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Synthesis and characterization of new organotin(IV) complexes with polyfunctional ligands

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Abstract

New mono-, di- and tri-organotin(IV) derivatives containing the neutral bis(2-pyridylthio)methane ligand, $[(pyS)_2CH_2]$ and tris(2-pyridylthio)methane ligand, $[(pyS)_3CH]$ have been synthesized from reaction with SnR_nCl_{4-n} (R = Me, ^{n}Bu, Ph and Cy, $n = 1$–3) acceptors. Mono-nuclear adducts of the type $\{[(pyS)_2CH_2]R_nSnCl_{4-n}\}$ and $\{[(pyS)_3CH]R_nSnCl_{4-n}\}$ have been obtained and characterized by elemental analyses, FT-IR, ESI-MS, multinuclear (^{1}H and ^{119}Sn) NMR spectral data. The ^{1}H and ^{119}Sn NMR and ESI-MS data suggest for the triorganotin(IV) derivatives a complete dissociation of the compounds in solution. The mono- and di-organotin(IV) derivatives show a greater stability in solution, and their spectroscopic data are in accordance with the existence of six-coordinated $RSnCl_3N_2$ or $R_2SnCl_2N_2$ species.

Keywords: Organotin(IV); Bis(2-pyridylthio)methane; Tris(2-pyridylthio)methane; 2-Mercaptopyridine; Tin-119 NMR; Electrospray ionization mass spectroscopy

1. Introduction

The interest in the coordination chemistry of tin and organotin acceptors with poly(azolyl)alkanes, β-diketones and poly(azolyl)borates dates from a long time. Organotin(IV) compounds are of interest in view of the considerable structural diversity that they possess and an additional reason for this research field is based on the biological activity, antifouling paints and antitumor activity displayed by many organotin(IV) derivatives containing mixed N,X-ligands (X = O, S, P) [1,2].

Recently, we have reported the synthesis and the spectroscopic characterization of new poly(pyrazolyl)borate [3,4] and poly(imidazolyl)borate [5,6] complexes containing organotin(IV) acceptors. It has been our endeavor to develop the chemistry of organotin compounds bearing co-ligands of ambidentate character. The primary impetus has been to comprehend competitive coordination modes of scorpionate ligands to the tin atom and find a rationale related to the stability and structural motifs of this class of compounds [7]. As an extension of this research field, we are now interested in the development of the chemistry of some new organotin compounds obtained from the interaction of a number of organotin(IV) halides with polyfunctional S,N-ligands, containing two or three pyridine groups.

In recent years a number of authors [8–17] have synthesized S,N-ligands of the type $(CH_2)_n(SAz)_2$ (Fig. 1) based on a nitrogenated aromatic ring system such as pyridine (Fig. 1(a)). These ligands are able to coordination by both S and the neighbouring N atom, and hence the formation of stable chelate rings of five or more atoms [18–25]. In particular the bis(2-pyridylthio)methane (Fig. 1(b)) has a rich coordination chemistry as recently reported for Zn(II), Hg(II), Cu(I), Ag(I) [26], Cd(II) [27] and Cu(II) [28]

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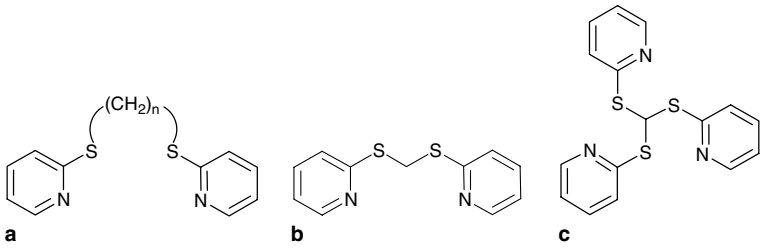

Fig. 1. Structure of S,N-ligands of type $(CH_2)_n(SAz)_2$.

complexes. Tris(2-pyridylthio)methane (Fig. 1(c)) has also been synthesized by Kinoshita et al. [28,29] and they have shown that this ligand reacts with copper(II) halide forming the first example of compounds containing a Cu(II)–C(sp^3) bond [30].

Recently, we have reported the synthesis, characterization and hydrolytic behavior of some new complexes obtained from the interaction of a number of organotin(IV) halides with the novel sodium bis(2-pyridylthio)acetate ligand [31]. The spectroscopic and structural data suggest for these derivatives a strong bonding of the tin atom to the carboxylate group of the ligand.

We have extended this research to the coordination chemistry of two neutral pyridine-2-thiolate ligands, bis- and tris-(2-pyridylthio)methanes; they are particularly versatile sulphur-containing ligands suitable for the assembly of metallosupramolecular materials and of relevance in biological systems.

