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Tin(IV) and organotin(IV) complexes containing mono or bidentate N-donor ligands. V. Imidazole and imidazoline-2-thione derivatives: synthesis and spectroscopic characterization. Comparison with other imidazole tin(IV) complexes

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Abstract—The reactions of imidazole (L^1), benzimidazole (L^2), 2-phenylimidazole (L^3), 1-acetylimidazole (L^4), imidazoline-2(1,3*H*)-thione (L^5) and 1-methyl-imidazoline-2(3*H*)-thione (L^6) with R_nSnCl_{4-n} (R = Me, Bu^n or Ph; $n = 1$, 2 or 3) were investigated. Twenty-seven novel adducts were obtained and characterized by analytical (elemental analysis, conductivity and vaporimetric molecular weight measurements) and spectral (IR, far IR, ^{1}H and ^{119}Sn NMR) data. The ligands L^1, L^2, L^3 and L^4 behave in the monodentate N-donor fashion, whereas L^5 and L^6 behave as monodentate S-donor molecules. Breaking of the N–CO bonds and protonation of imidazolate moiety occurred when the donor L^4 reacts with organotin acceptors in not rigorously anhydrous conditions. The behavior of the adducts in acetone and chlorinated solvents is also discussed. Comparison was made with related organotin(IV) complexes of imidazoles. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: tin(IV) and organotin(IV) complexes; ligands; imidazole; imidazoline-2-thione derivatives

INTRODUCTION

Imidazole-type heterocycles represent an important class of ligands in coordination chemistry: the imidazole ring is an essential component of many biological systems such as proteins, nucleic acids and the vitamin B_{12} coenzyme.

Expanding the earlier studies carried out with mercury(II) [1] and copper(I) [2], we have recently initiated a systematic study of tin(IV) and organotin(IV) compounds of imidazoles, in order to evaluate the bonding ability of imidazoles, which is important for understanding the effect of these N-donor ligands on the physico–chemical properties of metal complexes.

To investigate the influence of the nature of the tin(IV) acceptors and of the substituents on the azole ring, we previously investigated the interaction of 1-benzyl- [3], 4-phenyl- [4], 4-methyl-, 2-methyl-, 2-isopropyl- [5] and 1-methyl-imidazole [6] with R_nSnX_{4-n} acceptors (R = Me, Et, Bu^n and Ph; $n = 1$, 2 or 3; X = Cl, Br, I, NO_3, ClO_4, NCS and BPh_4). The reactivity of these imidazoles towards organotin(IV) acceptors depends not only on the electronic and steric features of the groups bonded to tin, but also on the position of the alkylic or arylic substituent in the imidazole moiety and on the nature of the counterion: the ligand/metal ratio can range from 1:1, as in [(1-methylimidazole)$(C_6H_5)_3$SnCl] and to 4:1, as in [(4-methylimidazole)$_4(CH_3)_2$Sn]$(BPh_4)_2$. NMR data, molecular weight measurements and X-ray crystal and

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molecular structure determinations indicate that the bonding interaction between the imidazole donors and R_nSnX_{4-n} generally increases with the decreasing of *n*.

With the aim to complete our systematic study on tin(IV) and organotin(IV) complexes of imidazoles we report here the synthesis, spectroscopic characterization (IR and ^{1}H NMR data) and behavior in solution (conductivity and molecular weight measurements) of new adducts between organotin(IV) acceptors and the ligands in Fig. 1, i.e. imidazole (L^1), benzimidazole (L^2), 2-phenylimidazole (L^3), 1-acetylimidazole (L^4), imidazoline-2(1,3*H*)-thione (L^5) and 1-methyl-imidazoline-2(3*H*)-thione (L^6).

EXPERIMENTAL

General methods

The organotin(IV) halides were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligands imidazole (L^1), benzimidazole (L^2), 2-phenylimidazole (L^3), 1-acetylimidazole (L^4), imidazoline-2(1,3*H*)-thione (L^5), 1-methyl-imidazoline-2(3*H*)-thione (L^6) were obtained from Aldrich and were crystallized from diethyl ether/petroleum ether (1:2). Solvent evaporations were always carried out *in vacuo* (water aspirator). The samples for microanalysis were dried *in vacuo* to constant weight (20°C, approx. 0.1 Torr). Elemental analyses (C, H, N, S) were performed in house with a Carlo–Erba model 1106 instrument.

IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^{1}H and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^{1}H and 111.9 MHz for ^{119}Sn). The chemical shifts are reported in ppm from $SiMe_4$ (^{1}H calibration by internal deuterium solvent lock) and $SnMe_4$ (^{119}Sn).

Melting points were taken on an IA 8100 Electrothermal instrument. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature. The osmometric measurements were carried out at 40°C, over a range of concentrations, with a Knauer KNA0280 vapor pressure osmometer calibrated with benzil. The solvent was Baker Analyzed Spectrophotometric grade chloroform. The results were reproducible to $\pm 2\%$.

Syntheses

All experiments were carried out under a dinitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium, dichloromethane from calcium hydride and tetrahydrofuran from $LiAlH_4$. All solvents were outgassed with dry dinitrogen prior to use.

