

Organotin(IV) polypyrazolylborates. IX. Tetrakis(4-methyl-1*H*-pyrazol-1-yl) borates. Characterisation, Mössbauer study and X-ray crystal structure of $\text{Cl}_3\text{Sn}(\mu\text{-4-MePz})_3\text{B}(4\text{-MePz})$

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Abstract

Tin(IV) and organotin(IV) compounds containing tetrakis(4-methyl-1*H*-pyrazol-1-yl)borate ($\text{pzTp}^{4\text{Me}}$), $\text{R}_n\text{SnCl}_{4-n} \cdot \text{pzTp}^{4\text{Me}}$ ($\text{R} = \text{Me}$ or Ph , $n = 0-2$) have been synthesised and characterised by ^1H , ^{13}C , ^{119}Sn NMR and ^{119}Sn Mössbauer spectroscopies. The compounds are fluxional (except when $n = 0$) and contain six-coordinate tin(IV) with a tridentate ligand. The crystal structure of $\text{SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$ ($\text{C}_{16}\text{H}_{20}\text{Cl}_3\text{N}_8\text{BSn}$) has been determined by single crystal X-ray diffraction methods.

Keywords: Boron; Tin; Pyrazolylborates; X-ray; Mössbauer

1. Introduction

Trispyrazolylborates, among the polypyrazolylborates, have been widely used in coordination chemistry [1]. The bispyrazolylborates are generally only bidentate and as such are not comparable. The tetrakis pyrazolylborates, which are mainly tridentate, have received comparatively little attention [2–7]. Among such ligands only $\text{B}(\text{Pz})_4 (= \text{pzTp})$ [8] and $\text{B}(3\text{-MePz})_4 (= \text{pzTp}^{\text{Me}})$ [9] are known. Several studies from these laboratories have been devoted to (organo)tin(IV) polypyrazolylborates [10–16]. Donors $\text{B}(\text{pz})_4$ were employed with tin(II) [2,5] and tin(IV) [4,11]. Here we present the results of a study concerning a new donor with the 4-Me-pyrazole ring, $\text{B}(4\text{-MePz})_4 (= \text{pzTp}^{4\text{Me}})$ ¹, and its interaction with (organo)tin(IV) species. The

resulting complexes may be compared with those previously obtained with pzTp . While the latter is a weaker donor than Tp [17], owing to a hydride being replaced by a pyrazolate, the 4-Me in $\text{pzTp}^{4\text{Me}}$ should increase its donating power without increasing steric hindrance. It is therefore interesting to compare the results with those previously obtained with pzTp , to ascertain the effect of the 4-Me substituent.

2. Results and discussion

The IR data show all the bands required for the presence of the donor tetrakis(4-Me-pyrazolyl)borate and the acceptor chloro(organo)tin(IV): a weak band at ca. 3110 cm^{-1} (C–H stretching vibration(s) characteristic of the pyrazole ring), a strong or very strong band at ca. 1510 cm^{-1} (ring “breathing”), other strong bands due to ring out-of-plane vibrations appear at ca. 805 cm^{-1} , in addition, some low frequency absorptions are due to Sn–C (for **2** (monomethyl derivative) 527 cm^{-1} , for **3** (dimethyl) 588 cm^{-1} , for **4** (monophenyl) 276

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¹ The ligand abbreviations are according to Trofimenko (Ref. [1]) and the symbol Tp^* stands for any pyrazolylborate.

Table 1
Yields, analyses, and physical properties of the compounds

Compound ^a	Yield (%)	Elemental analysis (Found/Calc.) (%)			MW (Found/Calc.)	m.p.	Λ ^b
		C	H	N			
K · pzTp ^{4Me}	72	51.11/51.34	5.52/5.39	29.70/29.94		247–249	
1 SnCl ₃ · pzTp ^{4Me}	64	33.98/34.30	3.30/3.36	19.76/20.00		^c	3.5(1.0)
2 MeSnCl ₂ · pzTp ^{4Me}	74	37.63/37.82	4.32/4.29	20.50/20.76	522 ^d /540	306–308 ^e	5.8(1.1)
3 Me ₂ SnCl · pzTp ^{4Me}	73	41.77/41.62	5.16/5.05	21.39/21.57		258–260 ^e	10.1(1.0)
4 PhSnCl ₂ · pzTp ^{4Me}	88	44.12/43.90	4.34/4.19	18.47/18.62	589 ^d /602	204–207	7.9(0.9)
5 Ph ₂ SnCl · pzTp ^{4Me}	82	51.96/52.26	4.85/4.70	17.17/17.41		172–174	12.4(1.0)

^a pzTp^{4Me} is tetrakis(4-methyl-1H-pyrazol-1-yl)borate C₁₆H₂₀N₈B. ^b Specific conductivity (ohm⁻¹ cm² mol⁻¹) in acetone solution at room temperature; the molar concentration $\times 10^{-3}$ is indicated in parentheses in the lower line. ^c Chars without melting. ^d Monomer according to molecular weight determination by osmometry in dichloromethane. ^e Melted with decomposition.

cm⁻¹ and for **5** (diphenyl) 295 cm⁻¹) and Sn–Cl stretching at ca. 280–298 cm⁻¹.