2. Experimental

2.1. Materials and methods

All reagents were purchased from Aldrich (Milwaukee) and used as received. All syntheses were carried out under a nitrogen atmosphere. All solvents were distilled and degassed with dry nitrogen prior to use. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). 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 instrument operating at room temperature (respectively, at 300 MHz for ^1H and 111.9 MHz for ^{119}Sn). Melting points were taken on an SMP3 Stuart Scientific Instrument. The electrical conductivity measurements (Λ_m, reported as $\Omega^{-1}\,cm^2\,mol^{-1}$) of acetone or dichloromethane solutions were taken with a Crison CDTM 522 conductimeter at room temperature. Electrospray mass spectra (ESI-MS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetone 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 $\mu l\,min^{-1}$, 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 ESI-MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the ISOPRO computer program [32].

2.2. Synthesis

2.2.1. Synthesis of $[(pyS)_2CH_2]$ (1)

The bis(2-pyridylthio)methane ligand was prepared by modification of the literature method [29]. The crude product was recrystallized in acetone/dichloromethane (1:1) yielding $[(pyS)_2CH_2]$ (**1**) as pale yellow microcrystalline needles. Yield: 88%. M.p. 92–95 °C. ^1H NMR ($CDCl_3$, 293 K): δ 5.07 (s, 2H, CH_2), 7.02 (m, 2H, 5-C*H*), 7.19 (d, 2H, 3-C*H*), 7.48 (m, 2H, 4-C*H*), 8.51 (d, 2H, 6-C*H*). IR (nujol, cm^{-1}): 3111w, 3070w, 3045w (CH), 1577s, 1557s (C=C + C=N), 665m, 620s, 477s, 444s, 419m, 397s, 378m, 356w, 257sbr. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 233 (100) $[(pyS)_2CH]^-$, 110 (50) $[(pyS)]^-$. Calc. for $C_{11}H_{10}N_2S_2$: C, 56.38; H, 4.30; N, 11.95; S, 27.36. Found: C, 56.23; H, 4.25; N, 11.83; S, 26.99%.

2.2.2. Synthesis of $[(pyS)_3CH]$ (2)

The tris(2-pyridylthio)methane ligand was prepared by modification of the literature method [29]. The crude product was recrystallized from diethyl ether. Yield: 66%. M.p. 106–109 °C. ^1H NMR ($CDCl_3$, 293 K): δ 7.02 (m, 3H, 5-C*H*), 7.25 (d, 3H, 3-C*H*), 7.52 (m, 3H, 4-C*H*), 7.91 (s, 1H, C*H*), 8.52 (d, 3H, 6-C*H*). IR (nujol, cm^{-1}): 3144w, 3107w, 3048w (CH), 1572s, 1555s (C=C + C=N), 616s, 481s, 452s, 395s, 344s, 322s, 279w, 264w, 235s, 224w, 206w. ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 344 (100) $[\{(pyS)_3CH\} + H]^+$, 366 (30) $[\{(pyS)_3CH\} + Na]^+$, 710 (60) $[2\{(pyS)_3CH\} + Na]^+$. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 379 (100) $[(pyS)_3CH + Cl]^-$, 342 (20) $[(pyS)_3C]^-$, 110 (10) $[(pyS)]^-$. Calc. for $C_{16}H_{13}N_3S_3$: C, 55.95; H, 3.81; N, 12.23; S, 28.00. Found: C, 55.90; H, 3.70; N, 12.00; S, 27.80%.

*2.2.3. {[(pyS)$_2$CH$_2$]Sn(CH$_3$)Cl$_3$} (**3**)*

To a CH_2Cl_2 solution (50 ml) of $(CH_3)SnCl_3$ (0.240 g, 1.0 mmol), $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) was added. The mixture reaction was stirred for 20 h at room temperature, then solvent was removed on a rotary evaporator and the residue was washed with chloroform/petroleum ether (1:5). The colourless product obtained was dried to constant weight under reduced pressure. Yield: 62%. M.p. 181–183 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.97 (s, 3H, Sn–C*H*$_3$, $J(^{117}Sn–^1H) = 73.0$ Hz, $J(^{119}Sn–^1H) = 77.0$ Hz), 5.01 (s, 2H, C*H*$_2$), 7.05 (t, 2H, 5-C*H*), 7.20 (d, 2H, 3-C*H*), 7.51 (t, 2H, 4-C*H*), 8.54 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): −472.45 (s). IR (nujol, cm^{-1}): 3170w, 3105w (CH), 1579m (C=C + C=N), 482s (Sn–C), 399m (Sn–N), 293sbr, 282sh (Sn–Cl). Anal. Calc. for $C_{12}H_{13}Cl_3N_2S_2Sn$: C, 30.39; H, 2.76; N, 5.91; S, 13.49. Found: C, 30.59; H, 2.97; N, 6.10; S, 13.80%.