[*Trimethylbis*(*imidazole*)*tin*(*IV*)]*chloride* (***I***). To a stirred refrigerated (0°C) petroleum ether/diethyl ether (10/1) solution (100 cm^3) of imidazole (L^1) (272 mg, 4.0 mmol), $(CH_3)_3SnCl$ (398 mg, 2.0 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 12 h. The solution was stored in freezer overnight. A colorless precipitate was formed, which was separated from the solution, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, approx. 0.1 Torr) and shown to be com-

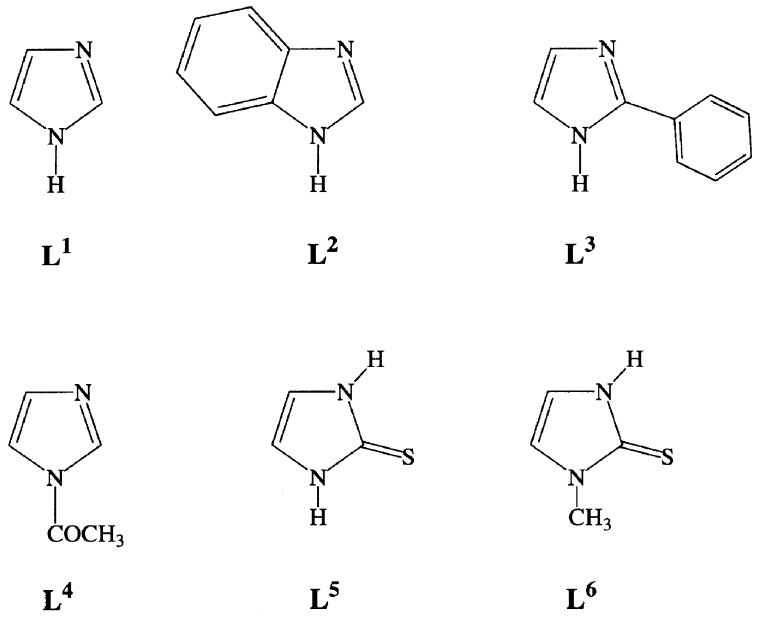

Fig. 1. Ligands employed in this work.

pound **1**. Yield: 70%, m.p. 54–56°C (Found: C, 32.4; H, 5.2; N, 16.6. Calc. for $C_9H_{17}ClN_4Sn$: C, 32.2; H, 5.1; N, 16.7%). NMR (Acetone-d_6): ^{1}H, δ 10.8 (br, 2H, N–*H*), 7.82 (s, 2H, 2-C*H*), 7.13 (s, 4H, 4-, 5-C*H*), 0.66 [$|^2J(^{119}Sn–H)| = 70.8$ Hz, $|^2J(^{117}Sn–H)| = 67.8$ Hz, s, 9H, SnCH_3]; ^{119}Sn, δ −83.5 ppm. IR: 3162 w, 3100 w [ν(C–H)], 549 s [ν(Sn–C)]. Λ (acetone, 25°C, 1.1×10^{-3} M): $1.4\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Triphenylbis*(*imidazole*)*tin*(*IV*)]*chloride* (***2***). To a stirred refrigerated (0°C) diethyl ether solution (100 cm^3) of imidazole (L^1) (272 mg, 4.0 mmol), $(C_6H_5)_3SnCl$ (385 mg, 1.0 mmol) was added under N_2 stream. The mixture was stored at 0°C and stirred for 12 h. A white precipitate was formed, which was filtered off, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **2**. Yield: 39%, m.p. 155–157°C (Found: C, 55.0; H, 4.2; N, 10.4. Calc. for $C_{24}H_{23}ClN_4Sn$: C, 55.3; H, 4.4; N, 10.7%). NMR (Acetone-d_6): ^{1}H, δ 7.84 [$|^2J(^{119}Sn–H)| = 69.0$ Hz, $|^2J(^{117}Sn–H)| = 66.3$ Hz, d, 2H, Sn-*o*-C_6H_5)], 7.81 [$|^2J(^{119}Sn–H)| = 67.1$ Hz, $|^2J(^{117}Sn–H)| = 64.2$ Hz, d, 2H, Sn-*o*-C_6H_5)], 7.52 (s, 2H, 2-C*H*), 7.43 (m, 6H, Sn-*m*-, Sn-*p*-C_6H_5), 6.97 (s, 4H, 4-, 5-C*H*); ^{119}Sn, δ −225 ppm. IR: 3131 w, 3049 w [ν(C–H)], 463 s, 453 s [δ(Ph)], 290 m [ν(Sn–C)]. Λ (acetone, 25°C, 1.0×10^{-3} M): $2.6\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Trichloromethylbis*(*imidazole*)*tin*(*IV*)]·H_2O (***3***). To a stirred diethyl ether/ethanol (1/1) solution (100 cm^3) of imidazole (L^1) (272 mg, 4.0 mmol), $(CH_3)SnCl_3$ (240 mg, 1.0 mmol) was added at room temperature. The mixture was stirred for 12 h. The solvent was removed with a rotary evaporator and diethyl ether/petroleum ether 1:1 were added until an oil was formed, which was separated from the solution. The oily residue was washed with diethyl ether/petroleum ether 1:1 (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **3**. Yield: 75% (Found: C, 21.6; H, 3.5; N, 14.6. Calc. for $C_7H_{13}Cl_3N_4OSn$: C, 21.3; H, 3.3; N, 14.2%). NMR (CD_3OD): ^{1}H, δ 8.71 s (2H, 2-C*H*), 7.50 s (4H, 4- and 5-C*H*), 1.21 s, 3H, SnCH_3]. IR: 3400 br [ν(O–H)], 3140 w, 3103 w [ν(C–H)], 569 sh br [ν(Sn–C)], 287 m, 275 m [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): $19.7\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Trichlorobutylbis*(*imidazole*)*tin*(*IV*)] (***4***). To a stirred diethyl ether solution (100 cm^3) of imidazole (L^1) (272 mg, 4.0 mmol), $(C_4H_9)SnCl_3$ (564 mg, 2.0 mmol) was added at room temperature. A colorless precipitate was formed immediately, which was filtered off after 6 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **4**. Yield: 95%, m.p. 93–95°C (Found: C, 28.7; H, 4.2; N, 13.3. Calc. for $C_{10}H_{17}Cl_3N_4Sn$: C, 28.7; H, 4.1; N, 13.4%). NMR (Acetone-d_6): ^{1}H, δ 12.2 (br, 2H, N–*H*), 8.70 (br, 2H, 2-C*H*), 7.50 (br, 4H, 4- and 5-C*H*), 1.6–1.8 (m, 4H, Sn–C_4H_9), 1.32 (ps, 2H, Sn–C_4H_9), 0.85 (t, 3H, Sn–C_4H_9). IR: 3126 m, 3047 w [ν(C–H)], 618 m [ν(Sn–C)], 284 m, 274 m [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.1×10^{-3} M): $24.3\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Trichlorophenylbis*(*imidazole*)*tin*(*IV*)] (***5***). Compound **5** was prepared similarly to compound **4**. Yield: 47%, m.p. 128–132°C (Found: C, 33.0; H, 3.2; N, 12.6. Calc. for $C_{12}H_{13}Cl_3N_4Sn$: C, 32.9; H, 3.0; N, 12.8%). NMR (Acetone-d_6): ^{1}H, δ 12.3 (br, 2H, N–*H*), 8.74, 8.67 (br, 2H, 2-C*H*), 7.54 (br, 4H, 4- and 5-C*H*), 8.2, 7.9, 7.8, 7.5, 7.3 (m, 5H, Sn–C_6H_5). IR: 3134 w [ν(C–H)], 462 m [δ(Ph)], 318 br, 310 m, 286 m, 270 m, 260 m [ν(Sn–C) and ν(Sn–Cl)]. Λ (acetone, 25°C, 1.1×10^{-3} M): $41.0\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Chlorotriphenyl*(*benzimidazole*)*tin*(*IV*)] (***6***). To a stirred diethyl ether solution (100 cm^3) of benzimidazole (L^2) (236 mg, 2.0 mmol), $(C_6H_5)_3SnCl$ (385 mg, 1.0 mmol) in dichloromethane (20 cm^3) was added at 40°C. A colorless precipitate was formed immediately, which was filtered off after 6 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **6**. Yield: 40%, m.p. 149–152°C (Found: C, 59.5; H, 4.4; N, 5.8. Calc. for $C_{25}H_{21}ClN_4Sn$: C, 59.6; H, 4.2; N, 5.6%). NMR (Acetone-d_6): ^{1}H, δ 8.06 (s, 1H, 2-C*H*), 7.83 [$|^2J(^{119}Sn–H)| = 65.0$ Hz, d, 6H, Sn-*o*-C_6H_5)], 7.40–7.55 (m, 11H, Sn-*m*-, Sn-*p*-C_6H_5 and 4- and 7-C*H*), 7.17 (m, 2H, 5- and 6-C*H*). IR: 3360 br [ν(N–H)], 3157 w, 3129 w [ν(C–H)], 455 s, 426 s, 422 sh [δ(Ph)], 290 m [ν(Sn–C)], 226 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 0.9×10^{-3} M): $1.3\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Dichlorodimethylbis*(*benzimidazole*)*tin*(*IV*)] (***7***). To a stirred dichloromethane solution (100 cm^3) of benzimidazole (L^2) (473 mg, 4.0 mmol), $(CH_3)_2SnCl_2$ (220 mg, 1.0 mmol) was added at room temperature. A colorless precipitate was formed immediately, which was filtered off after 6 h, washed with dichloromethane (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **7**. Yield: 98%, m.p. 171–174°C (Found: C, 42.2; H, 4.0; N, 12.2. Calc. for $C_{16}H_{18}Cl_2N_4Sn$: C, 42.1; H, 4.0; N, 12.3%). NMR (Acetone-d_6): ^{1}H, δ 11.1 (br, 2H, N–*H*), 8.77 (s, 2H, 2-C*H*), 7.82 (m, 4H, 4- and 7-C*H*), 7.39 (m, 4H, 5- and 6-C*H*), 1.22 [$|^2J(^{119}Sn–H)| = 92.1$ Hz, $|^2J(^{117}Sn–H)| = 87.9$ Hz, s, 6H, SnCH_3]; ^{119}Sn, δ −147.2 ppm. IR: 3150 br [ν(N–H)], 3134 w [ν(C–H)], 573 s [ν(Sn–C)], 435 s, 422 s [δ(Ph)], 228 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 0.9×10^{-3} M): $35.8\,\Omega^{-1}\,cm^2\,mol^{-1}$.

