₂] (XXXVI)	2.159(3) 2.161(3)	2.306(3) 2.374(3)	2.493(1) 2.507(1)	108.7(1)	161.4(1)	69.1(1)	[77]
[(4,4-Dimethyl-2,2'-bipyridyl)(<i>p</i> -ClC ₆ H ₅) ₂ -SnCl ₂] (XXXVII)	2.139(18) 2.170(13)	2.311(12) 2.327(12)	2.459(4) 2.491(4)	106.2(6)	163.5(1)	69.8(4)	[61]
[(4,4-Dimethyl-2,2'-bipyridyl)(<i>p</i> -ClC ₆ H ₅) ₂ -SnCl ₂] (XXXVIII)	2.158(7) 2.183(8)	2.322(6) 2.294(6)	2.509(2) 2.475(2)	106.3(3)	163.0(1)	69.4(2)	[61]

ically non-equivalent N-atom donors, namely **XXIV**–**XXX**, **XXXIII** and **XXXV**, generally have more distorted configurations and longer Sn–N bonds than those found in the derivatives of symmetrical chelating ligands.

The Sn–C and Sn–N bond distances in the adducts with monodentate ligands are slightly shorter than those found in complexes with bidentate donors, probably owing to greater steric requirements of the latter molecules.

In our compound, the Sn–C (2.131(9) and 2.111(8) Å) and Sn–Cl (2.498(2) Å) distances are shorter and longer respectively than those reported in the crystal structure of the starting dimethyldichlorotin(IV) (Sn–C, 2.21(8) Å; Sn–Cl, 2.40(4) Å) [78]. The shortening of the Sn–C bond on going from tetracoordinated to penta-coordinated or hexacoordinated tin(IV) derivatives, which is a consequence of the greater σ -electron density in this bond, is typical of dialkyltin(IV) compounds, whereas an opposite trend is found in the complexes with greater electron withdrawing groups such as the phenyl. The Sn–N distance in [(L⁴)(CH₃)₂SnCl₂] (2.436(6) Å) is longer not only with respect to that found in the derivatives with monodentate ligand (e.g. it is 2.338(6) Å in **II**), but also with respect to those found

Table 12

Compounds obtained from various poly(pyrazol-1-yl)alkanes and tin(IV) and organotin(IV) salts

Acceptor	Molar ratio n^a for the following ligands							
	L ¹	L ²	L ³	L ⁴	L ⁵	L ^T	L ^A	L ^B
Me ₂ SnCl ₂	1 ^{b,c,d}	1 ^{b,e,h}	1 ^g	1 ^b	1 ^g (1)			
Me ₂ SnBr ₂				1 ^g				
Et ₂ SnCl ₂	1 ^{b,c}	1 ^b		1 ^g	1 ^b			
Et ₂ SnBr ₂				1 ^g				
Pr ₂ SnCl ₂	1 ^b							
Ph ₂ SnCl ₂	1 ^d	1 ^e		1 ^g	1 ^g (1)	1 ^g		
Ph ₂ SnBr ₂	1 ^d							
MeSnCl ₃	1 ^{c,d}	1 ^e	1 ^e	1 ^g	1 ^g	1 ^g	1 ^g (2)	
BuSnCl ₃	1 ^c		f,i	1 ^g	1 ^g	1 ^g	1 ^g (1.5)	
PhSnCl ₃	1 ^d	1 ^e	1 ^e	1 ^g	1 ^g (1)	1 ^g	1 ^g (1)	
SnCl ₄	1 ^d	1 ^e		1 ^g	g ^l	1 ^{g,m}	$\frac{2}{3}$ g [$\frac{1}{2}$ Et ₂ O]	
SnBr ₄	1 ^d	e,n	f,i	1 ^g	g ⁿ	1 ^g	1 ^g	
SnI ₄	1 ^d	1 ^e	1 ^e (1)	1 ^g	1 ^g	g ⁿ	1 ^g	

^a See text for definition: L⁵ is tris(pyrazol-1-yl)methane. Water: metal molar ratio in parentheses.

^b From [7].

^c From [4].

^d From [5].

^e From [8].

^f From [26].

^g From this work.

^h 3:2 adduct was also obtained.

ⁱ Breaking of the C(sp³)–N bond occurred. 2:1 adduct of neutral pyrazole was obtained.

^j Breaking of the C(sp³)–N bond occurred. 2:1 adduct of neutral 3,4,5-trimethylpyrazole was obtained.

^m 5:4 adduct was also obtained.

ⁿ Substitution of one or two halides by OH groups occurred.

in the adducts of bipyridyl and phen (**XIII**, 2.368(4) Å; **XVIII**, 2.391(3) Å) consistent with the well-known lower donating ability of this type of ligand with respect to bipy and phen derivatives. The bond angles C–Sn–C (173.8(6)°, Cl–Sn–Cl (100.2(1)°), C–Sn–Cl (91.0(3) and 93.0(3)°) and C–Sn–N (86.3(4) and 88.9(4)°) are comparable with those reported for the analogous diorganotin(IV) derivatives, whereas the N–Sn–N bond angle is larger. This difference is due to the fact that a six-membered chelate ring is present in $[(L^4)(CH_3)_2-SnCl_2]$, whereas all the other compounds with bidentate nitrogen donor ligands reported in Table 11 have a five-membered chelate ring.

3.6. Conclusion

In all the tin(IV) and organotin(IV)poly(pyrazol-1-yl)alkane derivatives reported to date (Table 12), the ligand:metal ratio n goes from 2:3 in $(L^B)_2(SnCl_4)_3 \cdot \frac{1}{2}[Et_2O]$ to 3:2 in $[(L^4)_3(Me_2SnCl_2)_2]$.

A ligand can bind to an acceptor in more than one way; for example, treatment of an excess of L^2 with dimethyldichlorotin(IV) gave a deep-yellow 3:2 adduct whereas, when an equimolar quantity of L^2 and Me_2SnCl_2 was used, a colourless 1:1 adduct was found.

The solubility of the compounds obtained is limited to chlorinated solvents (diorganotin(IV)halides), acetone and DMSO (organotin(IV)trihalides and tin(IV)tetrahalides). The existence of adducts of L^1 , L^2 and L^4 but not of L^A and L^B with the low acid diorganotin(IV) acceptors, suggests that the poly(pyrazol-1-yl)methanes are better donors than poly(pyrazol-1-yl)ethanes. The sterically hindered L^3 is probably the weakest donor studied by us to date.

The weakness of the bonding between this family of ligands and tin and organotin(IV) acceptors is demonstrated by the fact that all the complexes reported are partially or completely dissociated in acetone and in chlorinated solvents, but it is also demonstrated by the longer Sn–N bond distances observed in the solid state in the crystal structure of $[(L^4)(CH_3)_2SnCl_2]$. This is of particular interest because it has been reported [6] that diorganotin(IV) compounds active towards P388 lymphocytic leukaemia tumour generally have average Sn–N bond lengths of 2.39 Å or greater, while those averaging in 2.39 Å or less were inactive.

4. Supplementary material

Tables of anisotropic thermal parameters for non-hydrogen atoms, tables of the least-squares planes of the two pyrazole ring and the displacements of atoms from it, tables of atomic coordinates and isotropic thermal parameters, as well as hydrogen atom parameters have been deposited at the Cambridge Crystallographic Data Centre.

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