*2.2.4. {[(pyS)$_2$CH$_2$]Sn(CH$_3$)$_2$Cl$_2$} (**4**)*

Compound **4** was prepared similarly to compound **3**, by using $(CH_3)_2SnCl_2$ (0.220 g, 1.0 mmol) and $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) in dichloromethane solution (50 ml). The colourless product was recrystallized from diethyl ether. Yield: 93%. M.p. 73–75 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.22 (s, 6H, Sn–C*H*$_3$, $J(^{117}Sn–^1H) = 67.0$ Hz, $J(^{119}Sn–^1H) = 70.0$ Hz), 5.07 (s, 2H, C*H*$_2$), 7.03 (t, 2H, 5-C*H*), 7.20 (d, 2H, 3-C*H*), 7.51 (t, 2H, 4-C*H*), 8.52 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): −20.5 (s). IR (nujol, cm^{-1}): 3179w, 3078w (CH), 1578s, 1558m (C=C + C=N), 569sh (Sn–C), 352m (Sn–N), 279s (Sn–Cl). ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 235 (100) $[\{(pyS)_2CH_2\} + H]^+$, 257 (60) $[\{(pyS)_2CH_2\} + Na]^+$. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 110 (10) $[(pyS)]^-$, 233 (100) $[(pyS)_2CH]^-$, 489 (20) $[\{(pyS)_2CH_2\}\{Sn(CH_3)_2Cl_2\} + Cl]^-$. Anal. Calc. for $C_{13}H_{16}Cl_2N_2S_2Sn$: C, 34.37; H, 3.55; N, 6.17; S, 14.09. Found: C, 34.03; H, 3.63; N, 5.93; S, 13.97%.

*2.2.5. {[(pyS)$_2$CH$_2$]Sn(CH$_3$)$_3$Cl} (**5**)*

To a Et_2O solution (50 ml) of $(CH_3)_3SnCl$ (0.199 g, 1.0 mmol), $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) was added. The mixture reaction was stirred for 6 h at room temperature, then solvent was removed on a rotary evaporator. The product was filtered off and recrystallized from dichloromethane/petroleum ether solution (1:4). Yield: 51%. M.p. 134–136 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.54 (s, 9H, Sn–C*H*$_3$, $J(Sn–^1H) = 57.0$ Hz), 5.07 (s, 2H, C*H*$_2$), 7.02 (t, 2H, 5-C*H*), 7.19 (d, 2H, 3-C*H*), 7.48 (t, 2H, 4-C*H*), 8.50 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): 153.11 (s). IR (nujol, cm^{-1}): 3170w (CH), 1573m, 1557m (C=C + C=N), 546sbr (Sn–C), 352m (Sn–N), 238sbr (Sn–Cl). ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 434 (100) $[\{(pyS)_2CH_2\}\{Sn(CH_3)_3Cl\} + H]^+$, 907 (40) $[\{(pyS)_2CH_2\}_2\{Sn(CH_3)_3Cl\}_2 + K]^+$. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 110 (100) $[(pyS)]^-$, 233 (40) $[(pyS)_2CH]^-$. Anal. Calc. for $C_{14}H_{19}ClN_2S_2Sn$: C, 38.71; H, 4.41; N, 6.45; S, 14.73. Found: C, 39.01; H, 4.54; N, 6.20; S, 14.50%.

*2.2.6. {[(pyS)$_2$CH$_2$]Sn(C$_4$H$_9$)$_2$Cl$_2$} (**6**)*

To a dichloromethane solution (50 ml) of $(C_4H_9)_2SnCl_2$ (0.304 g, 1.0 mmol), $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) was added. The mixture reaction was stirred for 4 h at room temperature, then solvent was removed on a rotary evaporator, *n*-hexane was added (40 ml) and a precipitate afforded, which was filtered off, and recrystallized from chloroform/petroleum ether solution (1:2). Yield: 48%. M.p. 81–83 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.87–1.99 (m, 18H, Sn–C$_4$*H*$_9$), 5.07 (s, 2H, C*H*$_2$), 7.03 (t, 2H, 5-C*H*), 7.20 (d, 2H, 3-C*H*), 7.50 (t, 2H, 4-C*H*), 8.52 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): −139.30 (s), −91.98 (s), −65.27 (s). IR (nujol, cm^{-1}): 3170w, 3046w (CH), 1574s, 1558s (C=C + C=N), 619sbr (Sn–C), 350sbr (Sn–N), 289mbr (Sn–Cl). ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 235 (100) $[\{(pyS)_2CH_2\} + H]^+$, 327 (40) $[\{Sn(C_4H_9)_2Cl_2\} + Na]^+$. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 339 (40) $[\{Sn(C_4H_9)_2Cl_2\} + Cl]^-$, 537 (10) $[\{(pyS)_2CH_2\}\{Sn(C_4H_9)_2Cl_2\} - H]^-$, 841 (100) $[\{(pyS)_2CH_2\}\{Sn(C_4H_9)_2Cl_2\}_2 - H]^-$. Anal. Calc. for $C_{19}H_{28}Cl_2N_2S_2Sn$: C, 42.38; H, 5.25; N, 5.21; S, 11.89. Found: C, 42.63; H, 5.41; N, 5.45; S, 12.00%.