[*Dichlorodiphenylbis*(*benzimidazole*)*tin*(*IV*)] (***8***). To a stirred dichloromethane/diethyl ether (2/1) solution (100 cm^3) of benzimidazole (L^2) (473 mg, 4.0 mmol), $(C_6H_5)_2SnCl_2$ (344 mg, 1.0 mmol) was added at room temperature. A pale brown precipitate was formed immediately, which was filtered off after 6 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **8**. Yield: 89%, m.p. 162–164°C (Found: C, 53.6; H, 3.9; N, 9.9. Calc. for $C_{26}H_{22}Cl_2N_4Sn$: C, 53.8; H, 3.8; N, 9.7%). NMR (Acetone-d_6): ^{1}H, δ 10.0 (br, 2H, N–*H*), 8.41 (s, 2H, 2-C*H*), 7.98 [$|^2J(^{119}Sn–H)| = 108.4$ Hz, $|^2J(^{117}Sn–H)| = 107.7$, d, 4H, Sn-*o*-

C_6H_5)], 7.67, 7.24 (m, 10H, Sn-*m*-, Sn-*p*-C_6H_5 and 4-, 5-, 6- and 7-C*H*). IR: 3150 br [ν(N–H)], 3127 w [ν(C–H)], 463 s, 458 s, 432 s, 424 s [δ(Ph)], 293 s [ν(Sn–C)], 244 s, 234 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 0.9×10^{-3} M): 19.9 Ω^{-1} cm^2 mol^{-1}.

