

Studies on some di- and triorganotin(IV) derivatives of bis(1-pyrazolyl) borates and some related compounds

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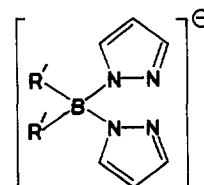
Abstract

A number of di- and triorganotin(IV) complexes of dihydrobis(1-pyrazolyl)borate and diphenylbis(1-pyrazolyl)borate have been synthesized. The complexes derived from dihydrobis(1-pyrazolyl)borate have been converted to their dihalobis(1-pyrazolyl)borate analogues by halogenation reactions. The compounds have been characterized by elemental analysis, infrared and ¹H, ¹¹B and ¹¹⁹Sn NMR spectra. © 1997 Elsevier Science S.A.

Keywords: Diphenyltin(IV); Dibutyltin(IV); Dimethyltin(IV); Bis(1-pyrazolyl)borates; Infrared spectroscopy; ¹¹B/¹¹⁹Sn NMR spectroscopy

1. Introduction

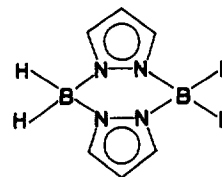
The poly(1-pyrazolyl)borate ions, [R_nB(pz)_{4-n}]⁻ (Hpz^{*} = pyrazole or C-substituted derivative thereof, R = a non-coordinating group, n = 0–2), have found extensive use as chelating ligands towards metals in general and transition metal in particular [1,2]. Poly(1-pyrazolyl)borate derivatives of tin(IV) [3–11] and tin(II) [12,13] have also attracted considerable attention in recent years, yet organotin(IV) derivatives of dihydrobis(1-pyrazolyl)borate, H₂B(pz)₂⁻ (**Ia**), and diphenylbis(1-pyrazolyl)borate, [Ph₂B(pz)₂]⁻ (**Ib**), are rather quite limited [13]. Moreover, no organotin(IV) complexes of dihalobis(1-pyrazolyl)borates, [X₂B(pz)₂]⁻ (X = Cl, Br, I), are known, nor the parent ligands themselves. Therefore, syntheses of haloderivatives of organotin(IV) complexes from their dihydrobis(1-pyrazolyl)borate complexes by halogenation was undertaken, considering the latter to be structural analogues of pyrazobole, H₂B(μ-pz)₂BH₂ (**II**) [1]. The latter having a B(N₂)₂B six-membered ring system possesses considerable chemical stability and undergoes substitution of the hydrogen atoms on the boron by halogens [1,14].



I

R' = H (**Ia**)

R' = Ph (**Ib**)

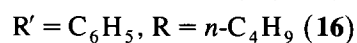
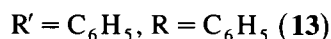
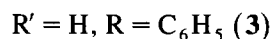
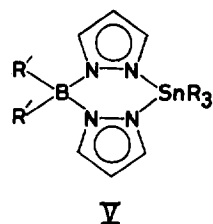
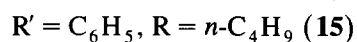
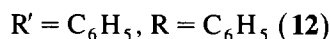
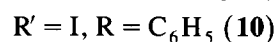
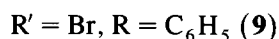
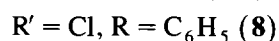
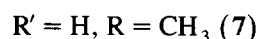
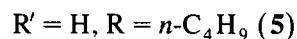
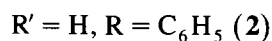
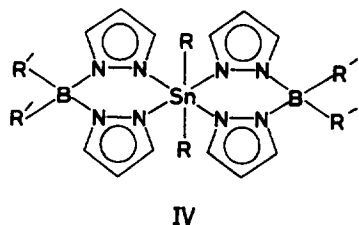
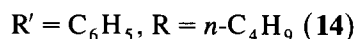
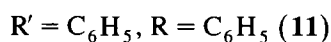
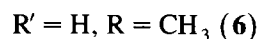
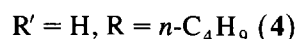
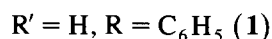
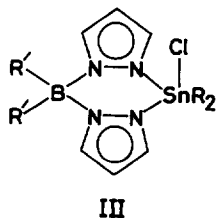


II

The present study describes the synthesis and characterization of some organotin(IV) complexes of dihydro- and diphenylbis(1-pyrazolyl)borates and dihaloderiva-

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tives of the former. Their structural formulae are given in III, IV and V.