*2.2.7. {[(pyS)$_2$CH$_2$]Sn(C$_4$H$_9$)$_3$Cl} (**7**)*

To a dichloromethane solution (50 ml) of $(C_4H_9)_3SnCl$ (0.326 g, 1.0 mmol), $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) was added. The mixture reaction was stirred for 4 h at room temperature, then solvent was removed on a rotary evaporator and diethyl ether was added (20 ml). A pale brown precipitate afforded, which was filtered off. Yield: 64%. M.p. 85–87 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.89–1.73 (m, 27H, Sn–C$_4$*H*$_9$), 5.07 (s, 2H, C*H*$_2$), 7.02 (t, 2H, 5-C*H*), 7.19 (d, 2H, 3-C*H*), 7.50 (t, 2H, 4-C*H*), 8.50 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): 156.16 (s). IR (nujol, cm^{-1}): 3064w, 3047w (CH), 1578s, 1555s (C=C + C=N), 603sbr (Sn–C), 332s (Sn–N), 258mbr (Sn–Cl). ESI-MS (major positive-ions, CH_3OH), *m*/*z* (%): 235 (95) $[\{(pyS)_2CH_2\} + H]^+$, 257 (70) $[\{(pyS)_2CH_2\} + Na]^+$, 291 (100) $[Sn(C_4H_9)_3]^+$, 524 (60) $[\{(pyS)_2CH_2\}\{Sn(C_4H_9)_3\}]^+$. ESI-MS (major negative-ions, CH_3OH), *m*/*z* (%): 361 (100) $[\{Sn(C_4H_9)_3Cl\} + Cl]^-$. Anal. Calc. for $C_{23}H_{37}ClN_2S_2Sn$: C, 49.28; H, 6.66; N, 5.00; S, 11.42. Found: C, 49.04; H, 6.60; N, 5.02; S, 11.17%.

*2.2.8. {[(pyS)$_2$CH$_2$]Sn(C$_6$H$_5$)$_2$Cl$_2$} (**8**)*

To a dichloromethane solution (50 ml) of $(C_6H_5)_2SnCl_2$ (0.344 g, 1.0 mmol), $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) was added. The mixture reaction was stirred for 4 h at room temperature, then solvent was removed on a rotary evaporator and a dichloromethane/petroleum ether solution (1:2) was added (50 ml); a colourless precipitate afforded, which was filtered off and dried to constant weight under reduced pressure. Yield: 45%. M.p. 87–89 °C. ^{1}H NMR ($CDCl_3$,

293 K): δ 5.03 (s, 2H, CH_2), 7.03 (m, 2H, 5-C*H*), 7.20 (d, 2H, 3-C*H*), 7.46–7.78 (m, 12H, 4-C*H* and Sn–C_6H_5), 8.52 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): −31.79 (s), −298.22 (s). IR (nujol, cm^{-1}): 3170w, 3046w (CH), 1577s, 1554m (C=C + C=N), 353m (Sn–N), 280m (Sn–Cl), 224sbr (Sn–C). ESI-MS (major positive-ions, CH_3OH), *m/z* (%): 235 (80) $[\{(pyS)_2CH_2\} + H]^+$, 959 (100) $[\{(pyS)_2CH_2\}\{Sn(C_6H_5)_2Cl_2\}_2 + K]^+$. ESI-MS (major negative-ions, CH_3OH), *m/z* (%): 379 (100) $[\{Sn(C_6H_5)_2Cl_2\} + Cl]^-$. Anal. Calc. for $C_{23}H_{20}Cl_2N_2S_2Sn$: C, 49.06; H, 3.79; N, 5.75; S, 13.06. Found: C, 49.56; H, 3.94; N, 5.94; S, 13.46%.