The electrical conductivities, measured in acetone solution for all the compounds listed in Table 1, show that like other complexes R(Ar)_nSnCl_{4-n-1} · Tp[#] [11–15], the new compounds are non-electrolytes.

2.1. NMR results

The ¹H, ¹³C, and ¹¹⁹Sn NMR spectra for compounds R(Ar)_nSnCl_{4-n-1} · Tp^{4Me} are summarised in Tables 2 and 3.

If the ligand is tridentate with the Sn octahedral and

Table 2
¹H NMR data ^a

Compound	δ ^a			R–Sn, ⁿ J (¹¹⁹ Sn–H) or ⁿ J (^{119,117} Sn–H) (Hz)
	3- or 5-H		4-Me	
K · pzTp ^{4Me}	7.24	6.94	1.97	
1 SnCl ₃ · pzTp ^{4Me}	8.00 ^{b,c}		7.56 ^{b,d}	2.06 ^b
		7.78	2.29	2.02
2 MeSnCl ₂ · pzTp ^{4Me}	7.78	7.67	2.03	Me: 1.34; 119.1, 111.2
	8.1 br ^b	7.1 br ^b	2.27	
3 Me ₂ SnCl · pzTp ^{4Me}	7.70	7.04	2.07	Me: 0.90; 69.0
	7.50	7.36	2.16	
4 PhSnCl ₂ · pzTp ^{4Me}	7.72 br	7.40 br	2.02 br	Ph: 7.52–7.28
			1.98	
5 Ph ₂ SnCl · pzTp ^{4Me}	8.19	7.62	1.99	Ph: 7.40–7.25
	7.79	7.72	2.99	

^a Not observed. ^a CDCl₃ solution (except K · pzTp^{4Me} in acetone) in ppm from Me₄Si, calibration from internal deuterium solvent lock. ^b The signal has three times the intensity of that in the lower line. ^c |³J| \cong 11.6 Hz. ^d |⁴J| \cong 7.4 Hz.

Table 3
¹³C and ¹¹⁹Sn NMR data

Compound	δ					¹¹⁹ Sn
	C-3 or C-5 ^{a,b}		C-4 ^{a,b}	Me-4 ^{a,b}	R–Sn ^a	
K · pzTp ^{4Me}	140.3	133.4	113.2	8.2		
1 SnCl ₃ · pzTp ^{4Me}	141.6	135.7	117.1	9.1		–620.2
	144.3	134.3	119.0	9.5		
2 MeSnCl ₂ · pzTp ^{4Me}	144.0	135.1	118.6	9.1	20.7 ^d	–479.7
	140.6	134.8	116.7	9.5		
3 Me ₂ SnCl · pzTp ^{4Me}	141.7	134.9	116.4	8.7	12.0	–229.4
		133.6	118.2			
4 PhSnCl ₂ · pzTp ^{4Me}	142.5	134.6	116.4	9.2	128.3; 128.7	–526.8
	^c	134.3	116.3		129.7; 135.6	
5 Ph ₂ SnCl · pzTp ^{4Me}	141.2	135.1	116.1	8.6	128.2; 129.3	–451.1
	141.8	134.0	118.2	9.0	133.8; 134.3	

^a In ppm from Me₄Si, calibration from internal deuterium solvent lock; when coupling constants are detected they are reported by a footnote.

^b The signals in the upper line are more intense than those in the lower line. ^c The signal is seen as a shoulder of the main peak.

^d |¹J(¹¹⁹Sn–¹³C)| = 667 Hz. * Not observed.

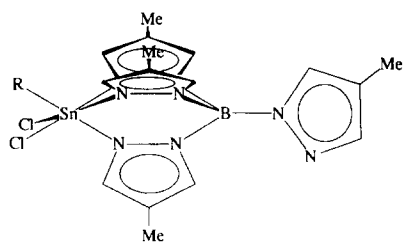


Fig. 1. Octahedral coordination around tin(IV).

there is a rigid structure as found in the corresponding compounds containing the unsubstituted pzTp [11], the pyrazole ring protons H-3, Me-4, and H-5 (or carbons C-3, C-4, Me-4, and C-5) should give rise to three sets of signals in the ratio 2:1:1, except when $n = 0$ (ratio 3:1). This is due to the presence of one free pz group and the fact that (when $n \neq 0$) the pyrazole rings opposed to a Cl are not equivalent to those opposed to an Me (or Ph), see Fig. 1.