2. Experimental

2.1. Materials

Pyrazole (Sigma), diphenyltin dichloride (Aldrich), dimethyltin dichloride (Fluka), dibutyltin dichloride (Alfa), tri-*n*-butyltin chloride (Alfa), sodium tetraphenylborate (Loba, India), potassium borohydride (Sigma), bromine (S.D. Fine Chemicals, India) were used as-received. Iodine (BDH) was purified by sublimation prior to use. Solvents were purified and dried by standard procedures.

2.2. Physical measurements

Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded on a Perkin-Elmer Model 883 or 597 spectrophotometer as KBr discs under standard operating conditions. The spectra were calibrated with respect to the 1601 cm^{-1} band of a polystyrene film. The ^1H NMR spectra were recorded on a Varian EM-360 (60 MHz) or a Jeol JNM-FX-90 (90 MHz) instrument and the ^{11}B and ^{119}Sn NMR spectra were recorded on a Jeol JNM-FX-90 instrument at 28.89 MHz and 33.35 MHz respectively, using CHCl_3 (locking with D_2O) as solvent unless otherwise noted. The chemical shift data are given in parts per million with positive values indicating downfield from the references (internal $(\text{CH}_3)_4\text{Si}$ for ^1H NMR, external $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$ for ^{11}B NMR and external $(\text{CH}_3)_4\text{Sn}$ for ^{119}Sn NMR). Carbon and hydrogen analyses were performed on a Perkin-Elmer 240C elemental analyser. Boron was estimated volumetrically and tin was estimated gravimetrically as SnO_2 after precipitation as metastannic acid. Melting points (uncorrected) were determined on an electrical heating-coil apparatus. Preparation and handling of materials were generally done in anhydrous atmosphere under nitrogen cover.

2.3. Preparation of poly(1-pyrazolyl)borate ligands

$\text{K}[\text{H}_2\text{B}(\text{pz})_2]$ (Hpz = pyrazole) [15] was prepared from KBH_4 and Hpz; m.p. $170\text{--}172^\circ\text{C}$ (Ref. [15] $171\text{--}172^\circ\text{C}$); $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ was prepared from $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ and Hpz [16].

2.4. Preparation of organotin(IV) bis(1-pyrazolyl)borates

All the compounds except a few were prepared in similar fashion by stirring the reactants at room temperature in dichloromethane; however, the work-up procedures differed in details, and are, therefore, given under individual heads.

2.4.1. $[H_2B(pz)_2]SnCl(C_6H_5)_2$ (**1**)

A mixture of $(C_6H_5)_2SnCl_2$ (1.89 g, 5.5 mmol), and $K[H_2B(pz)_2]$ (1.022 g, 5.5 mmol) and 80 ml of dichloromethane was stirred at room temperature for 8 h. The mixture was filtered to remove the alkali halide and the solvent was evaporated from clear filtrate to leave 2.30 g (92.2%) of crude product which was recrystallized from benzene; m.p. 97–99 °C. Anal. Found: C, 47.14; H, 3.65; B, 2.27; Sn, 25.94. Calcd. for $C_{18}H_{18}BClN_4Sn$ (formula weight, 455.33): C, 47.48; H, 3.98; B, 2.37; Sn, 26.07.

2.4.2. $[H_2B(pz)_2]Sn(C_6H_5)_2$ (**2**)

2 was obtained by the reaction of 0.95 g (2.75 mmol) of $(C_6H_5)_2SnCl_2$ and 1.03 g (5.5 mmol) of $K[H_2B(pz)_2]$ (70 ml of dichloromethane, 10 h stirring) to give 1.24 g (79.3%) of crude material after drying in vacuum. The compound could not be further purified by recrystallization due to its decomposition during recrystallization. M.p. 100–103 °C; Anal. Found: C, 51.29; H, 4.49; B, 3.88; Sn, 20.47. Calcd. for $C_{24}H_{26}B_2N_8Sn$ (formula weight, 566.84): C, 50.85; H, 4.62; B, 3.81; Sn, 20.94.

2.4.3. $[H_2B(pz)_2]Sn(C_6H_5)_3$ (**3**)

3 was prepared from 1.06 g (5.70 mmol) of $K[H_2B(pz)_2]$ and 2.192 g (5.69 mmol) of $(C_6H_5)_3SnCl$ (80 ml of dichloromethane, 12 h stirring) as a crude gelatinous mass which solidified after several hours of vacuum. The crude solid product was extracted with dry chloroform. M.p. of the resulting extracted material, 182–184 °C. Anal. Found: C, 57.52; H, 4.80; B, 1.99; Sn, 23.48. Calcd. for $C_{24}H_{23}BN_4Sn$ (formula weight, 496.98): C, 58.00; H, 4.66; B, 2.17; Sn, 23.88.