[*Trichloromethylbis*(*benzimidazole*)*tin*(*IV*)] (***9***). Compound **9** was prepared similarly to compound **7**. Yield: 84%, m.p. 280°C dec. (Found: C, 38.0; H, 3.1; N, 11.6. Calc. for $C_{15}H_{15}Cl_3N_4Sn$: C, 37.8; H, 3.2; N, 11.8%). NMR (Acetone-d_6): ^{1}H, δ 8.95 (br, 2H, 2-C*H*), 7.90 (m, 4H, 4- and 7-C*H*), 7.30 (m, 4H, 5- and 6-C*H*), 1.46 [$|^2J(^{119}Sn–H)| = 131.4$ Hz, $|^2J(^{117}Sn–H)| = 121.2$ Hz, s, 3H, SnCH_3]. IR: 3340 m, 3278 br [ν(N–H)], 3139 w [ν(C–H)], 592 s, 546 m, 533 m [ν(Sn–C)], 439 s, 420 s [δ(Ph)], 304 s, 295 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 44.1 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorobutylbis*(*benzimidazole*)*tin*(*IV*)] (***10***). Compound **10** was prepared similarly to compound **8**. Yield: 75%, m.p. 158–160°C (Found: C, 41.7; H, 4.1; N, 10.5. Calc. for $C_{18}H_{21}Cl_3N_4Sn$: C, 41.7; H, 4.1; N, 10.8%). NMR (Acetone-d_6): ^{1}H, δ 9.68 (s, 2H, 2-C*H*), 8.02 (m, 4H, 4- and 7-C*H*), 7.69 (m, 4H, 5- and 6-C*H*), 1.8–2.2 (m, 4H, Sn–C_4H_9), 1.47 (ps, 2H, Sn–C_4H_9), 0.93 (t, 3H, Sn–C_4H_9). IR: 3200 br [ν(N–H)], 3085 w [ν(C–H)], 597 s [ν(Sn–C)], 419 s, 403 s [δ(Ph)], 291 s, 251 s, 230 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.3×10^{-3} M): 76.4 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorophenylbis*(*benzimidazole*)*tin*(*IV*)] (***11***). Compound **11** was prepared similarly to compound **8**. Yield: 80%, m.p. 121–124°C (Found: C, 44.5; H, 3.1; N, 10.5. Calc. for $C_{20}H_{17}Cl_3N_4Sn$: C, 44.6; H, 3.2; N, 10.4%). NMR (Acetone-d_6): ^{1}H, δ 12.5 (br, 2H, N–*H*), 8.95 (br, 2H, 2-C*H*), 7.96 (br, 2H, Sn-*o*-C_6H_5), 7.72, 7.26 (br, 7H, Sn-*m*-, Sn-*p*-C_6H_5 and 4-, 5-, 6- and 7-C*H*). IR: 3278 br [ν(N–H)], 3134 w [ν(C–H)], 455 s, 437 s, 420 s, 408 s [δ(Ph)], 285 m [ν(Sn–C)], 266 sh, 257 br, 250 br, 236 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 0.8×10^{-3} M): 30.5 Ω^{-1} cm^2 mol^{-1}.

[*Dichlorodimethylbis*(2-*phenylimidazole*)*tin*(*IV*)] (***12***). To a stirred dichloromethane/diethyl ether (2/1) solution (100 cm^3) of 2-phenylimidazole (L^3) (577 mg, 4.0 mmol), $(CH_3)_2SnCl_2$ (439 mg, 2.0 mmol) was added at room temperature. A colorless precipitate was formed immediately, which was filtered off after 6 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **12**. Yield: 52%, m.p. 130–132°C (Found: C, 47.4; H, 4.4; N, 10.9. Calc. for $C_{20}H_{22}Cl_2N_4Sn$: C, 47.3; H, 4.4; N, 11.0%). NMR ($CDCl_3$): ^{1}H, δ 8.22 (d, 4H, *o*-C_6H_5), 7.41 (t, 2H, *p*-C_6H_5), 7.31 (t, 4H, *m*-C_6H_5), 7.24 (s, 4H, 4- and 5-C*H*), 1.25 [$|^2J(^{119}Sn–H)| = 71.7$ Hz, $|^2J(^{117}Sn–H)| = 69.0$ Hz, s, 6H, SnCH_3]. IR: 3140 br [ν(N–H)], 3110 w, 3048 w [ν(C–H)], 575 m [ν(Sn–C)], 438 s [δ(Ph)], 233 s br [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.1×10^{-3} M): 67.3 Ω^{-1} cm^2 mol^{-1}.

[*Dichlorodibutylbis*(2-*phenylimidazole*)*tin*(*IV*)] (***13***). To a stirred ethanol/diethyl ether (2/1) solution (100 cm^3) of 2-phenylimidazole (L^3) (577 mg, 4.0 mmol), $(C_4H_9)_2SnCl_2$ (304 mg, 1.0 mmol) was added at room temperature. A colorless precipitate was formed immediately, which was filtered off after 6 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **13**. Yield: 93%, m.p. 109–111°C (Found: C, 53.0; H, 6.0; N, 10.0. Calc. for $C_{26}H_{34}Cl_2N_4Sn$: C, 52.7; H, 5.8; N, 9.5%). NMR ($CDCl_3$): ^{1}H, δ 10.6 (br, 2H, N*H*), 7.96 (d, 4H, *o*-C_6H_5), 7.27 (m, 6H, *m*- and *p*-C_6H_5), 7.11 (s, 4H, 4- and 5-C*H*), 1.8 (m, 4H, Sn–C_4H_9), 1.39 (ps, 2H, Sn–C_4H_9), 0.93 (t, 3H, Sn–C_4H_9). IR: 3400 br [ν(N–H)], 3155 w [ν(C–H)] 600 v br [ν(Sn–C)], 445 m, 418 m [δ(Ph)], 230 m [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.3×10^{-3} M): 23.4 Ω^{-1} cm^2 mol^{-1}.

