CRYSTAL STRUCTURE OF [TETRAKIS(4-METHYL-1H-PYRAZOL-1-YL)BORATO]DICHLOROMETHYLTIN(IV) $\text{MeCl}_2\text{Sn}(\mu\text{-4-MePz})_3\text{B(4-MePz)}$

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Abstract: The organotin(IV) compound $\text{CH}_3\text{SnCl}_2\cdot\text{pzTp}^{4\text{Me}}$ containing the tetrakis(4-methyl-1H-pyrazol-1-yl)borate ($\text{pzTp}^{4\text{Me}}$) ligand has been synthesised and characterised by ^1H , ^{13}C , ^{119}Sn NMR spectra and ^{119}Sn Mössbauer spectroscopy. The crystal structure determined by X-ray diffraction, shows the presence of a distorted octahedral tin(IV) coordination geometry with one facial *N*-tridentate ligand. Crystal data are as follows: monoclinic, space group $\text{P2}_1/\text{n}$ (No. 14), with $a = 9.217(1)$, $b = 15.925(2)$, $c = 15.908(2)$ Å, $\beta = 99.1(1)^\circ$.

Introduction

The poly(pyrazolyl)borates are the most studied among the pyrazole derived chelating agents [1]. While these ligands are well-suited for the formation of metal complexes, *e.g.* of tin(IV) and organotin(IV) [2-9], their steric and electronic properties can be easily modified by changing the number of pyrazole rings and/or the substituents thereon. The possibility of changing the ring- and/or *B*-substituents make them highly customisable. Indeed, such variations have been shown to entail strong effects on the spectroscopic properties [10, 11] and reactivity of their derivatives.

In a recent paper, in order to have a comparison with the previous complexes from pzTp [3] (The notation of Trofimenko [1a] has been followed throughout, and $\text{Tp}^\#$ stands for any pyrazolylborate), we studied the ligand $\text{pzTp}^{4\text{Me}}$ and its interaction with (organo)tin(IV) species [9]. The presence of a 4-Me substituent in the substituted pyrazole groups in $\text{pzTp}^{4\text{Me}}$ is expected to result in differing behaviour. While the steric factors are not expected to differ substantially from those of pzTp , the electronic ones should affect the complexes from this ligand. Generally, the Lewis acidity of metal fragment can be easily controlled by exchanging electronegative halogen atoms with alkyl or aryl groups.

The monoorgano-dichlorotin(IV) complexes $\text{R}_n\text{SnCl}_{4-n-1}\cdot\text{Tp}^\#$ ($n = 1$) may be considered as a special case. Indeed, they are sufficiently stable in solution with respect to self-decomposition, at variance with the diorganochlorotin derivatives (which are prone to disproportionation, possibly followed by deboronation [12, 13]). Moreover, they are not so moisture sensitive as the "inorganic" $\text{Cl}_3\text{Sn}\cdot\text{Tp}^\#$ [14]. Nevertheless, the fragment RSnCl_2^+ is still a sufficiently strong electron acceptor to allow a distinction in the electron donating power of similar ligands within the polypyrazolylborato family.

In view of the availability of another crystal structure featuring the MeSnCl_2 unit linked to a pyrazolylborate [7], besides one more with a monoorgano-dichlorotin [15], it seemed interesting to compare these structures with that of the title complex.

Experimental

The synthesis of the polypyrazolylborates follows Trofimenko's classic methods by letting molten pyrazole react with an alkali metal borohydride.