2.4.4. $[H_2B(pz)_2]SnCl(n-C_4H_9)_2$ (**4**)

4 was prepared employing 0.52 g (2.76 mmol) of $K[H_2B(pz)_2]$ with 0.84 g (2.76 mmol) of $(n-C_4H_9)_2SnCl_2$ (60 ml of dichloromethane, 8 h stirring); 1.03 g (90.1%) of crude solid product was obtained, which was washed with dry *n*-pentane followed by recrystallization from benzene; m.p. 120–123 °C. Anal. Found: C, 40.02; H, 5.96; B, 2.76; Sn, 28.34. Calcd. for $C_{14}H_{26}BClN_4Sn$ (formula weight, 415.35): C, 40.48; H, 6.30; B, 2.60; Sn, 28.58.

2.4.5. $[H_2B(pz)_2]_2Sn(n-C_4H_9)_2$ (**5**)

5 was prepared from 1.03 g (5.54 mmol) of $K[H_2B(pz)_2]$ and 0.839 g (2.76 mmol) of $(n-C_4H_9)_2SnCl_2$ (60 ml of dichloromethane, 16 h stirring). After filtration and removal of the solvent under reduced pressure, crude solid product 1.36 g (93.5%) was obtained. This was then washed with dry ethanol and finally extracted with dry chloroform which was removed and the residue was dried in vacuum; m.p. 111–113 °C. Anal. Found: C, 45.56; H, 6.06; B, 4.25;

Sn, 22.48. Calcd. for $C_{20}H_{34}B_2N_8Sn$ (formula weight, 526.86): C, 45.59; H, 6.50; B, 4.10; Sn, 22.53.

2.4.6. $[H_2B(pz)_2]SnCl(CH_3)_2$ (**6**)

6 was prepared from 0.511 g (2.75 mmol) of $K[H_2B(pz)_2]$ and 0.604 g (2.75 mmol) of $(CH_3)_2SnCl_2$ (50 ml of dichloromethane, 6 h stirring). The colourless crude solid product, 0.89 g (97.8%), could not be further purified; m.p. 110–113 °C. Anal. Found: C, 29.56; H, 4.10; B, 2.99; Sn, 35.37. Calcd. for $C_8H_{14}BClN_4Sn$ (formula weight, 331.19): C, 29.01; H, 4.26; B, 3.26; Sn, 35.84.

2.4.7. $[H_2B(pz)_2]_2Sn(CH_3)_2$ (**7**)

7 was prepared from 0.605 g (2.75 mmol) of $(CH_3)_2SnCl_2$ and 1.03 g (5.5 mmol) of $K[H_2B(pz)_2]$ (60 ml of dichloromethane, 12 h stirring) as a crude solid product 1.09 g (89.0%). It was recrystallized from chloroform–petroleum ether mixture to give colourless crystals, m.p. 160–162 °C. Anal. Found: C, 37.54; H, 4.70; B, 4.59; Sn, 26.45. Calcd. for $C_{14}H_{22}B_2N_8Sn$ (formula weight, 442.70): C, 37.98; H, 5.00; B, 4.88; Sn, 26.81.

2.4.8. $[Cl_2B(pz)_2]_2Sn(C_6H_5)_2$ (**8**)

This was prepared by passing dry chlorine gas through a solution of 1.311 g (2.30 mmol) of $[H_2B(pz)_2]_2Sn(C_6H_5)_2$ (**2**) in 70 ml of dichloromethane with stirring until halogen colour persisted in the solution. A small amount of gelatinous material was removed by filtration and the clear filtrate was then evaporated to dryness. Thus 1.22 g (75%) of crude product was obtained, which was recrystallized from chloroform–petroleum ether mixture to give a colourless crystalline compound; m.p. 175–178 °C. Anal. Found: C, 40.48; H, 3.33; B, 2.38; Sn, 16.41. Calcd. for $C_{24}H_{22}B_2Cl_4N_8Sn$ (formula weight, 704.62): C, 40.91; H, 3.15; B, 2.06; Sn, 16.85.