[*Dichlorodiphenylbis*(2-*phenylimidazole*)*tin*(*IV*)] (***14***). To a stirred dichloromethane/methanol (1/1) solution (100 cm^3) of 2-phenylimidazole (L^3) (577 mg, 4.0 mmol), $(C_6H_5)_2SnCl_2$ (688 mg, 2.0 mmol) was added at 40°C. A colorless precipitate was formed immediately, which was filtered off after 6 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **14**. Yield: 54%, m.p. 171–173°C (Found: C, 57.2; H, 4.3; N, 8.7. Calc. for $C_{30}H_{26}Cl_2N_4Sn$: C, 57.0; H, 4.2; N, 8.9%). NMR ($CDCl_3$): ^{1}H, δ 7.0–8.0 (m br, 24H, Sn–C_6H_5, 2-C_6H_5, 4- and 5-C*H*). IR: 3350 br [ν(N–H)], 3061 w, 3039 w [ν(C–H)], 455 s, 444 m [δ(Ph)], 278 m, 269 s [ν(Sn–C)], 226 m [ν(Sn–Cl)]. Λ not available in acetone due to poor solubility.

[*Trichloromethylbis*(2-*phenylimidazole*)*tin*(*IV*)] (***15***). Compound **15** was prepared similarly to compound **12**. Yield: 70%, m.p. 135–138°C dec. (Found: C, 43.0; H, 3.7; N, 10.8. Calc. for $C_{19}H_{19}Cl_3N_4Sn$: C, 43.2; H, 3.6; N, 10.6%). NMR (Acetone-d_6): ^{1}H, δ 8.8 (br, 2H, N–*H*), 8.17 (d, 4H, *o*-C_6H_5), 7.60–7.72 (m, 10H, *m*-C_6H_5, *p*-C_6H_5, 4- and 5-C*H*), 1.41 [$|^2J(^{119}Sn–H)| = 117.5$ Hz, $|^2J(^{117}Sn–H)| = 113.0$ Hz, s, 3H, SnCH_3]. IR: 3150 br [ν(N–H)], 3103 w [ν(C–H)], 527 s [ν(Sn–C)], 442 s [δ(Ph)], 317 s, 300 sh, 288 m [ν(Sn–Cl)]. Λ (acetone, 25°C, 0.8×10^{-3} M): 95.0 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorobutylbis*(2-*phenylimidazole*)*tin*(*IV*)] (***16***). To a stirred dichloromethane solution (100 cm^3) of 2-phenylimidazole (L^3) (577 mg, 4.0 mmol), $(C_4H_9)SnCl_3$ (564 mg, 2.0 mmol) was added at room temperature. The mixture was stirred for 24 h; the solvent was removed with a rotary evaporator and diethyl ether was added. A colorless precipitate was formed immediately, which was filtered off, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **16**. Yield: 90%, m.p. 109–112°C (Found: C, 47.4; H, 4.2; N, 10.0. Calc. for $C_{22}H_{25}Cl_3N_4Sn$: C, 47.3; H, 4.4; N, 9.8%). NMR ($CDCl_3$): ^{1}H, δ 13.9 (br, 2H, N*H*), 8.11 (d, 4H, *o*-C_6H_5), 7.20–7.50 (m, 10H, *m*-C_6H_5, *p*-C_6H_5, 4- and 5-C*H*), 2.45 (m, 2H, Sn–C_4H_9), 1.96 (m, 2H, Sn–C_4H_9), 1.51 (ps, 2H, Sn–C_4H_9), 0.97 (t, 3H, Sn–C_4H_9); ^{119}Sn, δ −269.1 ppm. IR: 3150 br [ν(N–H)], 3085 w [ν(C–H)], 616 m [ν(Sn–C)], 457 w, 441 w, 422 w [δ(Ph)], 316 s, 303 sh [ν(Sn–

Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 88.9 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorophenylbis*(2-*phenylimidazole*)*tin*(*IV*)] (***17***). Compound **17** was prepared similarly to compound **12**. Yield: 65%, m.p. 128–130°C dec. (Found: C, 48.6; H, 3.4; N, 9.6. Calc. for $C_{24}H_{21}Cl_3N_4Sn$: C, 48.8; H, 3.6; N, 9.5%). NMR (Acetone-d_6): ^{1}H, δ 8.30 (d, 2H, Sn–C_6H_5), 8.19 (d, 4H, 2-C_6H_5) 7.71, 7.61, 7.33 (m, 13H, 2-C_6H_5, Sn–C_6H_5, 4- and 5-C*H*). IR: 3300 br [ν(N–H)], 3106 w [ν(C–H)], 458 s [δ(Ph)], 290 m [ν(Sn–C)], 323 m, 315 m, 303 m [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 85.4 Ω^{-1} cm^2 mol^{-1}.

Dichlorodimethylbis(1-*acetylimidazole*)*tin*(*IV*)] (***18***). Compound **18** was obtained similarly to compound **2**. The oily residue obtained was washed with diethyl ether (3×20 cm^3) and shown to be compound **18**. Yield: 90%. (Found: C, 32.5; H, 4.3; N, 12.4. Calc. for $C_{12}H_{18}Cl_2N_4O_2Sn$: C, 32.8; H, 4.1; N, 12.7%). NMR ($CDCl_3$): ^{1}H, δ 8.25 (br, 2H, 2-C*H*), 7.52 (br, 2H, 4- or 5-C*H*), 7.17 (br, 2H, 4- or 5-C*H*), 2.63 (s, 6H, N–CH_3), 1.23 [$|^2J(^{119}Sn–H)| = 75.9$ Hz, $|^2J(^{117}Sn–H)| = 72.3$ Hz, s, 6H, SnCH_3]. IR: 3170 w, 3147 w [ν(C–H)], 1747 s br [ν(C=O)], 564 s [ν(Sn–C)], 244 s, 217 m [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 0.9 Ω^{-1} cm^2 mol^{-1}.