In compound **1** ($n = 0$) signals in both ^1H and ^{13}C spectra fully support this. In the first set H-3 and H-5 resonances are flanked by ^{119}Sn satellites with $|^3J| \cong 11.6$ and $|^4J| \cong 7.4$ Hz. The other set of signals, besides not showing coupling constants, remains unchanged with temperature up to 55°C in CHCl_3 solution. This rules out fluxionality around boron.

In the other complexes two clearly distinct sets of signals are observed in the ratio 3:1. The less intense of them is attributable to the dangling pz group, so that here again the fluxionality around B can be excluded. The other set is split into two subsets (often broad and partially overlapping) in **2** and **4** (monomethyl, monophenyl), but not in **3** and **5** (dimethyl, diphenyl). Moreover, no couplings appear for H-3 or H-5. The possibility that two pz rings are free (tin 5-coordinate) can be excluded on the basis of signal intensity and multiplicity. Thus, assuming octahedral coordination, fluxionality around tin must take place in solution and the exchange rate must be rapid at room temperature on the NMR time scale. In the case of complexes **3** or **5**, because of the presence of much broader peaks, there

Table 4

Fractional coordinates with equivalent isotropic thermal parameters (\AA^2) for $1 \text{ SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso/eq}}$
Sn	0.58778(2)	0.31582(2)	0.19394(3)	0.0356(1)
Cl(1)	0.49190(7)	0.41039(8)	0.2819(1)	0.0636(4)
Cl(2)	0.51278(7)	0.30347(8)	-0.0491(1)	0.0584(4)
Cl(3)	0.52906(8)	0.19267(8)	0.2852(1)	0.0646(4)
B(1)	0.7994(3)	0.3490(3)	0.2558(4)	0.030(1)
N(1)	0.6618(2)	0.4192(2)	0.1254(3)	0.037(1)
N(2)	0.7483(2)	0.4211(2)	0.1661(3)	0.0295(9)
N(3)	0.6942(2)	0.2424(2)	0.1327(3)	0.037(1)
N(4)	0.7785(2)	0.2648(2)	0.1730(3)	0.0317(9)
N(5)	0.6788(2)	0.3306(2)	0.4007(3)	0.036(1)
N(6)	0.7655(2)	0.3419(2)	0.4034(3)	0.0313(9)
N(7)	0.8935(2)	0.3704(2)	0.2703(3)	0.033(1)
N(8)	0.9276(2)	0.4246(2)	0.3796(4)	0.043(1)
C(1)	0.6388(2)	0.4918(2)	0.0578(4)	0.042(1)
C(2)	0.7096(2)	0.5423(2)	0.0538(4)	0.038(1)
C(3)	0.7770(2)	0.4956(2)	0.1240(4)	0.035(1)
C(4)	0.7118(3)	0.6289(3)	-0.0084(5)	0.053(2)
C(5)	0.6938(3)	0.1648(2)	0.0744(5)	0.045(1)
C(6)	0.7765(3)	0.1370(2)	0.0747(4)	0.043(1)
C(7)	0.8277(2)	0.2005(2)	0.1399(4)	0.037(1)
C(8)	0.8054(3)	0.0544(3)	0.0179(6)	0.064(2)
C(9)	0.6651(3)	0.3258(2)	0.5392(4)	0.043(1)
C(10)	0.7414(3)	0.3330(2)	0.6350(4)	0.043(1)
C(11)	0.8030(2)	0.3428(2)	0.5459(4)	0.037(1)
C(12)	0.7552(4)	0.3300(4)	0.8003(5)	0.075(2)
C(13)	0.9459(3)	0.3657(3)	0.1670(4)	0.044(1)
C(14)	1.0164(3)	0.4145(3)	0.2089(5)	0.050(1)
C(15)	1.0017(3)	0.4489(3)	0.3421(5)	0.051(2)
C(16)	1.0921(4)	0.4284(5)	0.1319(7)	0.105(3)

$U_{\text{iso/eq}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

must be fluxionality around Sn, but the exchange rate is slower than in **2** or **4** and somewhat comparable with the NMR time scale.