*Dichloromethyltetrakis(4-Methyl-1*H*-pyrazol-1-yl-borate) :*

A dichloromethane solution (35 mL) of MeSnCl₃ (1 mmol, 0.24 g) was added dropwise to a ice-water cooled dichloromethane solution/suspension (35 ml) of K-pzTp^{4Me} (1 mmol, 0.374 g) under stirring. The resulting cloudy mixture was stirred for 18 min at 15 °C, filtered, and the filtrate evaporated under reduced pressure. The title complex was recrystallised from dichloromethane-toluene mixture (2:1 v/v) yielding crystals suitable for X-ray studies. *Analysis*. Found: C, 37.71; H, 4.31; N, 20.63%. Calc. for C₁₇H₂₃N₈BCl₂Sn: C, 37.82; H, 4.29; N, 20.76%. *M.W.* (Found/Calc.) 522/539.8. ¹H NMR (δ)(CDCl₃): 7.78 [8.10 br], 7.67 [7.10 br] (3- and 5-H, s); 2.03 [2.27] 4-Me); 1.34 (Me-Sn). ¹¹⁹Sn NMR (δ)(CDCl₃): 144.0 [140.6], 135.1 [134.8] (3- and 5-C); 118.6 [116.7] (4-C); 9.1 [9.5] (4-Me); 20.7 (Me-Sn). ¹³C NMR (δ)(CDCl₃): 144.0 [140.6], 135.1 [134.8] (3- and 5-C); 118.6 [116.7] (4-C); 9.1 [9.5] (4-Me); 20.7 (Me-Sn). ¹J(¹¹⁹Sn-¹³C) = 667 Hz. ¹¹⁹Sn NMR: -480 ppm. The signals in square brackets are those of the set of hydrogen or carbon atoms of the pyrazole ring not linked to tin; its intensity is one third of the corresponding set in the ¹H spectra, and lower in the ¹³C ones. IR: 3118vw, 3109w ν (C-H), 1510s (ring breathing), 527s ν (Sn-C), 290vs, br ν (Sn-Cl).

Crystal data for C₁₇H₂₃N₈BCl₂Sn, monoclinic, P2₁/n (No. 14), *a* = 9.217(1), *b* = 15.925(2), *c* = 15.908(2) Å, β = 99.1(1)°, *V* = 2305(8) Å³, *Z* = 4, *D*_c = 1.61 g/cm³, *F*(000) = 1112, λ = 0.71069 Å, μ = 13.56 cm⁻¹.

X-ray crystal structure procedure and Mössbauer spectroscopy

A crystal with approximate dimensions 0.2 x 0.2 x 0.6 mm was used. Intensity data were collected at 293 K with a Philips PW 1100 diffractometer by using Mo-K α radiation in the range 4.8° < 2 θ < 50.0°. 4207 reflections were read and 3093 reflections with *F* > 3 σ (*F*) were used in the structure analysis. Data were corrected for the Lorentz and polarisation effects. The structure was solved as implemented in the SHELXS86 program system with direct methods [16]. 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. During the refinement it was evident that for every molecule the two Cl and the Me ligands around tin(IV) are statistically distributed and indistinguishable. Consequently the occupancy of the X group = 2/3Cl + 1/3C(methyl) was 0.7843 of the Cl scattering factor. The position of the hydrogen atoms was partially located on the DF map but not refined. The final *R* value was 0.049 (*R*_w 0.053).

The molecular structure is displayed in the ORTEP plot of Fig. 2 together with the numbering scheme. Final atomic coordinates, selected bond distances and angles are reported in Tables 1-3. (Supplementary material including anisotropic thermal parameters, structural factors, inter atomic contacts, and fractional coordinates for non-hydrogen atoms is available on request from the Authors).

The Mössbauer collection of data and the subsequent data processing procedure are similar to those previously reported [9].

Results and Discussion

The compound have been prepared by the reaction :

The colorless solid shows good stability but in the air it is more moisture-sensitive than the corresponding ones with Tp, Tp*, or Tp^{Me}. The complex is soluble in chlorinated organic solvents, less in aromatic hydrocarbons, not appreciably in the aliphatic ones, and insoluble in water.

The electrical conductivity in dichloromethane solution shows it to be a non-electrolyte, and the molecular weight determinations in CHCl₃ indicate that discrete monomeric units are present in solution in agreement with its nature as a neutral, internal complex. The three pyrazole groups linked to tin should be, in the frame of octahedral geometry, not equivalent. The group opposing the Me-substituent should give rise to signals distinctly different from those from the other two. Solution NMR spectra fail to show such inequivalence, so that fluxionality around tin must take place at room temperature, as already observed in other organotin complexes of the same ligand [9] and at variance with the case of the corresponding trispyrazolylborato ligands [2, 4-8].

In Fig. 1 a comparison can be seen of the ¹¹⁹Sn chemical shifts for complexes with different pyrazolylborato ligands. The value for the title compound (-480 ppm) is located between the MeSnCl₂·Tp^{4Me} and MeSnCl₂·Tp and is clearly lower than the value for MeSnCl₂ pzTp. This is qualitatively in accordance with the expected donating power of the ligands. Indeed, the presence of electron-releasing Me groups make them better donating ones, while the presence of one more pyrazole group on B decreases their overall donating power [16]. This is also in agreement with the empirical observation [2-9] that correlates lower ¹¹⁹Sn chemical shifts for organotin(IV) polypyrazolylborates with better donating power of the ligand. According to such observation the positive effect of a 4-Me substituent cannot counterbalance the negative effect of a one more pz group on boron: $\delta(\text{MeSnCl}_2 \text{ pzTp}^{4\text{Me}}) < \delta(\text{MeSnCl}_2 \cdot \text{Tp})$.