Dichlorodiphenylbis(1-*acetylimidazole*)*tin*(*IV*)]·H_2O(***19***). Compound **19** was obtained similarly to compound **2**. The colorless precipitate formed was filtered after 24 h, washed with diethyl ether (3×30 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **19**. Yield: 95%, m.p. 140–144°C (Found: C, 43.8; H, 4.3; N, 9.5. Calc. for $C_{22}H_{26}Cl_2N_4O_4Sn$: C, 44.0; H, 4.4; N, 9.3%). NMR ($CDCl_3$): ^{1}H, δ 8.19 (br, 2H, 2-C*H*), 7.79 [$|^2J(^{119}Sn–H)| = 132$ Hz, $|^2J(^{117}Sn–H)| = 121$ Hz, m, 4H, Sn–C_6H_5], 7.51 (m br, 8H, Sn–C_6H_5, 4- or 5-C*H*), 7.13 (br, 2H, 4- or 5-C*H*), 2.60 (s, 6H, N–CH_3). IR: 3200–2800 br [ν(O–H)], 3170 w, [ν(C–H)], 1752 s br [ν(C=O)], 295 m [ν(Sn–C)], 264 sh, 256 s, 230 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.2×10^{-3} M): 15.0 Ω^{-1} cm^2 mol^{-1}.

[*Dichlorodiphenylbis*(*imidazoline*-2(1,3H)-*thione*)*tin* (*IV*)] (***20***). To a stirred diethyl ether solution (40 cm^3) of $(C_6H_5)_2SnCl_2$ (344 mg, 1.0 mmol), imidazoline-2-thione (L^5) (200 mg, 2.0 mmol) was added at room temperature. A colorless precipitate was formed immediately, which was filtered off after 24 h, washed with diethyl ether (3×20 cm^3), dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **20**. Yield: 92%, m.p. 213–214°C (Found: C, 39.6; H, 3.5; N, 10.2; S, 11.6. Calc. for $C_{18}H_{18}Cl_2N_4S_2Sn$: C, 39.7; H, 3.3; N, 10.3; S, 11.8%). NMR (Acetone-d_6): ^{1}H, δ 8.12 [$|^2J(^{119}Sn–H)| = 97.2$ Hz, $|^2J(^{117}Sn–H)| = 87.1$ Hz, d, 4H, Sn-*o*-C_6H_5)], 7.3–7.6 (m, 6H, Sn-*o*-C_6H_5), 7.10 (s, 4H, 4- and 5-C*H*). IR: 3220 br [ν(N–H)], 3050 w [ν(C–H)], 1077 s, 1060 m [ν(C–S)], 460 s [δ(Ph)], 289 m, 278 m [ν(Sn–C)], 238 m, 225 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 2.0 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorophenylbis*(*imidazoline*-2(1,3H)-*thione*)*tin* (*IV*)] (***21***). Compound **21** was prepared similarly to compound **20**. Yield: 79%, m.p. 291–293°C (Found: C, 29.0; H, 2.9; N, 11.0; S, 12.5. Calc. for $C_{12}H_{13}Cl_3N_4S_2Sn$: C, 28.7; H, 2.6; N, 11.1; S, 12.8%). NMR (Acetone-d_6): ^{1}H, δ 10.6 (br, 4H, N-*H*), 8.06 [$|^2J(^{119}Sn–H)| = 135.8$ Hz, $|^2J(^{117}Sn–H)| = 117.4$ Hz, d, 2H, Sn-*o*-C_6H_5)], 7.3–7.4 (m, 3H, Sn–C_6H_5), 7.28 (s, 4H, 4- and 5-C*H*). IR: 3250 br [ν(N–H)], 3120 w [ν(C–H)], 1124 w, 1102 w, 1076 m [ν(C–S)], 457 s [δ(Ph)], 301 w, 289 w [ν(Sn–C)], 255 br [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 6.5 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorobutylbis*(*imidazoline*-2(1,3H)-*thione*)*tin* (*IV*)] (***22***). Compound **22** was prepared similarly to compound **20**. Yield: 39%, m.p. 118–121°C (Found: C, 25.0; H, 3.3; N, 11.7; S, 13.3. Calc. for $C_{10}H_{17}Cl_3N_4S_2Sn$: C, 24.9; H, 3.5; N, 11.6; S, 13.3%). NMR (Acetone-d_6): ^{1}H, δ 9.2 (br, 4H, N-*H*), 7.23 (s, 4H, 4- and 5-C*H*), 0.91 t, 1.44 ps, 1.76–1.88 m, 2.02–2.08 m (9H, Sn–C_4H_9); ^{119}Sn, δ −330.6 ppm. IR: 3170 w, [ν(C–H)], 1083 m, 1073 m [ν(C–S)], 501 m [ν(Sn–C)], 268 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 14.0 Ω^{-1} cm^2 mol^{-1}.

[*Dichlorodimethyl*(1-*methyl*-*imidazoline*-2(3*H*)-*thione*)*tin*(*IV*)] (***23***). Compound **23** was prepared similarly to compound **20**. Yield: 95%, m.p. 122–125°C (Found: C, 22.0; H, 3.8; N, 8.6; S, 9.5. Calc. for $C_6H_{12}Cl_2N_2SSn$: C, 21.6; H, 3.6; N, 8.4; S, 9.6%). NMR (Acetone-d_6): ^{1}H, δ 11.8 (br, 1H, N-*H*), 6.98, 6.87 (2d, 2H, 4- and 5-C*H*), 3.51 (s, 3H, N–CH_3), 1.22 [$|^2J(^{119}Sn–H)| = 85.9$ Hz, $|^2J(^{117}Sn–H)| = 82.8$ Hz, s, 6H, Sn–CH_3). ^{119}Sn, δ −13.7 ppm. IR: 3125 w, 3085 w [ν(C–H)], 1165 s, 1109 s [ν(C–S)], 566 s [ν(Sn–C)], 240 s br [ν(Sn–Cl)]. Λ (acetone, 25°C, 0.9×10^{-3} M): 4.9 Ω^{-1} cm^2 mol^{-1}.