Increasing the number of Me groups on tin and lowering the number of chlorine atoms should decrease the positive charge on tin in the fragment $\text{Me}_n\text{SnCl}_{4-n}^+$ and its Lewis acidity. An analogous trend should hold for Ph groups, although attenuated because the difference in electronegativity between Cl and Ph is less than that between Cl and Me. In spite of the fact that the

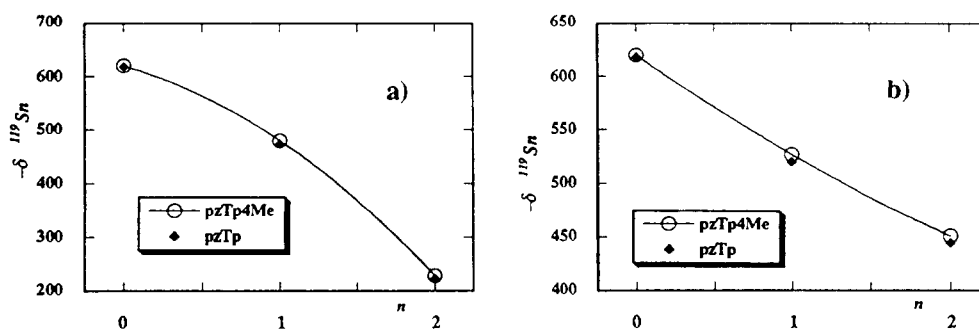


Fig. 2. Chemical shift (^{119}Sn) of (a) $\text{Me}_n\text{SnCl}_{4-n-1} \cdot \text{pzTp}^\#$ and (b) $\text{Ph}_n\text{SnCl}_{4-n-1} \cdot \text{pzTp}^\#$ as a function of n , where $\text{pzTp}^\#$ is pzTp or $\text{pzTp}^{4\text{Me}}$. The fitting line is drawn only for the complexes from $\text{pzTp}^{4\text{Me}}$.

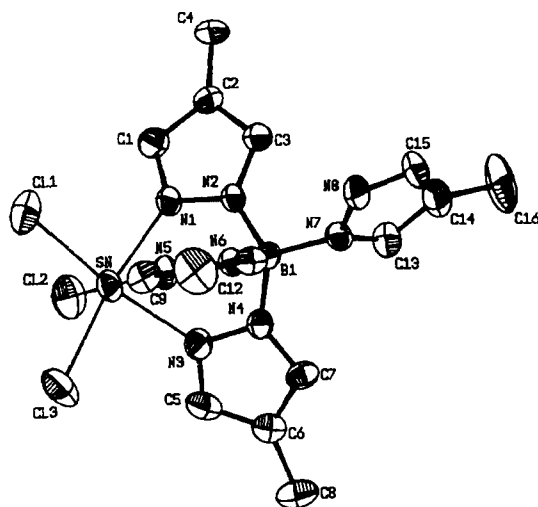


Fig. 3. ORTEP plot for the compound $1 \text{ SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$.

NMR chemical shift does not necessarily correlate with charge, it is empirically found that some correlation exists. Specifically, $\delta(^{119}\text{Sn})$ is a linear function of n for the series $\text{R}(\text{Ar})_n\text{SnCl}_{4-n-1} \cdot \text{Tp}^\#$. For different $\text{Tp}^\#$ these lines are parallel to each other. The distance between any given pair of lines is consistent with the difference in charge on tin, the higher the shift (absolute values of δ) the lower the charge. As shown in Fig. 2, the lines for the present series closely parallel those for the PzTp^2 , with $\text{R} = \text{Me}$ or $\text{Ar} = \text{Ph}$, although different lines are followed. Moreover, phenyl groups give rise to more negative shifts than Me ones for both ligands. This empirical observation, which correlates more negative shifts with the donor power of the ligand, infers that the $\text{pzTp}^{4\text{Me}}$ should be slightly more donating than pzTp . This is not unexpected. The only (possibly significant) difference is that the line for the Me series is not as straight as that for the corresponding trispyrazolylborates.

2.2. Description of the molecular structure

Crystal data are as follows: $\text{SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$ [Tetrakis(4-Me-1H-pyrazol-1-yl)borate]trichlorotin(IV) formula $\text{C}_{16}\text{H}_{20}\text{Cl}_3\text{N}_8\text{BSn}$, formula weight $M = 560.2$, monoclinic, space group $P2_1/n$ (No. 14), with $a = 15.797(1)$, $b = 15.925(1)$, $c = 9.205(1)$ Å, $\beta = 92.34^\circ$, $V = 2287.2(7)$ Å³, $Z = 4$, $D_c = 1.63$ g cm⁻³, $F(000) = 1112$, $\mu = 13.67$ cm⁻¹, crystal dimensions $0.50 \times 0.30 \times 0.10$ mm³.

