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Synthesis and solution studies by electrospray mass spectroscopy of new bis(imidazolyl)borate organotin(IV) complexes

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Abstract

New organotin(IV) derivatives containing the anionic dihydrobis(1-imidazolyl)borate $[H_2B(im)_2]^-$ have been synthesized from the reaction between SnR_nX_{4-n} (R = Me, Ph, ^{n}Bu or Cy; $n = 1–3$) acceptors and $[K\{H_2B(im)_2\}\cdot(DMAC)]$ (DMAC = dimethylacetamide). Mono-nuclear complexes of the type $\{[H_2B(im)_2]R_nSnCl_{4-n-1}\}$ have been obtained, which have been fully characterized by elemental analyses and FT-IR in the solid state and by NMR (^{1}H and ^{119}Sn) spectroscopy, conductivity measurements and electrospray ionization mass spectrometry (ESIMS) in solution. ESIMS spectra of a methanol solution of the complexes show the existence of hydrolysed species for mono- and di-organotin(IV) derivatives, while non-hydrolysed aggregates are detected for triorganotin(IV) derivatives.
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Keywords: Organotin(IV); Bis(imidazolyl)borate ligand; Tin-119 NMR; Electrospray mass spectroscopy

1. Introduction

The imidazole nucleus, and derivatives thereof, are known to play extremely crucial parts in the structures and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions [1]. The replacement of the pyrazole ring in the poly(pyrazol-1-yl)borate ligands [2] by imidazole and the formation of poly(imidazol-1-yl)borate ligands with different coordination characteristics offer the opportunity of a new and interesting chemistry paralleling that of the pyrazolyl arrays.

Poly(1-imidazolyl)borates have been described, but their metal complexes have never been structurally authenticated [3], with the exception of the ionic lithium salt of tetrakis(imidazolyl)borate [4], the hydrotris(imidazolyl)boratothallium(I) compound [5] and the representative arrays of some silver(I) complexes of dihydrobis- and tetrakis-(imidazol-1-yl)borates [6]. Recently, we have reported the synthesis and the spectroscopic characterization of new tetrakis(imidazol-1-yl)borate complexes containing organotin(IV) acceptors and the crystal structure of $[\mu\text{-}(im)_2B(im)_2SnMe_3]$, which represents the first poly(imidazolyl)borate organotin(IV) complex exhibiting a polymeric chain [7]. As an extension of this research field, we report here the synthesis, characterization and reactivity of some new complexes obtained from the interaction of potassium (dimethylacetamide)dihydrobis(1-imidazolyl)borate (Fig. 1), $K(DMAC)[H_2B(im)_2]$ (DMAC = dimethylacetamide), with a number of organotin(IV) halides, SnR_nX_{4-n} (R = Me, Ph, ^{n}Bu or Cy; $n = 1–3$). We also report spectroscopic and electrospray ionization mass studies of these complexes.

Electrospray ionization mass spectrometry (ESIMS) is a relatively new ionization method introduced in the mid-1980s by Fenn et al. [8]. Only recently has there been corresponding interest from inorganic chemists [9], the ESIMS gentle ionization process being particularly suitable for the study of labile organometallic systems in

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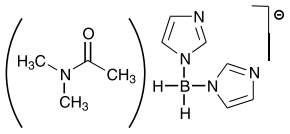

Fig. 1. Structure of the donor (DMAC)$[H_2B(im)_2]^-$.

solution [10]. Our main interests in the area of inorganic ESIMS lie in the development of the technique to probe the chemistry of poly(azolyl)borate ligands and their reactions toward organotin(IV) acceptors. The solution behaviour of organotin species is known to be complicated since a range of complex cations and anions may be formed [11,12]. Interconversion of these species can be rapid on the NMR time scale and so ESIMS would allow ready investigation of the ions present in hydrolysed solutions of the organotin moiety [13,14].

2. Experimental

2.1. General

All reactions were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C,H,N,S) were performed with a Fisons Instruments 1108 CHNS-O Elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H and 111.9 MHz for ^{119}Sn). The electrical resistance of acetone and CH_2Cl_2 solutions was measured with a Crison CDTM 522 conductimeter at room temperature. Electrospray mass spectra were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using a methanol mobile phase. The compounds were added to the reagent grade methanol to give solutions of approximate concentration 0.1 mM. These solutions were injected (1 μl) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 μl min^{-1}, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in this ESIMS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the ISOPRO computer program [15].

2.2. Synthesis

The organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received.