[*Dichlorodiphenylbis*(1-*methyl*-*imidazoline*-2(3*H*)-*thione*)*tin*(*IV*)] (***24***). Compound **24** was prepared similarly to compound **20**. Yield: 82%, m.p. 153–155°C (Found: C, 41.7; H, 4.0; N, 9.8; S, 10.9. Calc. for $C_{20}H_{22}Cl_2N_4S_2Sn$: C, 42.0; H, 3.9; N, 9.8; S, 11.2%). NMR ($CDCl_3$): ^{1}H, δ 7.90 [$|^2J(Sn–H)| = 88.9$ Hz, m, 10H, Sn–C_6H_5)], 6.74, 6.72 (2d, 4H, 4- and 5-C*H*), 3.61 (s, 3H, N–CH_3); ^{119}Sn, δ −232.1 ppm. IR: 3125 w [ν(C–H)], 1096 m, 1084 m, 1060 m [ν(C–S)], 461 s [δ(Ph)], 283 s [ν(Sn–C)], 227 s, 222 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 10.5 Ω^{-1} cm^2 mol^{-1}.

[*Trichloromethylbis*(1-*methyl*-*imidazoline*-2(3*H*)-*thione*)*tin*(*IV*)]·H_2O (***25***). Compound **25** was prepared similarly to compound **20**. Yield: 40%, m.p. 80°C dec. (Found: C, 21.9; H, 3.3; N, 11.7; S, 13.5. Calc. for $C_9H_{17}Cl_3N_4OS_2Sn$: C, 22.2; H, 3.5; N, 11.5; S, 13.2%). NMR (Acetone-d_6): ^{1}H, δ 7.35, 7.28 (2 s br, 4H, 4- and 5-C*H*), 3.76 (s br, 6H, N–CH_3), 1.4–2.2 (br, 3H, Sn–CH_3). IR: 3200 br [ν(N–H) and ν(O–H)], 3125 w [ν(C–H)], 1160 m, 1099 m [ν(C–S)], 514 m [ν(Sn–C)], 295 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 15.0 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorophenylbis*(1-*methyl*-*imidazoline*-2(3*H*)-*thione*)*tin*(*IV*)] (***26***). Compound **26** was prepared similarly to compound **20**. Yield: 92%, m.p. 80–83°C (Found: C, 30.3; H, 3.4; N, 9.9; S, 11.4. Calc. for

$C_{14}H_{19}Cl_3N_4OS_2Sn$: C, 30.7; H, 3.5; N, 10.2; S, 11.7%). NMR (Acetone-d_6): ^{1}H, δ 8.1–8.2, 7.4–7.6 (m, 5H, Sn–C_6H_5), 7.28, 7.35 (2d, 4H, 4- and 5-C*H*), 3.73 (s, 6H, N–CH_3); ^{119}Sn, δ −236.9, −330.3 ppm. IR: 3100 w [ν(C–H)], 1160 m, 1098 m [ν(C–S)], 456 s [δ(Ph)], 290 br [ν(Sn–C)], 262 br [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 15.8 Ω^{-1} cm^2 mol^{-1}.

[*Trichlorobutylbis*(1-*methyl-imidazoline*-2(3*H*)-*thione*)*tin*(*IV*)] (**27**). To a stirred diethyl ether solution (100 cm^3) of $(C_4H_9)SnCl_3$ (0.303 mg, 1.0 mmol) 1-methylimidazoline-2(3H)-thione (0.228 g, 2.0 mmol) was added at room temperature. The oily residue formed was separated from the solution and dissolved in dichloromethane (10 cm^3). To the clear solution diethyl ether was added (20 cm^3) and the colorless precipitate formed was filtered, washed with diethyl ether, dried *in vacuo* to constant weight (20°C, *ca.* 0.1 Torr) and shown to be compound **27**. Yield: 45%, m.p. 95–98°C (Found: C, 28.4; H, 4.3; N, 11.0; S, 12.7. Calc. for $C_{12}H_{21}Cl_3N_4S_2Sn$: C, 28.2; H, 4.1; N, 11.0; S, 12.6%). NMR ($CDCl_3$): ^{1}H, δ 7.00, 6.91 (2d, 4H, 4- and 5-C*H*), 3.72 (s, 6H, N–CH_3), 0.93 t, 1.45 ps, 1.80–1.96 m, 2.28 t (9H, Sn–C_4H_9); ^{119}Sn, δ −251.8 ppm. IR: 3154 w, 3125 w [ν(C–H)], 1133 m, 1096 m [ν(C–S)], 520 s, 512 sh [ν(Sn–C)], 276 s [ν(Sn–Cl)]. Λ (acetone, 25°C, 1.0×10^{-3} M): 4.6 Ω^{-1} cm^2 mol^{-1}.

RESULTS AND DISCUSSION

Synthesis, reactivity and properties of the organotin(IV) complexes

Interaction between R_nSnCl_{4-n} (R = Me, Bu^n or Ph; n = 1, 2 or 3) compounds and an excess of imidazole (L^1), benzimidazole (L^2) and 2-phenylimidazole (L^3) in organic solvents (alcohols, dichloromethane, diethyl ether or petroleum ether) at 0°C or at room temperature gave the compounds **1**–**17** in accordance with eq. (1):

$$x(L) + (R_nSnCl_{4-n}) \xrightarrow{\text{Solvent}} \underset{\mathbf{1–17}}{[(L)_x(R_nSnCl_{4-n})]\cdot zH_2O}. \quad (1)$$