² The values of $\delta(^{119}\text{Sn})$ reported in Ref. [11] for compounds $\text{R}_2\text{SnCl} \cdot \text{pzTp}$ ($\text{R} = \text{Me}$, Et, or ⁿBu) were reported as read from the spectra, which display a scale shift of just 100 ppm more negative than the actual values.

Table 5
Selected bond distances (Å) for $1 \text{ SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$

Sn–Cl(1)	2.367(2)	Sn–Cl(2)	2.371(2)
Sn–Cl(3)	2.378(1)	Sn–N(1)	2.169(3)
Sn–N(3)	2.192(3)	Sn–N(5)	2.211(3)
B(1)–N(2)	1.564(5)	B(1)–N(4)	1.552(5)
B(1)–N(6)	1.541(5)	B(1)–N(7)	1.510(5)
N(1)–N(2)	1.359(4)	N(1)–C(1)	1.336(5)
N(2)–C(3)	1.348(5)	N(3)–N(4)	1.373(4)
N(3)–C(5)	1.347(5)	N(4)–C(7)	1.348(5)
N(5)–N(6)	1.378(4)	N(5)–C(9)	1.328(5)
N(6)–C(11)	1.352(5)	N(7)–N(8)	1.370(4)
N(7)–C(13)	1.357(5)	N(8)–C(15)	1.329(6)
C(1)–C(2)	1.383(5)	C(2)–C(3)	1.375(5)
C(2)–C(4)	1.496(6)	C(5)–C(6)	1.380(6)
C(6)–C(7)	1.373(5)	C(6)–C(8)	1.512(6)
C(9)–C(10)	1.384(6)	C(10)–C(11)	1.376(6)
C(10)–C(12)	1.504(6)	C(13)–C(14)	1.364(6)
C(14)–C(15)	1.396(6)	C(14)–C(16)	1.498(8)

The ORTEP plot of Fig. 3 shows the crystal structure of the compound **1** together with the numbering scheme. As expected, the Cl and C(methyl) atoms have large anisotropic thermal parameters. The cell contains four discrete covalent molecules. The tin atom displays distorted octahedral coordination, with bond angles Cl–Sn–Cl ranging from 95.62(7) to 97.11(6)° and N–Sn–N from 81.8(1) to 82.1(1)°. The bond lengths Sn–Cl range from 2.367(2) to 2.378(1) Å and Sn–N from 2.169(3) to 2.211(3) Å. Additional bond distances and angles are given in Tables 5 and 6.

The weighted least-squares planes **I** N1N2C1C2C3 and **III** N5N6C9C10C11 deviate significantly from the planarity. However, the pyrazole rings **II** N3N4C5C6C7 and **IV** N7N8C13C14C15 are planar. The dihedral angles between the planes **I/II**, **I/III**, **I/IV**, **II/III**, **II/IV**, **III/IV** are 48, 63, 89, 111, 46 and 143° respectively. For comparison, structural data for some corresponding pyrazolylborato complexes are reported in Table 7.

As can be seen from Table 7, Sn–N and Sn–Cl bond distances are in the range typical of analogous complexes containing different pyrazolylborates. The α value for the present ligand is the greatest, the β value the smallest for all analogues reported.

This may derive from a steric interaction with the fourth uncoordinated pyrazole ring.