2.2.1. Synthesis of the ligand

2.2.1.1. K[$H_2B(im)_2$](DMAC). The ligand $K[H_2B(im)_2]\cdot(DMAC)$ (85% yield) was obtained according to the published method [6]. Mp: 138–140 °C. ^1H NMR ($CDCl_3$, 293 K): δ 2.08 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 3.06 (s, 3H, CH_3), 6.79 (s, 2H, 4- or 5-CH), 6.84 (s, 2H, 4- or 5-CH), 7.39 (s, 2H, 2-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 21.61 (s, CH_3), 35.80 (s, CH_3), 38.72 (s, CH_3), 124.38 (s, 4- or 5-CH), 127.62 (s, 4- or 5-CH), 142.25 (s, 2-CH), 173.68 (s, CO). Calc. for $C_{10}H_{17}BKN_5O$; C, 44.0; H, 6.3; N, 25.6. Found: C, 43.7; H, 6.2; N, 25.3%. ESIMS (CH_3OH): (+) 126 (50) $[K(DMAC)]^+$, 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 187 (35) $[KH\{H_2B(im)_2\}]^+$, 197 (15) $[Na(DMAC)_2]^+$, 297 (25) $[(H)_3\{H_2B(im)_2\}_2]^+$, 319 (5) $[K(H)_2\{H_2B(im)_2\}_2]^+$, 335 (10) $[K(H)_2\{H_2B(im)_2\}_2]^+$. (−): 147 (100) $[H_2B(im)_2]^-$, 295 (20) $[H\{H_2B(im)_2\}]^-$.

2.2.2. Synthesis of the organotin(IV) complexes

*2.2.2.1. $[H_2B(im)_2(CH_3)SnCl_2]$ (**1**).* To a CH_2Cl_2 solution (50 ml) of $MeSnCl_3$ (0.240 g, 1.0 mmol), $K[H_2B(im)_2]\cdot(DMAC)$ (0.273 g, 1 mmol) was added. The solution was stirred for 3 h, then the KCl formed was filtered off and the solution concentrated under reduced pressure to give a colourless oil. Purification from petroleum ether gives complex **1** as an oil. Yield: 56%. ^1H NMR (CD_3OD, 293 K): δ 0.98 (s, 3H, Sn–CH_3, $^2J(Sn-^1H) = 123$ Hz), 7.31 (d, 2H, 4- or 5-CH), 7.36 (d, 2H, 4- or 5-CH), 8.50 (s, 2H, 2-CH). ^{119}Sn NMR (CD_3OD, 293 K): δ −313.4 (s). IR (nujol, cm^{-1}): 3150w, 3123w [ν(C–H)], 2432sbr, 2365sh, 2244sh [ν(B–H)], 1558m, 1525m (C=C,C=N), 493s [ν(Sn–C)], 265s [ν(Sn–Cl)]. *Anal.* Calc. for $C_7H_{11}BCl_2N_4Sn$: C, 23.9; H, 3.1; N, 15.9. Found: C, 24.0; H, 3.3; N, 15.8%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (35) $[(H)_3\{H_2B(im)_2\}_2]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (35) $[H\{H_2B(im)_2\}]^-$.

*2.2.2.2. $[H_2B(im)_2(CH_3)_2SnCl]$ (**2**).* To a CH_2Cl_2 solution (50 ml) of Me_2SnCl_2 (0.220 g, 1.0 mmol), $K[H_2B(im)_2]\cdot(DMAC)$ (0.273 g, 1 mmol) was added. The solution was stirred for 3 h, then the KCl formed was filtered off and the solution concentrated under reduced pressure to give a colourless precipitate of **2**. It was filtered off, washed with diethyl ether and recrystallized from diethyl ether/petroleum ether (1/1). Yield: 65%. Mp: 163–165 °C. ^1H NMR (CD_3OD, 293 K): δ 0.80 (s, 6H, Sn–CH_3, $^2J(^{119}Sn-^1H) = 91.3$ Hz,

$^2J(^{117}Sn-^1H) = 87.5$ Hz), 7.17 (d, 2H, 4- or 5-C*H*), 7.21 (d, 2H, 4- or 5-C*H*), 8.27 (s, 2H, 2-C*H*). ^{119}Sn NMR (CD_3OD, 293 K): δ −160.1 (s). IR (nujol, cm^{-1}): 3133w, 3120w [ν(C–H)], 2435s, 2360m, 2296m [ν(B–H)], 1557m, 1520m (C=C,C=N), 519s [ν(Sn–C)], 260s [ν(Sn–Cl)]. *Anal*. Calc. for $C_8H_{14}BClN_4Sn$: C, 29.0; H, 4.3; N, 16.9. Found: C, 28.8; H, 4.0; N, 16.8%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (15) $[(H)_3\{H_2B(im)_2\}_2]^+$, 555 (5) $[Na\{H_2B(im)_2\}\{(CH_3)_2SnCl\}_2OH]$, 571 (5) $[K\{H_2B(im)_2\}\{(CH_3)_2SnCl\}_2OH]$. (−): 147 (100) $[H_2B(im)_2]^-$.