2.2.9. {[(pyS)$_2$CH$_2$]Sn(C$_6$H$_5$)$_3$Cl} (9)

Compound **9** was prepared similarly to compound **8**, by using $(C_6H_5)_3SnCl$ (0.386 g, 1.0 mmol) and $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) in dichloromethane solution (50 ml). Yield: 90%. M.p. 77–79 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 5.03 (s, 2H, CH_2), 7.02 (m, 2H, 5-C*H*), 7.19 (d, 2H, 3-C*H*), 7.40–7.80 (m, 17H, 4-C*H* and Sn–C_6H_5), 8.50 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): −72.28 (s). IR (nujol, cm^{-1}): 3170w, 3059w (CH), 1578s, 1558s (C=C + C=N), 333sbr (Sn–N), 269sbr (Sn–Cl), 230sbr (Sn–C). ESI-MS (major positive-ions, CH_3OH), *m/z* (%): 235 (80) $[\{(pyS)_2CH_2\} + H]^+$, 584 (60) $[\{(pyS)_2CH_2\}\text{-}\{Sn(C_6H_5)_3\}]^+$, 717 (60) $[\{Sn(C_6H_5)_3\}O\{Sn(C_6H_5)_3\}_3 + H]^+$. ESI-MS (major negative-ions, CH_3OH), *m/z* (%): 421 (100) $[\{Sn(C_6H_5)_3Cl\} + Cl]^-$. Anal. Calc. for $C_{29}H_{25}ClN_2S_2Sn$: C, 56.13; H, 4.06; N, 4.52; S, 10.31. Found: C, 56.01; H, 4.24; N, 4.39; S, 10.07%.

2.2.10. {[(pyS)$_2$CH$_2$]Sn(C$_6$H$_{11}$)$_3$Cl} (10)

Compound **10** was prepared similarly to compound **8** by using $(C_6H_{11})_3SnCl$ (0.404 g, 1.0 mmol) and $[(pyS)_2CH_2]$ (0.234 g, 1.0 mmol) in dichloromethane solution (50 ml). Yield: 55%. M.p. 94–96 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.25–1.98 (m, 33H, Sn–C_6H_{11}), 5.06 (s, 2H, CH_2), 7.02 (m, 2H, 5-C*H*), 7.19 (d, 2H, 3-C*H*), 7.50 (t, 2H, 4-C*H*), 8.50 (d, 2H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): 73.07 (s). IR (nujol, cm^{-1}): 3170w, 3046w (CH), 1577s, 1553s (C=C + C=N), 478m (Sn–C), 355m (Sn–N), 266sbr (Sn–Cl). ESI-MS (major positive-ions, CH_3OH), *m/z* (%): 235 (80) $[\{(pyS)_2CH_2\} + H]^+$, 369 (20) $[\{Sn(C_6H_{11})_3\}]^+$, 603 (30) $[\{(pyS)_2CH_2\}\{Sn(C_6H_{11})_3\}]^+$. ESI-MS (major negative-ions, CH_3OH), *m/z* (%): 439 (100) $[\{Sn(C_6H_{11})_3Cl\} + Cl]^-$. Anal. Calc. for $C_{29}H_{43}ClN_2S_2Sn$: C, 54.53; H, 6.79; N, 4.39; S, 10.02. Found: C, 54.03; H, 7.01; N, 4.14; S, 9.87%.

2.2.11. {[(pyS)$_3$CH]Sn(CH$_3$)$_2$Cl$_2$} (11)

To a diethyl ether solution (50 ml) of $[(pyS)_3CH]$ (0.343 g, 1.0 mmol), the tin(IV) acceptor $(CH_3)_2SnCl_2$ (0.220 g, 1.0 mmol) was added. The mixture reaction was stirred for 24 h at room temperature, then solvent was removed on a rotary evaporator and the residue was washed with diethyl ether. The pale brown product obtained was dried to constant weight under reduced pressure. Yield: 88%. M.p. 90–93 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.22 (s, 6H, Sn–CH_3, $J(^{117}Sn–^1H) = 71.0$ Hz, $J(^{119}Sn–^1H) = 73.7$ Hz), 7.09 (m, 3H, 5-C*H*), 7.29 (d, 3H, 3-C*H*), 7.58 (t, 3H, 4-C*H*), 7.87 (s, 1H, C*H*), 8.55 (d, 3H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): 39.59 (s). IR (nujol, cm^{-1}): 3189w, 3078w (CH), 1573m, 1556m (C=C + C=N), 556s, 566s (Sn–C), 370br (Sn–N), 289sbr (Sn–Cl). Anal. Calc. for $C_{18}H_{19}Cl_2N_3S_3Sn$: C, 38.39; H, 3.40; N, 7.46; S, 17.08. Found: C, 38.93; H, 3.53; N, 7.73; S, 17.57%.