Table 1. Fractional coordinates with equivalent isotropic thermal parameters ($\text{\AA}^2$) for $\text{MeSnCl}_2\cdot\text{pzTp}_{4\text{Me}}$. Uis/eq is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	Uis/eq
Sn	0.19208(4)	0.32014(2)	0.08400(2)	0.0436(2)
X(1) ^a	-0.0528(3)	0.3122(2)	0.0137(2)	0.0717(8)
X(2) ^a	0.2813(3)	0.4165(2)	-0.0054(2)	0.085(1)
X(3) ^a	0.2871(3)	0.1941(2)	0.0292(2)	0.0735(8)
N(1)	0.3994(5)	0.3330(3)	0.1787(3)	0.043(1)
N(2)	0.4046(4)	0.3449(2)	0.2649(3)	0.034(1)
N(3)	0.1271(5)	0.4229(3)	0.1629(3)	0.039(1)
N(4)	0.1683(4)	0.4247(3)	0.2490(3)	0.035(1)
N(5)	0.1322(5)	0.2472(3)	0.1930(3)	0.045(1)
N(6)	0.1729(5)	0.2680(3)	0.2763(3)	0.037(1)
N(7)	0.2717(5)	0.3716(3)	0.3925(3)	0.037(1)
N(8)	0.3822(5)	0.4233(3)	0.4279(3)	0.048(2)
C(1)	0.5461(6)	0.3471(3)	0.3024(4)	0.042(2)
C(2)	0.6366(6)	0.3368(3)	0.2414(4)	0.049(2)
C(3)	0.5400(7)	0.3288(4)	0.1650(4)	0.049(2)
C(4)	0.8012(7)	0.3348(5)	0.2534(6)	0.082(3)
C(5)	0.1259(6)	0.4976(3)	0.2786(3)	0.038(2)
C(6)	0.0567(6)	0.5456(3)	0.2118(4)	0.043(2)
C(7)	0.0589(6)	0.4955(4)	0.1410(4)	0.049(2)
C(8)	-0.0079(8)	0.6314(4)	0.2150(4)	0.058(2)
C(9)	0.1416(6)	0.2038(3)	0.3255(4)	0.043(2)
C(10)	0.0743(6)	0.1405(3)	0.2738(4)	0.049(2)
C(11)	0.0715(7)	0.1703(3)	0.1925(5)	0.054(2)
C(12)	0.0200(9)	0.0581(4)	0.3031(6)	0.075(3)
C(13)	0.3447(7)	0.4460(4)	0.5024(4)	0.055(2)
C(14)	0.2098(7)	0.4133(4)	0.5144(4)	0.056(2)
C(15)	0.1658(6)	0.3669(4)	0.4439(4)	0.050(2)
C(1 6)	0.133(1)	0.4250(7)	0.5902(6)	0.102(4)
B(1)	0.2567(6)	0.3516(3)	0.2988(4)	0.034(2)

^a X = 2/3Cl + 1/3C(methyl)

The tin coordination site is roughly regular: the bond angles range from 79.3(2) to 90.7(1)° (Table 2) and the bond lengths Sn–N from one side and the Sn–X ones from the other are practically identical (Table 3). Selected bond distances and angles are summarised in Tables 2 and 3.

Fig. 1 - Trend of ^{119}Sn chemical shift within the various ligands for the complexes $\text{MeSnCl}_2\cdot\text{Tp}^\#$.

Molecular structure of MeSnCl₂pzTp^{4Me}

The cell content consists of four covalent molecules of MeSnCl₂pzTp^{4Me} with no significant intra- and intermolecular interactions. As shown in Fig. 2, the tin atom displays an octahedral coordination geometry.

Fig. 2. Molecular structure for MeSnCl₂pzTp^{4Me}. In the figure X = 2/3 Cl + 1/3 C (methyl).

Table 2. Bond lengths (Å) for MeSnCl₂pzTp^{4Me}.