*2.2.2.3. [$H_2B(im)_2(CH_3)_3Sn$] (**3**).* Compound **3** was prepared similarly to compound **2**, by using Me_3SnCl (0.199 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot$(DMAC) (0.273 g, 1 mmol) in dichloromethane solution (30 ml). Re-crystallization from petroleum ether gives complex **3** as a micro-crystalline solid (60% yield). Mp: 190–192 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.60 (s, 9H, Sn–C*H*$_3$, $^2J(^{119}Sn-^1H) = 69.5$ Hz, $^2J(^{117}Sn-^1H) = 66.6$ Hz), 6.80 (d, 2H, 4- or 5-C*H*), 6.91 (d, 2H, 4- or 5-C*H*), 7.40 (s, 2H, 2-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −134.2 (s). IR (nujol, cm^{-1}): 3122w, 3096w [ν(C–H)], 2398m, 2363m, 2273m [ν(B–H)], 1585m (C=C,C=N), 513s [ν(Sn–C)]. *Anal*. Calc. for $C_9H_{17}BN_4Sn$: C, 34.8; H, 5.5; N, 18.0. Found: C, 37.7; H, 5.3; N, 17.7%. ESIMS (CH_3OH): (+) 313 (60) $[H(CH_3)_3Sn\{H_2B(im)_2\}]^+$, 475 (100) $[\{(CH_3)_3Sn\}_2\{H_2B(im)_2\}]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (5) $[H\{H_2B(im)_2\}_2]^-$, 459 (60) $[(CH_3)_3Sn\{H_2B(im)_2\}_2]^-$.

*2.2.2.4. [$H_2B(im)_2(C_6H_5)SnCl_2(DMAC)$] (**4**).* Compound **4** was prepared similarly to compound **2**, by using $(C_6H_5)SnCl_3$ (0.302 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot$(DMAC) (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Re-crystallization from petroleum ether gives complex **4** as a micro-crystalline solid (57% yield). Mp: 92–94 °C. ^{1}H NMR (CD_3OD, 293 K): δ 2.09 (s, 3H, C*H*$_3$), 2.92 (s, 3H, C*H*$_3$), 3.07 (s, 3H, C*H*$_3$), 7.31 (d, 2H, 4- or 5-C*H*), 7.37 (d, 2H, 4- or 5-C*H*), 7.44–7.50 (mbr, 5H, Sn–C_6H_5), 8.50 (s, 2H, 2-C*H*). ^{119}Sn NMR (CD_3OD, 293 K): δ −235.2 (s). IR (nujol, cm^{-1}): 3118w, 3086w [ν(C–H)], 2440mbr, 2283m [ν(B–H)], 1670m, 1619sh [ν(C=O)], 1556m (C=C,C=N), 476m, 458s, [δ(Ph)], 291s [ν(Sn–C)], 207m [ν(Sn–Cl)]. *Anal*. Calc. for $C_{16}H_{22}BCl_2N_5OSn$: C, 38.4; H, 4.4; N, 14.0. Found: C, 38.2; H, 4.6; N, 14.1%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (35) $[(H)_3\{H_2B(im)_2\}_2]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (30) $[H\{H_2B(im)_2\}]^-$.

*2.2.2.5. [$H_2B(im)_2(C_6H_5)_2SnCl(DMAC)$] (**5**).* Compound **5** was prepared similarly to compound **2**, by using $(C_6H_5)_2SnCl_2$ (0.344 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot$(DMAC) (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Re-crystallization from diethyl ether gives complex **5** as a micro-crystalline solid (70% yield). Mp: 135–137 °C. ^{1}H NMR (CD_3OD, 293 K): δ 2.08 (s, 3H, C*H*$_3$), 2.92 (s, 3H, C*H*$_3$), 3.05 (s, 3H, C*H*$_3$), 7.29 (d, 2H, 4- or 5-C*H*), 7.33 (d, 2H, 4- or 5-C*H*), 7.40–7.60 (mbr, 10H, Sn–C_6H_5), 8.43 (s, 2H, 2-C*H*). ^{119}Sn NMR (CD_3OD, 293 K): δ −271.3 (s). IR (nujol, cm^{-1}): 3151w, 3127w [ν(C–H)], 2417s, 2374m, 2325m [ν(B–H)], 1619sbr [ν(C=O)], 1561m (C=C,C=N), 460s, 450s, 445sh [δ(Ph)], 283s [ν(Sn–C)], 204s [ν(Sn–Cl)]. *Anal*. Calc. for $C_{22}H_{27}BClN_5OSn$: C, 48.7; H, 5.0; N, 12.9. Found: C, 49.0; H, 4.8; N, 12.8%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (25) $[(H)_3\{H_2B(im)_2\}_2]^+$, 439 (20) $[(C_6H_5)_2Sn(OH)H\{H_2B(im)_2\}]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (10) $[H\{H_2B(im)_2\}]^-$, 361 (60) $[(C_6H_5)_2SnCl_2(OH)]^-$.