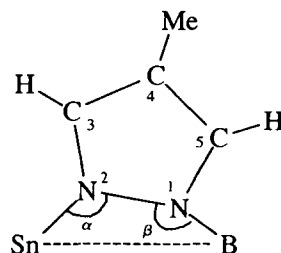


Table 6
Selected bond angles (°) for **1** SnCl₃ · pzTp^{4Me}

N(3)–Sn–N(5)	81.8(1)	N(1)–Sn–N(5)	82.1(1)
N(1)–Sn–N(3)	81.9(1)	Cl(3)–Sn–N(5)	91.20(9)
Cl(3)–Sn–N(3)	90.47(9)	Cl(3)–Sn–N(1)	170.5(1)
Cl(2)–Sn–N(5)	169.4(1)	Cl(2)–Sn–N(3)	90.2(1)
Cl(2)–Sn–N(1)	90.06(9)	Cl(2)–Sn–Cl(3)	95.75(5)
Cl(1)–Sn–N(5)	90.12(9)	Cl(1)–Sn–N(3)	170.0(1)
Cl(1)–Sn–N(1)	91.13(9)	Cl(1)–Sn–Cl(3)	95.62(7)
Cl(1)–Sn–Cl(2)	97.11(6)	N(6)–B(1)–N(7)	114.3(3)
N(4)–B(1)–N(7)	111.7(3)	N(4)–B(1)–N(6)	107.1(3)
N(2)–B(1)–N(7)	107.5(3)	N(2)–B(1)–N(6)	107.3(3)
N(2)–B(1)–N(4)	108.8(3)	Sn–N(1)–C(1)	132.2(3)
Sn–N(1)–N(2)	120.1(2)	N(2)–N(1)–C(1)	107.3(4)
B(1)–N(2)–N(1)	122.8(3)	N(1)–N(2)–C(3)	108.1(3)
B(1)–N(2)–C(3)	129.0(4)	Sn–N(3)–C(5)	129.5(3)
Sn–N(3)–N(4)	122.9(2)	N(4)–N(3)–C(5)	106.8(4)
B(1)–N(4)–N(3)	118.7(3)	N(3)–N(4)–C(7)	108.1(3)
B(1)–N(4)–C(7)	132.9(4)	Sn–N(5)–C(9)	129.6(3)
Sn–N(5)–N(6)	122.7(2)	N(6)–N(5)–C(9)	107.5(4)
B(1)–N(6)–N(5)	118.4(3)	N(5)–N(6)–C(11)	107.6(3)
B(1)–N(6)–C(11)	134.0(4)	B(1)–N(7)–C(13)	128.7(3)
B(1)–N(7)–N(8)	118.4(4)	N(8)–N(7)–C(13)	109.6(3)
N(7)–N(8)–C(15)	104.8(3)	N(1)–C(1)–C(2)	110.7(4)
C(1)–C(2)–C(4)	127.9(4)	C(1)–C(2)–C(3)	104.1(4)
C(3)–C(2)–C(4)	128.0(4)	N(2)–C(3)–C(2)	109.9(4)
N(3)–C(5)–C(6)	110.4(4)	C(5)–C(6)–C(8)	128.0(4)
C(5)–C(6)–C(7)	104.9(4)	C(7)–C(6)–C(8)	127.1(5)
N(4)–C(7)–C(6)	109.7(4)	N(5)–C(9)–C(10)	110.5(4)
C(9)–C(10)–C(12)	128.1(5)	C(9)–C(10)–C(11)	104.9(4)
C(11)–C(10)–C(12)	127.1(5)	N(6)–C(11)–C(10)	109.5(4)
N(7)–C(13)–C(14)	109.4(4)	C(13)–C(14)–C(16)	128.9(4)
C(13)–C(14)–C(15)	103.4(4)	C(15)–C(14)–C(16)	127.8(5)
N(8)–C(15)–C(14)	112.8(4)		

2.3. Mössbauer spectroscopy results

Except for the compound **1**, which exhibits a single line, the Mössbauer spectra exhibit one or two quadrupole-split doublets, as shown in Fig. 4.

For the inorganic compound **1** (Table 8) the s-electron density at the tin nucleus and the small p-electronic asymmetry around the tin atom are consistent with octahedral coordination found in the present X-ray crystal structure. The non-zero electric quadrupole splitting depends mainly on the N–Sn–N angular deviations from 90°, as a consequence of the N–Sn–N bite angle shown in Table 7.

For the organotin compounds **2** and **5** the spectra

reported in Table 8 can be attributed to the octahedral tin(IV) site with a facial *N*-tridentate pyrazolylborate, because of the agreement between experimental and calculated quadrupole splittings [19,20]. This is also true of the predominant feature in the Mössbauer spectra of **3** and **4**. For these compounds the minor component implies an increase in the s-electron density at tin nucleus and less delocalised s-electronic charge together with the greater tin p-electron asymmetry. In addition, the second component has a quadrupole splitting too large to correspond to a distorted octahedral coordination with a facial *N*-tridentate or *N*-bidentate ligand [20,21].

The large difference in the Mössbauer parameters

Table 7
Comparison of structural data for SnCl₃ · Tp[#]

Tp [#]	Sn–N (Å)	Sn–Cl (Å)	N–Sn–N (°)	Cl–Sn–Cl (°)	α (°)	β (°)	Ref.
pzTp ^{4Me}	2.191	2.372	81.9	96.2	121.9	118.5	*
Tp ^{*Cl}	2.213	2.345	81.8	96.9	120.2	121.3	[15]
Tp [*]	2.198	2.382	83.9	93.6	118.9	120.4	[18]
Tp	2.234	2.376	81.6	98.5	121.4	119.5	[16]

* This work.