2.2.12. {[(pyS)$_3$CH]Sn(C$_6$H$_5$)$_3$Cl} (12)

To a dichloromethane solution (20 ml) of $[(pyS)_3CH]$ (0.343 g, 1.0 mmol) a diethyl ether solution (20 ml) of $(C_6H_5)_3SnCl$ (0.385 g, 1.0 mmol) was added. The mixture reaction was stirred for 12 h at room temperature, then solvent was removed on a rotary evaporator. The product was dissolved in dichloromethane (2 ml), then diethyl ether was added (20 ml) and a brown precipitate afforded, which was filtered off and dried to constant weight under reduced pressure. Yield: 47%. M.p. 101 °C dec. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.03 (m, 3H, 5-C*H*), 7.12–7.90 (mc, 21H, 3-C*H*, 4-C*H*, Sn–C_6H_5), 7.92 (s, 1H, C*H*), 8.53 (d, 3H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): −84.78 (s). IR (nujol, cm^{-1}): 3137w, 3046w (CH), 1574s, 1556m (C=C + C=N), 374mbr (Sn–N), 265mbr (Sn–Cl), 233m (Sn–C). ESI-MS (major positive-ions, CH_3OH), *m/z* (%): 344 (20) $[\{(pyS)_3CH\} + H]^+$, 366 (90) $[\{(pyS)_3CH\} + Na]^+$, 752 (10) $[\{(pyS)_3CH\}Sn(C_6H_5)_3Cl + Na]^+$. ESI-MS (major negative-ions, CH_3OH), *m/z* (%): 421 (100) $[\{Sn(C_6H_5)_3Cl\} + Cl]^-$. Anal. Calc. for $C_{34}H_{28}ClN_3S_3Sn$: C, 56.02; H, 3.87; N, 5.76; S, 13.19. Found: C, 55.71; H, 3.70; N, 5.39; S, 12.87%.

2.2.13. {[(pyS)$_3$CH]Sn(C$_6$H$_{11}$)$_3$Cl} (13)

To a dichloromethane solution (20 ml) of $[(pyS)_3CH]$ (0.343 g, 1.0 mmol) a diethyl ether solution (20 ml) of $(C_6H_{11})_3SnCl$ (0.404 g, 1.0 mmol) was added. The mixture reaction was stirred for 5 h at room temperature, then solvent was removed on a rotary evaporator. The brown precipitate obtained was washed with a dichloromethane/diethyl ether solution (1:1) and dried to constant weight under reduced pressure. Yield: 72%. M.p. 111–115 °C. ^{1}H NMR ($CDCl_3$, 293 K): δ 1.33–2.00 (mc, 33H, Sn–C_6H_{11}), 7.08 (m, 3H, 5-C*H*), 7.24 (d, 3H, 3-C*H*), 7.53 (m, 3H, 4-C*H*), 7.90 (s, 1H, C*H*), 8.52 (d, 3H, 6-C*H*). ^{119}Sn NMR ($CDCl_3$, 293 K): 73.02 (s). IR (nujol, cm^{-1}): 3157w, 3070w (CH), 1574s, 1553s (C=C + C=N), 446m (Sn–C), 330m (Sn–N), 246sbr (Sn–Cl). ESI-MS (major positive-ions, CH_3OH), *m/z* (%): 344 (15) $[\{(pyS)_3CH\} + H]^+$, 366 (100) $[\{(pyS)_3CH\} + Na]^+$, 712 (20) $[\{(pyS)_3CH\}Sn(C_6H_{11})_3]^+$. ESI-MS (major negative-ions, CH_3OH), *m/z* (%): 439 (100) $[\{Sn(C_6H_{11})_3Cl\} + Cl]^-$. Anal. Calc. for $C_{34}H_{46}ClN_3S_3Sn$: C, 54.66; H, 6.21; N, 5.62; S, 12.87. Found: C, 54.37; H, 6.53; N, 5.34; S, 12.57%.

3. Results and discussion

The bis(2-pyridylthio)methane, $[(pyS)_2CH_2]$ (**1**) and tris(2-pyridylthio)methane $[(pyS)_3CH]$ (**2**) ligands were prepared modifying the literature method [29]. Compounds **1** and **2** are air- and moisture-stable yellow microcrystalline solids; they are soluble in chlorinated solvents, diethyl ether, acetone and DMSO, but insoluble in acetonitrile, aromatic and aliphatic hydrocarbons and water. The infrared spectra showed weak absorptions near 3100 cm^{-1} due to the pyS ring C–H stretching, and medium to strong absorptions in the range 1550–1580 cm^{-1} related to ring "breathing" vibrations. In the negative-ion spectrum of **1** the major peak at *m/z* 233 (100%) is due to the deprotonated species $[(pyS)_2CH]^-$; an other minor peak is attributable to the fragment $[(pyS)]^-$ (50%). Analogously in the negative-ion spectrum of **2** the major peak at *m/z* 379 (100%) is due to the fragment attributable to the aggregation of one chloride ion to the free ligand; other minor peaks are attributable to the deprotonated species $[(pyS)_3C]^-$ (20%) and to the fragment $[(pyS)]^-$ (10%). The ESI-MS positive-ion spectrum of **2** in methanol is dominated by the protonated ligand $[(pyS)_3CH + H]^+$ (100%) and by the fragments attributable to the aggregation of one sodium ion to one (*m/z* = 355, 30%) or two molecules of the free ligand (*m/z* = 710, 60%).