*2.2.2.6. [$H_2B(im)_2(C_6H_5)_3Sn$] (**6**).* Compound **6** was prepared similarly to compound **2**, by using $(C_6H_5)_3SnCl$ (0.385 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot$(DMAC) (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Re-crystallization from diethyl ether gives complex **6** as a micro-crystalline solid (72% yield). Mp: 209–211 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 6.35 (d, 2H, 4- or 5-C*H*), 6.51 (d, 2H, 4- or 5-C*H*), 6.95 (s, 2H, 2-C*H*), 7.30–7.50 (mbr, 15H, Sn–C_6H_5). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −311.8 (s). IR (nujol, cm^{-1}): 3123w, 3080w, 3063w [ν(C–H)], 2363sbr, 2276m [ν(B–H)], 1601m, 1579sh (C=C,C=N), 460s, 447s [δ(Ph)], 276s [ν(Sn–C)]. *Anal*. Calc. for $C_{24}H_{23}BN_4Sn$: C, 58.0; H, 4.7; N, 11.3. Found: C, 57.8; H, 4.8; N, 11.5%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (15) $[(H)_3\{H_2B(im)_2\}_2]^+$, 499 (60) $[(C_6H_5)_3Sn(H)\{H_2B(im)_2\}]^+$, 847 (40) $[\{(C_6H_5)_3Sn\}_2\{H_2B(im)_2\}]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (10) $[H\{H_2B(im)_2\}]^-$, 643 (40) $[(C_6H_5)_3Sn\{H_2B(im)_2\}_2]^-$.

*2.2.2.7. [$H_2B(im)_2(C_4H_9)SnCl_2(DMAC)$] (**7**).* Compound **7** was prepared similarly to compound **2**, by using $(C_4H_9)SnCl_3$ (0.282 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot$(DMAC) (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Re-crystallization from petroleum ether gives complex **7** as a micro-crystalline solid (53% yield). Mp: 202–204 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.95–1.60 (mbr, 9H, Sn–Bu^n), 2.09 (s, 3H, C*H*$_3$), 2.93 (s, 3H, C*H*$_3$), 3.02 (s, 3H, C*H*$_3$), 7.07 (d, 2H, 4- or 5-C*H*), 7.19 (d, 2H, 4- or 5-C*H*), 8.20 (s, 2H, 2-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −381.4 (s). IR (nujol, cm^{-1}): 3140w, 3089w [ν(C–H)], 2400mbr, 2340mbr [ν(B–H)], 1636m [ν(C=O)], 1520m (C=C,C=N), 626mbr [ν(Sn–C)], 262m [ν(Sn–Cl)]. *Anal*. Calc. for $C_{14}H_{26}BCl_2N_5OSn$: C, 35.0; H, 5.4; N, 14.6. Found: C, 35.2; H, 5.6; N, 14.4%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (25) $[(H)_3\{H_2B(im)_2\}_2]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (35) $[H\{H_2B(im)_2\}]^-$.

*2.2.2.8. $[H_2B(im)_2(C_4H_9)_2SnCl]\cdot(DMAC)$ (**8**).* Compound **8** was prepared similarly to compound **2**, by using $(C_4H_9)_2SnCl_2$ (0.304 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot(DMAC)$ (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Re-crystallization from petroleum ether gives complex **8** as a micro-crystalline solid (63% yield). Mp: 163–165 °C. ^1H NMR ($CDCl_3$, 293 K): δ 0.88 (t, 6H, CH_3 of Sn–Bu^n), 1.34–1.73 (mbr, 12H, CH_2 of Sn–Bu^n), 2.06 (s, 3H, CH_3), 2.92 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 7.01 (d, 2H, 4- or 5-C*H*), 7.12 (d, 2H, 4- or 5-C*H*), 7.91 (s, 2H, 2-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −179.5 (s). IR (nujol, cm^{-1}): 3120w, 3081w [ν(C–H)], 2421mbr, 2358m [ν(B–H)], 1640m [ν(C=O)], 1558m (C=C,C=N), 601sbr [ν(Sn–C)], 271mbr [ν(Sn–Cl)]. *Anal*. Calc. for $C_{18}H_{35}BClN_5OSn$: C, 43.0; H, 7.0; N, 13.9. Found: C, 43.2; H, 6.8; N, 14.1%. ESIMS (CH_3OH): (+) 149 (100) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (15) $[(H)_3\{H_2B(im)_2\}_2]^+$, 416 (10) $[(C_4H_9)_2SnCl(H)\{H_2B(im)_2\}]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (30) $[H\{H_2B(im)_2\}]^-$, 562 (15) $[\{(C_4H_9)_2SnCl\}\{H_2B(im)_2\}_2]^-$.