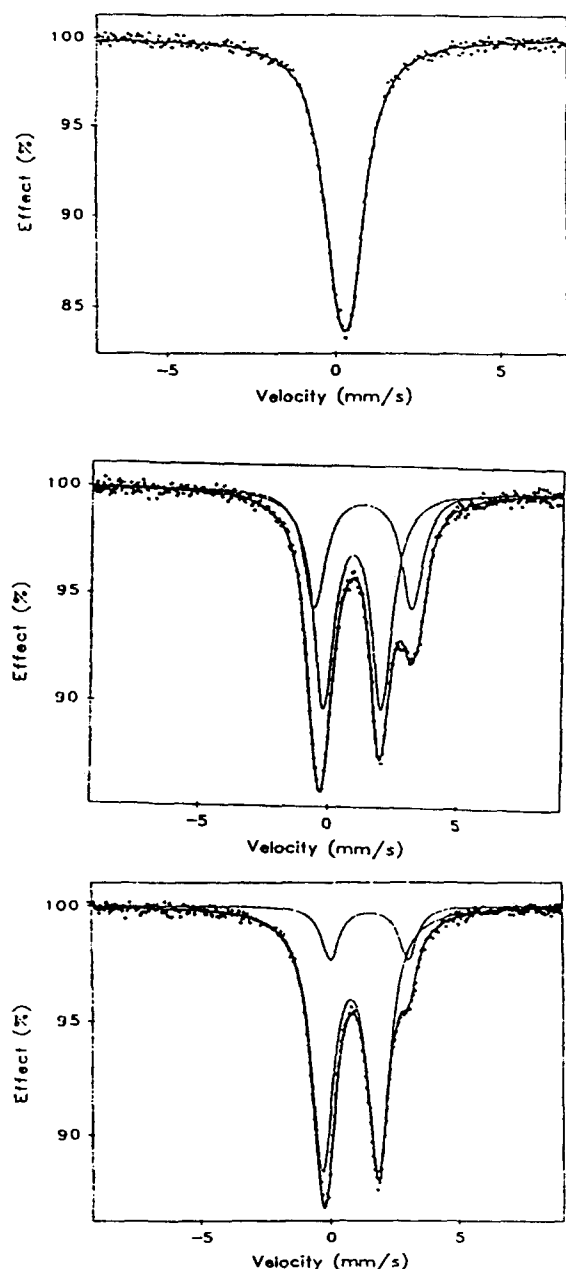


Fig. 4. Mössbauer spectra measured at 4.2 K (from top to bottom) for 1 $\text{SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$, 3 $\text{Me}_2\text{SnCl} \cdot \text{pzTp}^{4\text{Me}}$, 4 $\text{PhSnCl}_2 \cdot \text{pzTp}^{4\text{Me}}$.

between the two spectral components in 3 and 4 indicates that different coordination sites are present. The calculated splitting is close to the experimental if a ligand is *N*-monodentate in an all-*trans* octahedral geometry. This all-*trans* octahedral coordination, which is probably due to pyrazole released from decomposition of the pyrazolylborate, is consistent with that reported for bis(3,4,5-trimethyl-pyrazole)dichlorodimethyltin(IV) [21].

In conclusion, a distorted octahedral geometry for (organo)tin(IV) polypyrazolylborates $\text{R}_n\text{SnCl}_{4-n-1} \cdot \text{pzTp}^{4\text{Me}}$ with a facial *N*-tridentate ligand appears to be the rule for $n = 0-2$. However, different arrangements are possible if decomposition takes place.

3. Experimental details

3.1. General laboratory equipment

Concentration was always carried out in vacuo (water aspirator). The samples were dried in vacuo to constant weight (20°C, ca. 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out at Camerino University; molecular weight determinations were performed at Pascher Mikroanalytisches Laboratorium, Remagen, Germany. IR spectra were recorded from 4000 to 250 cm^{-1} on a Perkin-Elmer 2000 FTIR instrument. ^1H -, ^{13}C - and ^{119}Sn -NMR spectra were recorded on a Varian VXR-300 spectrometer operating at room temperature (300 MHz for ^1H , 75 MHz for ^{13}C and 111.9 MHz for ^{119}Sn). Some spectra were also recorded on a Varian Gemini-200 (200 MHz for ^1H , 50 MHz for ^{13}C). The conductances of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

3.2. Syntheses

3.2.1. Potassium tetrakis(4-Me-1H-pyrazol-1-yl)borate

Potassium borohydride (2.70 g, 0.05 mol) and 4-methylpyrazole (20.53 g, 0.25 mol) were gradually