Sn-X(1)	2.358(3)	Sn-X(2)	2.329(3)
Sn-X(3)	2.407(3)	Sn-N(1)	2.248(5)
Sn-N(3)	2.202(4)	Sn-N(5)	2.228(5)
N(1)-N(2)	1.377(6)	N(1)-C(3)	1.349(8)
N(2)-C(1)	1.346(6)	N(2)-B(1)	1.547(7)
N(3)-N(4)	1.363(6)	N(3)-C(7)	1.335(7)
N(4)-C(5)	1.334(6)	N(4)-B(1)	1.563(7)
N(5)-N(6)	1.360(6)	N(5)-C(11)	1.346(7)
N(6)-C(9)	1.345(7)	N(6)-B(1)	1.552(7)
N(7)-N(8)	1.360(6)	N(7)-C(15)	1.371(8)
N(7)-B(1)	1.509(7)	N(8)-C(13)	1.335(8)
C(1)-C(2)	1.386(9)	C(2)-C(3)	1.394(8)
C(2)-C(4)	1.499(9)	C(5)-C(6)	1.380(7)
C(6)-C(7)	1.382(8)	C(6)-C(8)	1.495(8)
C(9)-C(10)	1.385(8)	C(10)-C(11)	1.37(1)
C(10)-C(12)	1.503(9)	C(13)-C(14)	1.389(9)
C(14)-C(15)	1.350(9)	C(14)-C(16)	1.50(1)

The weighted least-squares pyrazole rings planes 1 (N1, N2, C1, C2, C3) and 2 (N3, N4, C5, C6, C7) do not deviate significantly from planarity. On the contrary, the planes 3 (N5, N6, C9, C10, C11) and 4 (N7, N8, C13, C14, C15) deviate from planarity. (In addition the isotropic thermal variations of the

C(methyl) atoms connected to these last pyrazole rings are the largest in Table 1). The dihedral angles between the planes 1/2, 1/3, 1/4, 2/3, 2/4, and 3/4 are 63.3(2)°, 111.6(2)°, 33.7(2)°, 48.3(2)°, 89.4(2)° and 132.9(2), respectively.

Examination of Table 4 reveals some notable features. The average Sn–N distance in the present complex MeSnCl₂·pzTp^{4Me} (A) is longer than in the corresponding one SnCl₃·pzTp^{4Me} (B), but shorter than MeSnCl₂·Tp^{Me} (C); the complex is somewhat similar to that in D (which can be assimilated to a complex of the type RSnCl₂·Tp). In addition, the N–Sn–N angles shrink, while the Cl–Sn–Cl ones open up in A compared to B.

Substituting a Me group for a Cl atom on tin, the MeSnCl₂⁺ fragment becomes less electron demanding than the SnCl₃⁺ one, and this explains the weakening and the consequent lengthening of the Sn–N bonds. A greater Sn–N elongation allows an increase in Cl–Sn–Cl angles (together with the Me–Sn–Cl bond angles) and a decrease in the N–Sn–N ones. Such angle widening releases non-bonded Cl···Cl interactions, while the closing of the ligand bite permits a reduction of the back strain due to the fourth pyrazole ring.