2.4.9. $[Br_2B(pz)_2]_2Sn(C_6H_5)_2$ (**9**)

9 was prepared by adding dropwise a solution of 1.24 g (7.77 mmol) of bromine in dichloromethane with stirring to a solution of 1.1 g (1.94 mmol) of $[H_2B(pz)_2]_2Sn(C_6H_5)_2$ (**2**) in 50 ml of dichloromethane at room temperature. The resulting mixture was refluxed for 30 min to complete the reaction. A light yellow precipitate was formed, which was filtered, washed with dry chloroform and collected, 1.59 g (92.8%). The crude product was washed with water and finally recrystallized from benzene; m.p. 138–140 °C. Anal. Found: C, 32.35; H, 2.42; B, 2.27; Sn, 13.64. Calcd. for $C_{24}H_{22}B_2Br_4N_8Sn$ (formula weight, 882.43): C, 32.67; H, 2.51; B, 2.45; Sn, 13.45.

2.4.10. $[I_2B(pz)_2]_2Sn(C_6H_5)_2$ (**10**)

10 was prepared in analogous manner by adding dropwise, with stirring, a solution of 2.16 g (8.51 mmol)

of iodine in dichloromethane to a solution of 1.20 g (2.12 mmol) of $[\text{H}_2\text{B}(\text{pz})_2]_2\text{Sn}(\text{C}_6\text{H}_5)_2$ (**2**) in 50 ml of dichloromethane at room temperature and the resulting mixture was stirred for 12 h. Any trace of solid material was separated by filtration and the solvent was evaporated on a rotary evaporator to leave 1.98 g (87%) of crude yellow solid product. It was washed with dry ethanol to remove traces of iodine and recrystallized from hot toluene, m.p. > 258 °C. Anal. Found: C, 26.55; H, 2.29; B, 2.14; Sn, 11.05. Calcd. for $\text{C}_{24}\text{H}_{22}\text{B}_2\text{I}_4\text{N}_8\text{Sn}$ (formula weight, 1070.41): C, 26.93; H, 2.07; B, 2.02; Sn, 11.09.

2.4.11. $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{SnCl}(\text{C}_6\text{H}_5)_2$ (**11**)

A mixture of 0.96 g (2.98 mmol) of $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ and 1.025 g (2.98 mmol) of $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ and 50 ml of dichloromethane was stirred at room temperature for 6 h. The mixture was filtered and the solvent was evaporated from the clear filtrate under reduced pressure to leave 1.73 g (95%) of colourless crude product. It could not be recrystallized because of its decomposition during recrystallization. The crude material melted over a range 165–170 °C. Anal. Found: C, 58.84; H, 4.59; B, 1.47; Sn, 19.76. Calcd. for $\text{C}_{30}\text{H}_{26}\text{BClN}_4\text{Sn}$ (formula weight, 607.52): C, 59.31; H, 4.31; B, 1.78; Sn, 19.54.

2.4.12. $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]_2\text{Sn}(\text{C}_6\text{H}_5)_2$ (**12**)

12 was prepared from 1.024 g (3.18 mmol) of $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ and 0.547 g (1.59 mmol) of $(\text{C}_6\text{H}_5)_2\text{SnCl}_2$ (60 ml of dichloromethane, 8 h stirring) to give 1.29 g (93.6%) of crude material, sintering at 75 °C and melting at 112–116 °C. Anal. Found: C, 65.78; H, 5.12; B, 2.29; Sn, 13.54. Calcd. for $\text{C}_{48}\text{H}_{42}\text{B}_2\text{N}_8\text{Sn}$ (formula weight, 871.23): C, 66.17; H, 4.85; B, 2.48; Sn, 13.62.

2.4.13. $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{Sn}(\text{C}_6\text{H}_5)_3$ (**13**)

13 was obtained from the reaction of 1.1 g (3.4 mmol) of $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ and 1.32 g (3.42 mmol) of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ (70 ml of dichloromethane 6 h stirring) as a crude solid product, 2.14 g (96%). Any trace of pyrazole was removed by sublimation and the residue was extracted with dry chloroform. The extracted product melted at 168–170 °C. Anal. Found: C, 66.48; H, 4.87; B, 1.68; Sn, 17.87. Calcd. for $\text{C}_{36}\text{H}_{31}\text{BN}_4\text{Sn}$ (formula weight, 649.18): C, 66.60; H, 4.81; B, 1.66; Sn, 18.28.