*2.2.2.9. $[H_2B(im)_2(C_4H_9)_3Sn]$ (**9**).* Compound **9** was prepared similarly to compound **1**, by using $(C_4H_9)_3SnCl$ (0.325 g, 1.0 mmol) and $K[H_2B(im)_2]\cdot(DMAC)$ (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Purification from petroleum ether gives complex **9** as an oil (42% yield). ^1H NMR ($CDCl_3$, 293 K): δ 0.82 (t, 9H, CH_3 of Sn–Bu^n), 1.22–1.47 (mbr, 18H, CH_2 of Sn–Bu^n), 6.84 (d, 2H, 4- or 5-C*H*), 6.90 (d, 2H, 4- or 5-C*H*), 7.49 (s, 2H, 2-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ −140.2 (s). IR (nujol, cm^{-1}): 3122w [ν(C–H)], 2392sbr, 2277s [ν(B–H)], 1586m (C=C,C=N), 605sbr [ν(Sn–C)]. *Anal*. Calc. for $C_{18}H_{35}BN_4Sn$: C, 49.5; H, 8.1; N, 12.8. Found: C, 49.2; H, 8.0; N, 13.0%. ESIMS (CH_3OH): (+) 149 (15) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (10) $[(H)_3\{H_2B(im)_2\}_2]^+$, 439 (60) $[(H)(C_4H_9)_3Sn\{H_2B(im)_2\}]^+$, 727 (100) $[\{(C_4H_9)_3Sn\}_2\{H_2B(im)_2\}]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (15) $[H\{H_2B(im)_2\}]^-$, 583 (80) $[(C_4H_9)_3Sn\{H_2B(im)_2\}_2]^-$.

*2.2.2.10. $[H_2B(im)_2(C_6H_{11})_3Sn]$ (**10**).* Compound **10** was prepared similarly to compound **2**, by using $(C_6H_{11})_3SnCl$ (0.404 g, 1.0 mmol), and $K[H_2B(im)_2]\cdot(DMAC)$ (0.273 g, 1 mmol) in dichloromethane solution (50 ml). Re-crystallization from chloroform/*n*-hexane 1 (1/1) gives complex **10** as a micro-crystalline solid (75% yield). Mp: 185–187 °C. ^1H NMR ($CDCl_3$, 293 K): δ 1.37–2.00 (m, 33H, Sn–C_6H_{11}), 7.02 (d, 2H, 4- or 5-C*H*), 7.05 (d, 2H, 4- or 5-C*H*), 7.84 (s, 2H, 2-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): δ 11.2 (s). IR (nujol, cm^{-1}): 3116w, 3090w [ν(C–H)], 2403sbr, 2276m [ν(B–H)], 1596m, 1576m (C=C,C=N), 487s [ν(Sn–C)]. *Anal*. Calc. for $C_{24}H_{41}BN_4Sn$: C, 56.0; H, 8.0; N, 10.9. Found: C, 56.1; H, 8.2; N, 10.6%. ESIMS (CH_3OH): (+) 149 (15) $[(H)_2\{H_2B(im)_2\}]^+$, 297 (10) $[(H)_3\{H_2B(im)_2\}_2]^+$, 517 (25) $[H(C_6H_{11})_3Sn\{H_2B(im)_2\}]^+$, 883 (40) $[\{(C_6H_{11})_3Sn\}_2\{H_2B(im)_2\}]^+$. (−) 147 (100) $[H_2B(im)_2]^-$, 295 (15) $[H\{H_2B(im)_2\}]^-$, 439 (15) $[(C_4H_9)_3SnCl_2]^-$.