Complexes **3**–**10** have been synthesized by reaction of $[(pyS)_2CH_2]$ with SnR_nX_{4-n} acceptors in dichloromethane solution in the following equation:

$$[(pyS)_2CH_2] + SnR_nCl_{4-n} \rightarrow \underset{\mathbf{3-10}}{[(pyS)_2CH_2]R2_nSnCl_{4-n}] \quad (1)}$$

3 R = CH_3 $n = 1$

4 R = CH_3 $n = 2$

5 R = CH_3 $n = 3$

6 R = ^{n}Bu $n = 2$

7 R = ^{n}Bu $n = 3$

8 R = Ph $n = 2$

9 R = Ph $n = 3$

10 R = Cy $n = 3$

Complexes **11–13** have been synthesized by reaction of $[(pyS)_3CH]$ with SnR_nX_{4-n} acceptors in diethyl ether or dichloromethane solution in the following equation:

$$[(pyS)_3CH] + SnR_nCl_{4-n} \rightarrow \underset{\mathbf{11-13}}{[(pyS)_3CH]R_nSnCl_{4-n}] \quad (2)}$$

11 R = CH_3 $n = 2$

12 R = Ph $n = 3$

13 R = Cy $n = 3$

We were not able to isolate any monoalkyl- or monoaryl-tin(IV) adduct with the tris(2-pyridylthio)methane ligand, by using different solvents or different ligand-to-metal ratio. Analogously no other di- or tri-alkyl/aryl derivative has been obtained also modifying the reaction conditions.

The derivatives **4**–**10** are stable in air; they are soluble in chlorinated solvents, acetone, methanol and DMSO, but are insoluble in aromatic and aliphatic hydrocarbons and they are non-electrolytes in CH_2Cl_2 solution. Derivative **3** is soluble in chloroform and DMSO and insoluble in other chlorinated solvents, acetone, methanol, acetonitrile, diethyl ether and aromatic and aliphatic hydrocarbons. The derivatives **11**–**13** are soluble in chlorinated solvents, acetone, methanol, but are insoluble in diethyl ether, acetonitrile, water and aromatic and aliphatic hydrocarbons and they are non-electrolytes in CH_2Cl_2 solution. The identity of these compounds has been established by elemental analysis, ESI-MS, IR, and multinuclear (^1H, ^{119}Sn) NMR spectral studies.

The infrared spectra carried out on the solid samples (nujol mull) showed all the expected bands for the ligands and the tin moieties: weak absorptions near 3100 cm^{-1} are due to the pyS ring C–H stretching and medium to strong absorptions in the range 1550–1580 cm^{-1} are related to ring "breathing" vibrations.

In the far-IR region medium to strong absorptions appear upon coordination, due to stretching modes of Sn–N, Sn–R and Sn–Cl [33]. The Sn–N stretching frequencies appear as strong or medium absorptions in the range 330–400 cm^{-1}. The Sn–Cl stretching frequencies in the trichloride-, dichloride- and monochloride–alkyl tin(IV) derivatives **3**–**7**, **10**, **11** and **13** fall as strong or medium broad bands in the range 282–293, 279–289 and 238–266 cm^{-1}, respectively. The corresponding frequencies in the dichloride- and monochloride–phenyl tin(IV) derivatives **8**, **9** and **12** fall as strong broad bands at 280, 269 and 265 cm^{-1}, respectively: this trend can be explained on the basis of higher inductive effect of electron-withdrawing chlorine with respect to alkyls or phenyls, which strengthen the Sn–N bond. In the far-IR spectra the Sn–C stretching frequencies fall as strong or medium broad bands in the range 446–619 cm^{-1} for alkyl derivatives **3**–**7**, **10**, **11** and **13**, and in the range 224–233 cm^{-1} for phenyl complexes **8**, **9**, and **12**; these absorptions agree well with the trends previously observed in similar N-donor complexes [34].

The room-temperature ^1H NMR spectra of derivatives **3**–**13**, in $CDCl_3$ solution (see Section 2), exhibit only one set of signals for the protons of the pyridyl rings of the $[(pyS)_2CH_2]$ or $[(pyS)_3CH]$ ligands [35]. Upon interaction of ligands **1** and **2** with mono-and di-organotin(IV) acceptors, only small shifts were evident for the proton atoms of the pyridyl rings, in particular detectable for the 6-CH protons: this observation implies a weak interaction of these rings with the metal. In the ^1H NMR spectra of the triorganotin(IV) derivatives, the positions of the signals are practically identical to those found in the free ligands, suggesting a dissociation of the complexes in solution.