2.4.14. $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{SnCl}(n\text{-C}_4\text{H}_9)_2$ (**14**)

14 was obtained from 0.87 g (2.70 mmol) or $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ and 0.82 (2.70 mmol) of $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$ (60 ml of dichloromethane, 6 h stirring) as a crude gelatinous product which after several hours of drying in vacuum yielded 1.3 g (85%) of the product.

Anal. Found: C, 55.54; H, 5.73; B, 1.73; Sn, 20.12. Calcd. for $\text{C}_{26}\text{H}_{34}\text{BClN}_4\text{Sn}$ (formula weight, 567.54): C, 55.02; H, 6.04; B, 1.90; Sn, 20.91.

2.4.15. $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]_2\text{Sn}(n\text{-C}_4\text{H}_9)_2$ (**15**)

15 was prepared by the reaction of 0.90 g (2.80 mmol) of $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ and 0.42 g (1.38 mmol) of $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$ in 40 ml of dichloromethane (12 h stirring) to give 0.90 g (78%) of crude product, which was washed with dry *n*-pentane to remove any traces of $(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$. It sinters at 152 °C and melts at 158–160 °C. Anal. Found: C, 64.03; H, 5.80; B, 2.67; Sn, 14.24. Calcd. for $\text{C}_{44}\text{H}_{50}\text{B}_2\text{N}_8\text{Sn}$ (formula weight, 831.25): C, 63.57; H, 6.06; B, 2.60; Sn, 14.28.

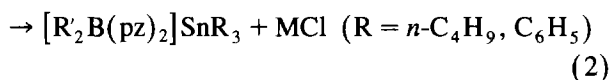
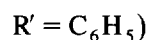
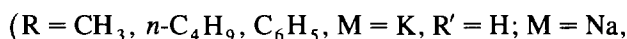
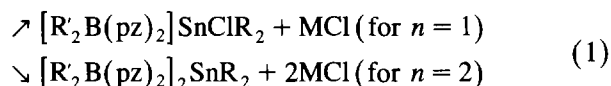
2.4.16. $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{Sn}(n\text{-C}_4\text{H}_9)_3$ (**16**)

16 was prepared by the reaction of 0.55 g (1.70 mmol) of $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ and 0.56 g (1.72 mmol) of $(n\text{-C}_4\text{H}_9)_3\text{SnCl}$ in 60 ml of dichloromethane (16 h stirring) to give 0.92 g (92%) of crude product which was washed with dry petroleum ether and dried under vacuum; m.p. 155–158 °C. Anal. Found: C, 61.18; H, 7.02; B, 1.89; Sn, 20.47. Calcd. for $\text{C}_{30}\text{H}_{43}\text{BN}_4\text{Sn}$ (formula weight, 589.20): C, 61.15; H, 7.35; B, 1.83; Sn, 20.14.

3. Results and discussion

3.1. Synthesis and general

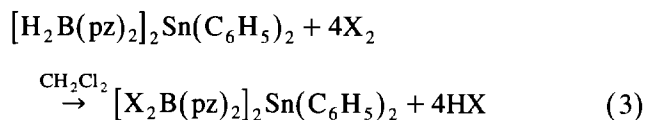
The reactions were carried out by stirring the reactants, R_2SnCl_2 and R_3SnCl , separately with $[\text{H}_2\text{B}(\text{pz})_2]$ or $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ at room temperature under an atmosphere of dry nitrogen and were carried out both in 1:1 and 1:2 molar proportions of organotin compounds to bis(1-pyrazolyl)borates.



The reactions of 1:1 molar proportions of organotin compounds and bis(1-pyrazolyl)borate took place with ease, whereas prolonged reaction times were required for the preparations of L_2SnR_2 and LSnR_3 [$\text{L} = \text{bis}(1-$

pyrazolyl)borate] and particularly more reaction times were required when $R = n\text{-C}_4\text{H}_9$. In most cases the complexes derived from $[\text{H}_2\text{B}(\text{pz})_2]^-$ were temperature sensitive and could not be purified by recrystallization without appreciable decomposition. Only two compounds (**1** and **7**) could be purified by recrystallization from appropriate solvents as described in Section 2. The complexes derived from $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]^-$ were also very sensitive to moisture and deteriorated on standing in solution as indicated by the appearance of a new signal in the ^1H NMR spectra in the range of δ 9.5–10.5 which was due to the presence of free pyrazole as a decomposition product [11]. But the ^1H spectra of fresh sample solutions gave no such signal in that range.