Table 3. Bond angles (°) for MeSnCl₂·pzTp^{4Me}

N(3)–Sn–N(5)	79.7(2)	N(1)–Sn–N(5)	79.3(2)
N(1)–Sn–N(3)	80.2(2)	X(3)–Sn–N(5)	89.8(1)
X(3)–Sn–N(3)	166.7(1)	X(3)–Sn–N(1)	90.0(2)
X(2)–Sn–N(5)	166.8(1)	X(2)–Sn–N(3)	90.7(1)
X(2)–Sn–N(1)	90.2(2)	X(2)–Sn–X(3)	98.3(1)
X(1)–Sn–N(5)	90.3(2)	X(1)–Sn–N(3)	89.1(2)
X(1)–Sn–N(1)	166.2(1)	X(1)–Sn–X(3)	99.2(1)
X(1)–Sn–X(2)	98.6(1)	Sn–N(1)–C(3)	128.5(4)
Sn–N(1)–N(2)	124.9(4)	N(2)–N(1)–C(3)	106.6(5)
N(1)–N(2)–B(1)	117.5(4)	N(1)–N(2)–C(1)	108.9(5)
C(1)–N(2)–B(1)	133.6(4)	Sn–N(3)–C(7)	130.9(4)
Sn–N(3)–N(4)	122.1(3)	N(4)–N(3)–C(7)	106.7(4)
N(3)–N(4)–B(1)	122.2(4)	N(3)–N(4)–C(5)	108.8(4)
C(5)–N(4)–B(1)	128.9(4)	Sn–N(5)–C(11)	128.6(4)
Sn–N(5)–N(6)	124.5(3)	N(6)–N(5)–C(11)	106.1(5)
N(5)–N(6)–B(1)	119.0(4)	N(5)–N(6)–C(9)	109.2(4)
C(9)–N(6)–B(1)	131.5(4)	C(15)–N(7)–B(1)	128.0(5)
N(8)–N(7)–B(1)	118.8(5)	N(8)–N(7)–C(15)	110.1(4)
N(7)–N(8)–C(13)	104.4(5)	N(2)–C(1)–C(2)	109.5(5)
C(1)–C(2)–C(4)	128.4(6)	C(1)–C(2)–C(3)	104.4(6)
C(3)–C(2)–C(4)	127.1(6)	N(1)–C(3)–C(2)	110.6(6)
N(4)–C(5)–C(6)	109.6(5)	C(5)–C(6)–C(8)	128.1(5)
C(5)–C(6)–C(7)	104.1(5)	C(7)–C(6)–C(8)	127.8(5)
N(3)–C(7)–C(6)	110.8(5)	N(6)–C(9)–C(10)	109.0(5)
C(9)–C(10)–C(12)	126.3(6)	C(9)–C(10)–C(11)	104.2(5)
C(11)–C(10)–C(12)	129.5(6)	N(5)–C(11)–C(10)	111.3(5)
N(8)–C(13)–C(14)	112.5(6)	C(13)–C(14)–C(16)	127.4(7)
C(13)–C(14)–C(15)	104.4(6)	C(15)–C(14)–C(16)	128.1(7)
N(7)–C(15)–C(14)	108.5(6)	N(6)–B(1)–N(7)	111.9(4)
N(4)–B(1)–N(7)	107.6(4)	N(4)–B(1)–N(6)	108.8(4)
N(2)–B(1)–N(7)	114.3(5)	N(2)–B(1)–N(6)	107.1(4)
N(2)–B(1)–N(4)	107.0(4)		

Table 4. Comparison of structural data for related organotin(IV) compounds R_nSnX_{4–n}·1·Tp[#]

Entry	Tp [#]	R	<i>n</i>	Sn–N (Å)	Sn–C (Å)	Sn–Cl (Å)	N–Sn–N (°)	Cl–Sn–Cl (°)	Me–Sn–Cl (°)	Ref.
A	pzTp ^{4Me}	Me	1	2.226	2.329	2.383	79.7	99.0 ^a		*
B	pzTp ^{4Me}	–	0	2.191	–	2.372	81.9	96.2	–	9
C	Tp ^{Me}	Me	1	2.242	2.244	2.438	82.0	94.5	96.5	6
D	Tp	R ^b	1	2.218	2.140	2.428	80.3	94.3	97.8	15

*Present paper. ^a As explained, the Sn–Me and the Cl atoms are indistinguishable.

^b R = MeO–OC–CH₂–CH₂–.

As often observed in comparing 3-substituted pyrazole ligands with 3-unsubstituted ones, the even longer Sn–N bond for C is attributable to some steric interaction of such rings with the tin-bonded groups.

Mössbauer Spectroscopy

The fit of the Mössbauer spectrum in Fig. 3 of MeSnCl₂·pzTp^{4Me} is consistent with the presence of one electric quadrupole doublet attributable to the octahedral tin(IV) site found in its crystal structure (IS = 0.71 mm/s relative to SnO₂, QS = 1.74 mm/s, LW = 1.10 mm/s [9]). The minor spectral component displayed in Fig. 3 with a relative resonance area of about 4% (IS = 1.33(2), QS = 4.22(4) and line width 0.76(7) mm/s) can be related, owing to its very large splitting, to a decomposition product containing an all-*trans* octahedral tin(IV) site previously observed in X-ray crystal structures of deboronated compounds [12].

Fig. 3. Mössbauer spectrum at the liquid helium temperature for MeSnCl₂·pzTp^{4Me}.

The Mössbauer parameters are similar to those reported for MeSnCl₂·Tp^{4Me} (IS = 0.72, QS = 1.72, LW = 1.01 mm/s, [13]). In spite of the peculiar steric requirements of the ligand pzTp^{4Me} in comparison with Tp^{4Me}, the Mössbauer parameters are practically unchanged.

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