3. Results and discussion

Complexes **1–10** have been synthesized by methathetic reaction of $K[H_2B(im)_2]\cdot(DMAC)$ with SnR_nX_{4-n} in CH_2Cl_2 at room temperature, Eq. (1).

$$K[H_2B(im)_2](DMAC) + SnR_nCl_{4-n} \xrightarrow{CH_2Cl_2/r.t.} \underset{\textbf{1-10}}{[H_2B(im)_2R_nSnCl_{4-n-1}(DMAC)_m]} + KCl \quad (1)$$

1	R = CH_3	$n = 1$	$m = 0$
2	R = CH_3	$n = 2$	$m = 0$
3	R = CH_3	$n = 3$	$m = 0$
4	R = Ph	$n = 1$	$m = 1$
5	R = Ph	$n = 2$	$m = 1$
6	R = Ph	$n = 3$	$m = 0$
7	R = ^{n}Bu	$n = 1$	$m = 1$
8	R = ^{n}Bu	$n = 2$	$m = 1$
9	R = ^{n}Bu	$n = 3$	$m = 0$
10	R = cy	$n = 3$	$m = 0$

Derivatives **1**, **2**, **4** and **5** show good solubility in alcohols and DMSO, but they are insoluble in chlorinated solvents, diethyl ether, aromatics and aliphatic hydrocarbons. Derivatives **3** and **6–10** show good solubility in acetone, chlorinated solvents and DMSO, and they are non-electrolytes in CH_2Cl_2 solution.

All complexes are significantly less stable than the corresponding tetrakis-(1-imidazolyl)borate ones [7], this property is relating to the high reducing power arising from the presence of the two hydrogen atoms linked to the boron atom.

All complexes have been characterized by analytical and spectral data. The infrared spectra of derivatives **1–10** (Section 2) are consistent with the formulations, showing all the bands required by the presence of the organotin(IV) acceptor and the organic nitrogen donor [16,17], the ligand absorptions being only slightly shifted with respect to those of the potassium salt of the same donor.

In the spectrum of $[K\{H_2B(im)_2\}\cdot(DMAC)]$, the CO stretching of DMAC appears as a strong and broad peak at approximately 1620 cm^{-1}; this value is lower shifted with respect to that observed for free DMAC ($\approx$ 1690 cm^{-1}), suggesting coordination of the oxygen atom to the potassium center [18].

In derivatives **1–10** the BH stretch region (2244–2440 cm^{-1}) exhibits a multiplicity of absorptions, consistent with the presence of both ^{10}B and ^{11}B in natural boron

[19], generally shifted to higher frequency with respect to the same absorptions observed in the free ligand.

In the far-IR spectra the Sn–C stretching frequencies fall as strong or medium broad bands in the range 487–626 cm^{-1} for alkyl derivatives **1**–**3** and **7**–**10**, and in the range 276–291 cm^{-1} for phenyl complexes **4**–**6**; these absorptions agree well with the trends previously observed in similar N-donor complexes [20]. The tin(IV) chloride stretching frequencies in the monochloride- and di-chloride-tin(IV) derivatives fall as strong or medium broad bands at 207 and 204 cm^{-1} for phenyl complexes **4** and **5** and in the range 260–271 cm^{-1} for the alkyl derivatives; these bands are lowered with respect to those found in the starting tin(IV) reagents [21]. The absence of Sn–Cl stretching vibrations in the spectra of derivatives **3**, **6**, **9** and **10** confirms the substitution of the chloride in the tin core by the $\{H_2B(im)_2\}^-$ ligand.

In the ^1H NMR spectra of complexes **1**–**10** in $CDCl_3$ or methanol solution (Section 2), the signals due to the imidazolyl rings are always deshielded with respect to those in the spectra of the free donors, confirming the existence of the complexes in solution. The chemical shifts of the imidazole protons are similar to those observed for analogous rings in organotin(IV) complexes [7,20]. The room-temperature ^1H NMR spectra of derivatives **1**–**10** exhibit only one set of signals for the protons of the imidazolyl rings of the poly(imidazolyl)borate ligand, resulting from dynamic exchange processes. This is common in complexes of corresponding poly(pyrazolyl)borates [22], suggesting highly fluxional species or complete dissociation and re-association of the imidazolyl nitrogens, which occur rapidly even at lower temperatures. On cooling the solutions of **1**–**10** to 223 K, no additional signals due to the imidazole ring appeared.

The tin-hydrogen $^2J(^{119,117}Sn,^1H)$ coupling constants in various cases can be correlated with the percentage of s-character which the Sn atom presents in the Sn–C bond [23] and hence $^2J(^{119,117}Sn,^1H)$ may give information about the coordination number of tin [24]. In compound **1** we have found that the tin-proton coupling constant $^2J(Sn,^1H)$ has a value of 123 Hz, not very different from those reported in the literature for six-coordinate organotin(IV) complexes [25,26]. Moreover, only one sharp signal is present in the ^{119}Sn NMR spectra of **1** and the δ value (−313.4 ppm) falls in the range typical for five-coordinated tin(IV) species [27]. The ^{119}Sn chemical shifts of the other monoorganotin(IV) derivatives **4** and **7**, at −235.2 and −381.4 ppm, respectively, provide an additional support for five coordinated tin atoms. A similar behaviour is observable in the ^{119}Sn NMR spectra of diorganotin(IV) derivatives; the ^{119}Sn chemical shifts of derivatives **2**, **5** and **8**, at −160.1, −271.3 and −179.5 ppm are in accordance with those of five coordinated diorganotin(IV)halides complexes involving S-, O- and N-donors [25,28,29]. In compound **2** the tin-proton coupling constants $^2J(^{119}Sn,^1H)$ and $^2J(^{117}Sn,^1H)$ are 91.3 and 87.5 Hz, respectively, falling in the range for an intermediate between penta- and hexa-coordinated dimethyltin(IV) species [26]. On the basis of Lockarts's equation [26] the Me–Sn–Me angle is estimated to be approximately 147°, which suggests a skewed penta-coordination around the tin atom in which the ligand is probably in a bridging form [6] (Fig. 2(a)).