Pyrazabole, $\text{H}_2\text{B}(\mu\text{-pz})_2\text{BH}_2$ is a very stable compound owing to the presence of four co-ordinate boron in the six-membered $\text{B}(\text{N}_2)_2\text{B}$ ring system. Its boron-bonded hydrogen atoms can be replaced by halogen atoms when reacted with elemental halogens—chlorine, bromine and iodine or boron trihalides. Organotin complexes having the $\text{B}(\text{N}_2)_2\text{Sn}$ structural unit may be considered to be similar to the pyrazabole in their structures. On the other hand, halo derivatives of $[\text{H}_2\text{B}(\text{pz})_2]^-$ are not known; so complexes derived from the halo derivatives of $[\text{H}_2\text{B}(\text{pz})_2]^-$ i.e. $[\text{X}_2\text{B}(\text{pz})_2]^-$, were not reported. We prepared halogenated complexes of dihydrobis(1-pyrazolyl)borate by halogenating the organotin complexes derived from $[\text{H}_2\text{B}(\text{pz})_2]^-$ by reacting them with elemental halogens (Eq. (3)). The halogenation reactions were found to proceed smoothly without any complications.



(X = Cl, Br, I)

3.2. Infrared spectra

Infrared spectra of the complexes were recorded in the region $4000\text{--}200\text{ cm}^{-1}$. The most prominent feature of the infrared spectra of the complexes derived from $[\text{H}_2\text{B}(\text{pz})_2]^-$ (**1–7**) is the presence of bands in the range $2614\text{--}2280\text{ cm}^{-1}$ due to the $\nu(\text{B-H})$ of the BH_2 group and the absence of any bands in this region for the complexes derived from $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]^-$ (**11–16**). The B-halogenated compounds (**8–10**) are also characterized by the absence of $\nu(\text{B-H})$ bands. The $\nu(\text{C-H})$ absorptions are found in two groups, in the ranges $3157\text{--}3000\text{ cm}^{-1}$ due to the phenyl and pyrazolyl groups and $2990\text{--}2823\text{ cm}^{-1}$ due to the alkyl groups. Ring breathing vibrations are found at $1525\text{--}1500\text{ cm}^{-1}$. Bands attributable to $\nu(\text{Sn-N})$, $\nu(\text{Sn-C})$ and $\nu(\text{Sn-Cl})$

are found in the low energy region. The asymmetric and symmetric $\nu(\text{Sn-C})$ (phenyl) modes in various phenyltin complexes were reported in the regions $382\text{--}261\text{ cm}^{-1}$ and $249\text{--}225\text{ cm}^{-1}$ respectively [17–19]. For the phenyltin bis(1-pyrazolyl)borate complexes, we have found bands in the regions $355\text{--}326\text{ cm}^{-1}$ and $278\text{--}266\text{ cm}^{-1}$ which may be assigned to the $\text{Sn-C}(\text{phenyl})$ asymmetric and symmetric stretching modes. The $\nu(\text{Sn-C})(\text{methyl})$ and $\nu(\text{Sn-C})(\text{butyl})$ modes in dialkylbis(diketonates), dibutylbis(hydroxamates) and dibutyldihydroxamates are found in the range $606\text{--}489\text{ cm}^{-1}$ [18–20]. The same are found in the ranges $595\text{--}520\text{ cm}^{-1}$ and $499\text{--}388\text{ cm}^{-1}$ for asymmetric and symmetric Sn-C stretching modes respectively. There is no general agreement on the values of the $\nu(\text{Sn-N})$ modes. For example, Lappert and co-workers assigned a band at 510 cm^{-1} to $\nu(\text{Sn-N})$ in N',N' -dimethyl- N -phenyl-ureidotrimethylstannane [21], whereas Sisido and Kozima assigned asymmetric $\nu(\text{Sn-N})$ modes to bands at $728\text{--}712\text{ cm}^{-1}$ for tris(tri- n -alkyltin)amine (alkyl = methyl, ethyl, propyl) [22]. Zuckerman and co-workers assigned the $\nu(\text{Sn-N})$ absorption to the 843 cm^{-1} band in N -trimethylstannylaniline [23], while Marchand et al. attributed a band at 600 cm^{-1} to Sn-N stretch in tributylstannylpyrazole [24]. We found bands consistently in the range $618\text{--}607\text{ cm}^{-1}$ by eliminating bands found in both the ligand bis(1-pyrazole)borates and the organotin starting materials. Considering the mass effect and close analogy of the complexes studied here with the tributylstannylpyrazole [24], we assign the bands in the region $616\text{--}607\text{ cm}^{-1}$ to Sn-N stretching modes. There are also discrepancies in the values of $\nu(\text{Sn-Cl})$ modes in the organotin halide complexes. These modes in compounds **1**, **4**, **6**, **11** and **14** have been assigned to the bands at $461\text{--}338\text{ cm}^{-1}$ in consonance with values reported in the literature [25].