Table 8
 ^{119}Sn Mössbauer parameters measured at 4.2 K

Sample	IS	QS	QS ^a	LW	Relative resonance area (%)	Sn site
1 $\text{SnCl}_3 \cdot \text{pzTp}^{4\text{Me}}$	0.30	0.43	0.00	1.13	100	O_h
2 $\text{MeSnCl}_2 \cdot \text{pzTp}^{4\text{Me}}$	0.71	1.74	+2.06	1.10	100	O_h
3 $\text{Me}_2\text{SnCl} \cdot \text{pzTp}^{4\text{Me}}$	0.89	2.23	-2.06	0.95	62	O_h
4 $\text{PhSnCl}_2 \cdot \text{pzTp}^{4\text{Me}}$	1.29	3.82	+3.93	1.02	38	O_h <i>trans</i> - $\text{Me}_2\text{Cl}_2\text{N}_2$
	0.78	2.16	+1.90	1.03	85	O_h
5 $\text{Ph}_2\text{SnCl} \cdot \text{pzTp}^{4\text{Me}}$	1.54	3.03	+3.62	0.84	15	O_h <i>trans</i> - $\text{Ph}_2\text{Cl}_2\text{N}_2$
	0.69	1.56	-1.90	1.02	100	O_h

^a Calculated by point-charge model assuming a regular geometry and using literature values [19,20].

heated with stirring in a 1 l flask at temperatures not exceeding 220°C. Potassium borohydride dissolved slowly with evolution of dihydrogen (0.2 mol, ca. 5 l), and the progress of the reaction was followed on a gas meter. After 48 h the melt was poured slowly into 300 ml of stirred hot xylene. The mixture was filtered, whereupon a solid precipitated. After recrystallization from ⁿhexane/diethyl ether (2:1) ca. 13.5 g (72%) m.p. 247–249°C were obtained.

3.2.2. [Tetrakis(4-Me-1H-pyrazol-1-yl)borate]trichlorotin(IV) (1)

An anhydrous solution of SnCl₄ in CH₂Cl₂ (1 M, 1 ml) was added by syringe under dinitrogen to a cooled (ca. –6°C) solution/suspension of K·pzTp^{4Me} (1 mmol, 0.374 g) in 40 ml of CH₂Cl₂ previously dried over NaH. The resulting mixture was purged with dry dinitrogen and stirred vigorously for 5 min. After filtration the solvent was removed in vacuo at room temperature, and the residue (yield 0.36 g, 64%) was recrystallised from dichloromethane/ethyl acetate (1:2, v/v) yielding crystals suitable for X-ray studies. Early experiments performed under less strictly anhydrous conditions led to mixtures containing more or less hydrolysed species.

3.2.3. [Tetrakis(4-Me-1H-pyrazol-1-yl)borato]dichloromethyltin(IV) (2–5)

A dichloromethane solution (35 ml) of MeSnCl₃ (1 mmol, 0.24 g) was added dropwise to a cooled stirred dichloromethane solution/suspension (35 ml) of K·pzTp^{4Me} (1 mmol, 0.374 g). The resulting cloudy mixture was stirred for 18 min at 15°C, filtered, and the filtrate evaporated under reduced pressure. Further purification of **2** was achieved by recrystallisation from ⁿheptane. Compounds **3–5** were prepared similarly. These compounds, especially **3** and **5**, are particularly prone to decomposition on standing in solution (as noted earlier [21]) and after one or two weeks decomposition products are visible even in the solid state. The yields of the reactions and some properties of compounds **2–5** are listed in Tables 1–3.

3.3. X-ray crystallographic analysis

Intensity data were collected at room temperature with a Philips PW 1100 diffractometer using Mo K α radiation in the range 4.8° < 2 θ < 50.0°. The data were corrected for Lorentz and polarisation effect, and for absorption following the North method.

4316 independent reflections were observed and 3060 with $F > 3\sigma(F)$ for **1** SnCl₃·Tp^{4Me} were used in the structure analysis. The structure was solved by SHELXL 86 direct methods. Blocked full-matrix least-squares refinement on F was computed and the function $\sum_w [|F_o| - |F_c|]^2$ minimised. The non-hydrogen atoms

were refined anisotropically. The positions of the hydrogen atoms were calculated but not refined. The final R value was 0.031 (R_w 0.032).

The molecule is displayed in the ORTEP plot of Fig. 3 together with its numbering scheme. The final atomic coordinates, selected bond distances, and angles are reported in Tables 4–6. (Supplementary material including anisotropic thermal parameters, structural factors, interatomic contacts, and fractional coordinates for non-hydrogen atoms are available from the Cambridge Crystallographic Data Centre).

3.4. Mössbauer spectroscopy

The Ca^{119m}SnO₃ Mössbauer source and the absorbers were kept at 4.2 K. A sinusoidal velocity waveform and a proportional detector were used. The spectra have been least-squares fitted with sets of Lorentzian lines by the program MOS 90. The hyperfine parameters such as isomer shift (IS) (relative to SnO₂), average line width (LW), experimental and calculated quadrupole splitting (QS), and relative resonance area in per cent are listed in Table 8, together with the coordination geometry attributed to the tin site. Some representative Mössbauer spectra are shown in Fig. 4.

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