The triorganotin(IV) derivatives **3**, **6** and **9** present in the ^{119}Sn NMR spectra a single sharp resonance at −134.2, −311.8 and −140.2 ppm, respectively, which are consistent with the range expected for five-coordinated organotin compounds [7]. Only the $[H_2B(im)_2(C_6H_{11})_3Sn]$ complex (**10**) exhibits a resonance at 11.2 ppm, being in the range expected for tetrahedral triorganotin compounds [26,30–32].

3.1. Electrospray ionization mass spectrometric data

The positive-ion spectrum of the ligand $[K\{H_2B(im)_2\}\cdot(DMAC)]$ shows five peaks decreasing in size with increasing mass, attributable to aggregates of $[H_2B(im)_2]^-$, H^+ and K^+ or Na^+: $[(H)_2\{H_2B(im)_2\}]^+$ (*m/z* 149), $[KH\{H_2B(im)_2\}]^+$ (*m/z* 187), $[(H)_3\{H_2B(im)_2\}_2]^+$ (*m/z* 297), $[Na(H)_2\{H_2B(im)_2\}_2]^+$ (*m/z* 319), $[K(H)_2\{H_2B(im)_2\}_2]^+$ (*m/z* 335). Weak signals at *m/z* 126 and *m/z* 197 are attributable to species including the *N*,*N*-dimethylacetamide (DMAC). The anionic spectrum of the ligand contains only two peaks attributable to aggregates of $H_2B(im)_2^-$ and H^+: $[H_2B(im)_2]^-$ (*m/z* 147) and $[H\{H_2B(im)_2\}_2]^-$ (*m/z* 295).

ESMS is particularly suitable for study of labile organotin systems in solution. Both positive-ion and negative-ion spectra of mono-organotin derivatives **1**, **4** and **7** dissolved in methanol are comparatively simple; the dominant fragments at *m/z* 149 (100%) and *m/z* 297 (35%) are attributable to aggregates of $H_2B(im)_2^-$ and H^+.

For compound **2** the major peaks in the positive-ion spectrum are those of protonated ligand at *m/z* 149 (100%) and *m/z* 297 (15%). Additionally, very weak

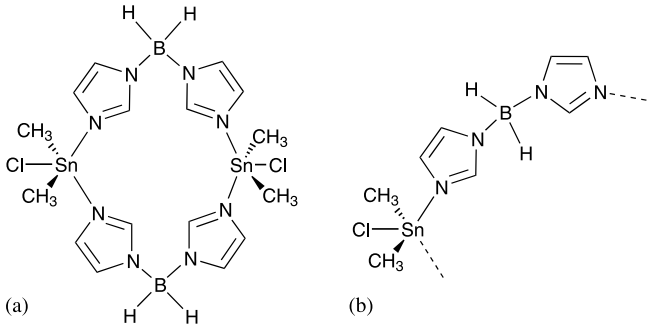

Fig. 2. Hypothesized dimeric (a) or polymeric (b) structures in solution for derivative **2**.

signals possibly due to the hydrolysed five-coordinate species $[Na\{H_2B(im)_2\}\{(CH_3)_2SnCl\}_2OH]$ (*m/z* 555) and $[K\{H_2B(im)_2\}\{(CH_3)_2SnCl\}_2OH]$ (*m/z* 571) are also detected and identified by the characteristic isotope distribution pattern. A plausible structure for these dimeric species presents the $H_2B(im)_2$ ligand bridging between the two tin centres $(CH_3)_2(Cl)Sn(OH)Sn(Cl)(CH_3)_2$. An evidence of these species is also available from tin-119 NMR investigation: the spectrum of compound **2** in methanol solution, shows a peak at −160.1 ppm, assignable to a five-coordinate tin site.