3.3. NMR spectra

The ^1H NMR spectra of the complexes containing five-coordinate tin (**1**, **3**, **4**, **6**, **11**, **13**, **14**, **16**) show two sets of signals (unresolved for **4**) for $\text{C}_4\text{-H}$ atoms in the range δ 6.00–6.56 indicating the presence of two inequivalent pyrazolyl groups, arising due to the trigonal bipyramidal arrangement around tin with bis(1-pyrazolyl)borate groups spanning the cis axial, equatorial positions, which structural arrangement is common with many organotin compounds [26]. In all other cases, the $\text{C}_4\text{-H}$ atoms of the pyrazolyl group appear as an unsymmetrical triplet in the range δ 6.2–6.6. The ^1H NMR spectra of the alkyltin derivatives are characterized by the presence of the alkyl group absorptions at appropriate positions and the absorptions owing to the phenyl groups of the phenyltin derivatives and the B-phenyl groups of the ligands are in most cases overlapped with

Table 1
Infrared spectral data of organotin poly(1-pyrazolyl)borates

IR data (cm ⁻¹) ^a						
Compound no.	$\nu(\text{B-H})$	$\nu(\text{C-H})$ (Ph + pz)	$\nu(\text{C-H})$ (alkyl)	$\nu(\text{Sn-N})$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-Cl})$
1	2482 m 2448 w	3141 3119 m 3062 m		613 s	330 m 270 m	442 m
2	2433 m 2383 m, sh 2280 m	3123 m 3061 w		614 s	334 m 278 m	
3	2500 m 2479 m 2459 m 2367 w	3135 m 3064 m 3050 w,sh		616 m	331 m 266 m	
4	2509 m	3140 w 3123 m 3108 m	2957 m 2927 m 2907 w,sh 2870 m	612 s	539 m 400 w	365 m
5	2495 s	3150 m 3135 w 3105 m	2962 s 2945 w 2880 m 2862 w	614 s	520 w 388 w	
6	2537 m 2486 m	3137 m 3121 m 3000 w	2979 w 2962 m 2920 w 2823 w	613 s	545 w 499 s	338 m
7	2614 w,sh 2535 s 2443 w	3140 m 3118 m	2988 m 2960 m 2913 m 2870 w	615 s	580 w 499 s	
8		3125 s		607 s	326 s 276 m,sh	
9		3141 ms 3118 s		611 s	342 w 275 w	
10		3157 w 3135 w 3113 s		610 s	339 m 267 w	
11		3141 m 3124 m 3069 m 3047 m 3006 w		617 s	355 s 275 s	461 m
12		3139 m 3115 m 3067 m 3043 m 3005 m		608 m	355 s 274 s	
13		3137 w,sh 3068 m 3047 m 3007 m		609 w	344 m 270 s	
14		3120 m	2960 ms 2930 m 2870 m	608 s	582 s 437 w	430 m

Table 1 (continued)

IR data (cm ⁻¹) ^a						
Compound no.	$\nu(\text{B-H})$	$\nu(\text{C-H}) (\text{Ph} + \text{pz})$	$\nu(\text{C-H}) (\text{alkyl})$	$\nu(\text{Sn-N})$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-Cl})$
15		3130 w,sh	2959 m			
		3115 m	2927 m	616 m	595 m	
		3095 w	2874 w		480 w	
		3060 m				
		3005 m				
16		3120 m	2990 m	610 s	595 m	
		3060 w	2880 w		480 w	

^a s = strong, m = medium, w = weak, sh = shoulder.