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 and hence $^2J(^{119,117}Sn, ^1H)$ may give information about

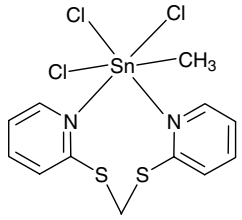

Fig. 2. Proposed structure for the derivative $\{[(pyS)_2CH_2]Sn(CH_3)Cl_3\}$ (**3**).

the coordination number of tin [36]. In the methyltin(IV) derivative **3** the tin-proton coupling constants $^2J(^{117}Sn, ^1H)$ and $^2J(^{119}Sn, ^1H)$ are 73.0 and 77.0 Hz, falling in the range for five- or six-coordinated species [37]. The ^{119}Sn chemical shift of **3** falls at −472.4 ppm, providing an additional support for six-coordinated tin atom [38] (Fig. 2), with the donor acting as *N*,*N*′-bidentate chelating ligand [26].

In the dimethyltin(IV) derivatives **4** and **11** the tin-proton coupling constants $^2J(^{117}Sn, ^1H)$ and $^2J(^{119}Sn, ^1H)$ fall in the range for five- or six-coordinated dimethyltin(IV) species [37]. The ^{119}Sn chemical shifts of diorganotin(IV) derivatives **4**, **8** and **11** are in accordance with those of five- or six-coordinated diorganotin(IV) halides complexes involving S-, O- or N-donors [31,39–42] (Figs. 3 and 4). The ^{119}Sn spectrum of $\{[(pyS)_2CH_2]Sn(C_4H_9)_2Cl_2\}$ (**6**) shows peaks at −139.30, −91.98 and −65.27 ppm, attributable to the dissociation of the complex and to the existence in solution of four- or five-coordinated species containing Sn–O bonds, due to the hydrolysis of the starting compounds [42,43]. The ^{119}Sn chemical shift of the triorganotin(IV) derivatives **5**, **7**, **9**, **10**, **12** and **13**, fall in the range typical of the R_3SnCl starting materials, suggesting a complete dissociation of the compounds in solution.

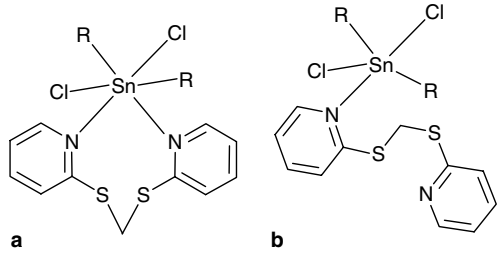

Fig. 3. Proposed structures for six-coordinated (a) or five-coordinated (b) diorganotin(IV) derivatives $\{[(pyS)_2CH_2]SnR_2Cl_2\}$.

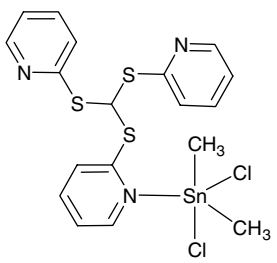

Fig. 4. Proposed structure for the derivative $\{[(pyS)_3CH]Sn(CH_3)_2Cl_2\}$ (**11**).

Electrospray ionization is considered a 'soft' ionization technique and is particularly suitable for the study of labile organotin systems in solution. Although ESI-mass spectra, dissolved in methanol solution and detected at fragmentation voltage of 30 V, do not show a molecular ion $[M]^+$ peak, structurally important fragment ions are clearly discernible.

Peaks at *m*/*z* 110, 233, 235 and 257 due to the free bis(2-pyridylthio)methane ligand or its decomposition fragments, are present in the spectra of all derivatives **3**–**11**. The cationic and anionic spectra of di-organotin derivatives **4**, **6** and **8** show peaks, at *m*/*z* 489, 537, 841 and 959 due to the mononuclear and dinuclear complexes, respectively, index of stability of the di-organotin complexes in methanol solution.

More complex fragmentation pattern has been detected in the positive- and negative-ion spectra of the triorganotin(IV) compounds **5**, **7**, **9** and **10**. In the positive-ion spectra of the trimethyl- and triphenyl-derivatives there are peaks attributable to the mononuclear complexes, while in the tributyl- and tricycloexyl-derivatives there are also peaks attributable to free $[Sn(R)_3]^+$ and $[\{Sn(R)_3Cl\} + Cl]^-$ acceptors, providing an additional support for the complete dissociation of these compounds in solution.

Peaks at *m*/*z* 344 and 366 due to the free tris(2-pyridylthio)methane ligand or its decomposition fragments, are present in the spectra of derivatives **12** and **13**, together with peaks due to the cationic mononuclear $[\{(pyS)_3CH\}Sn(C_6H_5)_3Cl + Na]^+$, $[\{(pyS)_3CH\}Sn(C_6H_{11})_3]^+$ complexes. The anionic spectra of derivatives **12** and **13** show peaks at *m*/*z* 421 and 439 attributable to free acceptors of the type $[\{Sn(R)_3Cl\} + Cl]^-$.

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