Kindred structures, as mixed distannoxane dimers, which exhibit bidentate Lewis acid coordination of tin toward halide ions have been identified recently in NMR and ESIMS studies [14,33]. In the anionic spectrum of **2** the major peak at *m/z* 147 (100%) is due to the $[H_2B(im)_2]^-$ ligand, while very weak signals at *m/z* 385–714 (< 3%) due to hydrolysed species are unassigned. A similar trend was observed for compounds **5** and **8**. The positive-ion spectrum of **5** shows, apart from the protonated ligand species, only a peak containing the tin atom at *m/z* 439 (20%), assignable to the hydrolysed species $[(C_6H_5)_2Sn(OH)H\{H_2B(im)_2\}]^+$. In the negative ion spectrum of **5** the major peak is due to the $(C_6H_5)_2SnCl_2(OH)$ complex (*m/z* 361, 60%), in accordance with the tin-119 NMR data [34]: the ^{119}Sn NMR spectrum of **5** in methanol solution displays a resonance at −271.3 ppm, which is indicative of the presence of penta-coordinate tin species [35].

The positive-ion spectrum of **8** displays a very weak peak containing the tin atom at *m/z* 416 (10%), assignable to the $(C_4H_9)_2SnCl(H)H_2B(im)_2$ complex; no hydrolysed species are observed.

In the positive ion spectrum of triorganotin complexes **3**, **6**, **9** and **10** no hydrolysed species are detected. For compound **3** the peaks in the positive-ion spectrum are attributable to the protonated $H(CH_3)_3Sn\{H_2B(im)_2\}$ complex at *m/z* 313 (60%) and to the dimeric $[\{(CH_3)_3Sn\}_2\{H_2B(im)_2\}$ species at *m/z* 475 (100%). Plausible structures for these species shows the $[H_2B(im)_2]^-$ ligand monodentate κ^1 or bridging μ^2 between the two four-coordinate tin centres, respectively (Fig. 3). No peaks due to the free ligand are detected in the positive ion spectrum; instead the negative ion spectrum presents a signal due to the free ligand as the

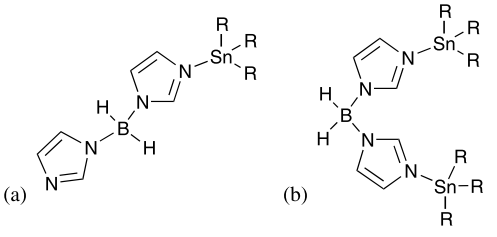

Fig. 3. Hypothesized monomeric (a) or dimeric (b) structures in solution for four-coordinate triorganotin derivatives.

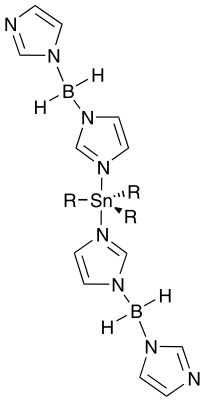

Fig. 4. Hypothesized structure in solution for five-coordinate triorganotin species.

major peak at *m/z* 147 (100%), together with a peak at *m/z* 459 (60%) due to the $(CH_3)_3Sn\{H_2B(im)_2\}_2$ species (Fig. 4).

Methanol solutions of **6**, **9** and **10** were also investigated. Overall, the positive-ion spectra bear a marked resemblance to that of compound **3**. In all spectra a peak due to the protonated $(H)R_3Sn\{H_2B(im)_2\}$ complex (Fig. 3(a)) was detected at *m/z* 499 (60%, R = Ph), *m/z* 439 (60%, R = Bu) and *m/z* 517 (25%, R = Cy); in addition the positive-ion spectra show a peak due to bridging coordinate stannyl cations $\{R_3Sn\}_2H_2B(im)_2$ (Fig. 3(b)) at *m/z* 847 (40%, R = Ph), *m/z* 727 (100%, R = Bu) and *m/z* 883 (40%, R = Cy).

The negative ion spectra of complexes **6** and **9** show a dominant peak due to $R_3Sn\{H_2B(im)_2\}_2$ complexes, with the two ligands probably monodentate κ^1 on the same five-coordinate tin atom (Fig. 4). A probable retention of these structures in $CHCl_3$ solution is evident from tin-119 NMR data of compounds **3**, **6** and **9**; however, it is worth nothing that the NMR spectra consist of a single tin resonance due to a mixture of species in rapid equilibrium [36].

A different behaviour is observable in the negative-ion electrospray spectrum of compound **10**, which shows only a weak peak due to a species containing a tin atom and attributable to the $(C_6H_{11})_3SnCl_2$ complex (*m/z* 439, 15%). This behaviour is probably due to the high steric demand of cyclohexyl groups, which excludes five- or six-coordinate structures. This conclusion is in agreement with results recently reported for analogous complexes obtaining by using the sodium tetrakis(imidazol-1-yl)borato ligand [7].

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