Table 2
¹H, ¹¹B and ¹¹⁹Sn NMR chemical shifts of organotin poly(1-pyrazolyl)borates

Compound no.	NMR data (δ ppm)				$\delta(^{11}\text{B})$	$\delta(^{119}\text{Sn})$
	¹ H) ^a					
	4-H (t)	3 or 5-H (d)	Phenyl (m)	Alkyl		
1	6.28 [2]	7.96 [2]	7.20–7.60 [10]		–3.56	–450.70
	6.46	8.20 [2]				
2	6.16 [4]	9.0 br [4]	7.30–8.06 [10]		–3.76	–289.56
		8.1 br [4]				
3	6.00 [2]		7.06–8.03 [19]		–1.69	–66.50
	6.23					
4		7.70 [4]			–3.23	–408.68
	6.39 [2]	7.84		0.94 t [18]		
		8.00		1.09–1.95 m		
		8.34				
5		7.66 [4]			–3.73	–57.59
	6.23 [4]	7.86 [4]		0.97 t [18]		
6	6.26 [2]	7.66 [2]		1.26 s [6]	–3.22	–329.12
	6.46	7.89 [2]				
7	6.26 [4]	7.64 [4]		0.83 s [6]	–3.73	–360.08
		7.70 [4]				
8	6.50 [4]		7.30 s,br [18]		–4.41	–103.19
			7.70 s,br			
9	6.43 [4]		7.66 s,br [18]		–3.22	–313.53
			8.06 s,br			
10 ^b					3.74	–289.7
11	6.30 [2]	8.06 [2]	6.70–7.83 [20]		6.11 br	–401.82
	6.56	8.39 [2]				
12	6.20 [4]	7.66 [4]	6.83–7.49 [34]			
13	6.12 [2]		6.53–7.39 [29]			
	6.24					
14	6.26 [2]	7.41 [2]	6.89–7.20 [10]	0.72 t [18]	3.50 br	
	6.79	8.06 [2]		0.94–1.73 m		
15	6.20 [4]	7.36 [4]	6.76–7.20 [20]	0.66 t [18]	3.30	–401.82
		7.53 [4]		0.78–1.53 m		
16	6.16 [2]	7.39 [2]	7.03–7.26 [10]	0.85 t [27]		
	6.39	7.56 [2]		1.03–1.59 m		

^a Measured as saturated solutions in CDCl₃ (99.8%) except 1 and 9 which were measured in (CH₃)₂CO-*d*₆ (99.9%); s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. All were measured at 60 MHz, except 1, which was measured at 90 MHz. Square bracketed quantities indicate the number of protons.

^b 10 was too insoluble in CDCl₃ or (CH₃)₂CO-*d*₆ for ¹H NMR study and decomposes in DMSO-*d*₆.

the C₃ and C₅ protons of pyrazolyl groups occurring in the range δ 6.9–8.20. The absorptions due to the C₃ and C₅ protons of the pyrazolyl groups in the butyltin and methyltin complexes appear as doublets in the range δ 7.64–8.34. The $\delta(^{11}\text{B})$ values in the ^{11}B NMR spectra are characteristic of four-coordinate boron and are in consonance with those of similar compounds found in the literature [4–12], and support the formation of the compounds. The $\delta(^{119}\text{Sn})$ values in the ^{119}Sn NMR spectra are characteristic of five- and six-coordinate tin(IV), and the δ values are in consonance with similar compounds derived from pyrazolylborate ligands [10,11] or other chelating ligands [27]. It is, however, found that they are dependent on the coordination number, the nature of the solvent in which spectra are recorded [28] and electronegativity of groups attached to both tin [10,11,29] and boron of the ligand [10,11]. The tin shielding increases with electronegativity of the substituents on it [29]. Thus the tin chemical shifts for compounds **1**, **4**, **11** having chloro substituents on tin appear at -450.70 ppm, -408.68 ppm and -313.53 ppm respectively, while for compounds **3** and **13** the δ values appear at -66.50 ppm and -289.7 ppm respectively, all being five-coordinate and the δ values are in consonance with those found in the literature [10,11,27,30]. Similarly, among the six-coordinate compounds, where no electronegative substituents are present, a wide range of δ values were obtained, which are in conformity with the values found in the literature [10,11,27,30]. Substituents on the boron atom of the ligand portion also affect the tin chemical shift values. For compound **5**, the $\delta(^{119}\text{Sn})$ is -57.59 ppm while for compound **15** having phenyl substituents on boron instead of hydrogen the same appears at -401.82 ppm. Electronegative substituents such as chlorine, iodine on boron also affect the tin chemical shift values, as seen for compound **2** the $\delta(^{119}\text{Sn})$ being at -289.58 ppm while for compounds **8** and **10** having chlorine and iodine substituents on boron, the δ values are -360.08 ppm and -103.19 ppm respectively. On the whole, in compounds such as these under study, where there are many variables, making clear-cut correlation is difficult. The infrared and NMR data are collected in Tables 1 and 2, while the analytical data and m.p.s are given along with the preparation of the compounds in Section 2.

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