No.	Ligand, L	R	x	n	z
1	L^1	Me	2	3	0
2	L^1	Ph	2	3	0
3	L^1	Me	2	1	1
4	L^1	Bu^n	2	1	0
5	L^1	Ph	2	1	0
6	L^2	Ph	1	3	0
7	L^2	Me	2	2	0
8	L^2	Ph	2	2	0
9	L^2	Me	2	1	0
10	L^2	Bu^n	2	1	0
11	L^2	Ph	2	1	0
12	L^3	Me	2	2	0
13	L^3	Bu^n	2	2	0
14	L^3	Ph	2	2	0
15	L^3	Me	2	1	0
16	L^3	Bu^n	2	1	0
17	L^3	Ph	2	1	0

In the same conditions no adduct was obtained from the interaction between L^1 and Bu$^n{}_3$SnCl, between L^2 and Me_3SnCl, Bu$^n{}_3$SnCl or Bu$^n{}_2$SnCl$_2$, and finally between L^3 and R_3SnCl (R = Me, Bu^n or Ph) or Me_2SnCl_2. On the other hand, even if different reaction conditions with respect to literature reports [7–10] were employed, from the interaction between L^1 and R_2SnCl_2 analogous 2:1 complexes were afforded.

With the exception of the derivative **6** (for which a ligand to metal ratio of 1:1 was observed) 2:1 adducts were obtained from the interaction between L^1 or L^2 and triorganotin(IV) acceptors. This fact further indicates the possibility of obtaining 2:1 adducts with triorganotin(IV) chlorides when imidazole type donors able to involve the halide group in a hydrogen bonding network were employed [4].

Interaction between R_2SnCl_2 (R = Me or Ph) and excess 1-acetylimidazole L^4 in diethyl ether produces the derivatives $[(L^4)_2(Me_2SnCl_2)]$ **18** and $[(L^4)_2(Ph_2SnCl_2)]\cdot H_2O$ **19**. Whereas L^4 reacts with other organotin acceptors yielding neutral adducts of unsubstituted imidazole L^1 upon hydrolysis of the N(1)–$COCH_3$ bond. The presence of a small quantity of water in the solvent is sufficient for the attack of the N(1)–C bond and formation of the donor L^1 which immediately coordinates the organotin acceptor. If rigorously anhydrous conditions were employed, no product afforded.

The reaction between imidazoline-2(1,3*H*)-thione (L^5) or 1-methyl-imidazoline-2(3*H*)-thione (L^6) and R_nSnCl_{4-n} acceptors (R = Me, Bu^n or Ph; n = 1, 2 or 3) was carried out in diethyl ether or diethyl ether/dichloromethane solutions from which compounds **20**–**27** were isolated as insoluble or sparingly soluble precipitates, in accordance with eq. (2) (see Table):

$$x(L) + (R_nSnCl_{4-n})\cdot zH_2O \xrightarrow{\text{Solvent}} \underset{\mathbf{20–27}}{[(L)_x(R_nSnCl_{4-n})]\cdot zH_2O}. \quad (2)$$

No.	Ligand, L	R	x	n	z
20	L^5	Ph	2	2	0
21	L^5	Ph	2	1	0
22	L^5	Bu^n	2	1	0
23	L^6	Me	1	2	0
24	L^6	Ph	2	2	0
25	L^6	Me	2	1	1
26	L^6	Ph	2	1	0
27	L^6	Bu^n	2	1	0

With the exception of the derivative **23** $[(L^6)(CH_3)_2SnCl_2]$ (for which a ligand to metal ratio

Table 1. Compounds obtained from various imidazoles and organotin(IV)chloride acceptors

	Organotin(IV) acceptor[b]									
Ligand[a]	Me_3SnCl	Me_2SnCl_2	$MeSnCl_3$	Bu_3SnCl	Bu_2SnCl_2	$BuSnCl_3$	Ph_3SnCl	Ph_2SnCl_2	$PhSnCl_3$	Ref.
L^1	2:1	2:1[c]	2:1	no reaction	2:1[d]	2:1	2:1	2:1[e]	2:1	This work
L^2	no reaction	2:1	2:1	no reaction	no reaction	2:1	1:1	2:1	2:1	This work
L^3	no reaction	no reaction	2:1	no reaction	2:1	2:1	no reaction	2:1	2:1	This work
L^4	N–CO break.	2:1	N–CO break.	N–CO break.	N–CO break.	N–CO break.	no reaction	2:1 (+1)	N–CO break.	This work
L^5	no reaction	2:1[f]	1:1,[f] 2:1[f]	no reaction	no reaction	2:1	no reaction	2:1	2:1	This work
L^6	no reaction	1:1	1:1,[f] 2:1 (+1)	no reaction	no reaction	1:1,[f] 2:1	1:1 anionic[g]	2:1	2:1	This work
L^7	1:1	2:1	2:1	no reaction	2:1	2:1	1:1	2:1 (+1)	2:1	[3]
L^8	2:1[h]	2:1	2:1	no reaction	2:1	3:2	2:1	2:1	3:2 (+1)	[4]
L^9	1:1	2:1[i]	2:1	1:1 (+1)	2:1 (+1)	2:1	1:1[l]	2:1	2:1	[6]
L^{10}	2:1	2:1	2:1 (+6)	2:1	2:1	3:1	1:1 (+1/3)	2:1 (+1)	3:1	[5]
L^{11}	2:1 (+1)	2:1	no reaction	no reaction	no reaction	2:1 (+2)	no reaction	no reaction	2:1 (+3)	[5]
L^{12}	1:1	2:1 (+1)	no reaction	no reaction	no reaction	no reaction	1:1	1:1 (+1)	no reaction	[5]
L^{13}	not inv.	2:1[m]	not inv.	not inv.	not inv.	not inv.	not inv	not inv.	not inv.	[28]
L^{14}	not inv.	1:1[n]	1:1[o]	not inv.	not inv.	not inv.	not inv.	1:1	not inv.	[29]

[a] L^1 = imidazole; L^2 = benzimidazole, L^3 = 2-phenylimidazole, L^4 = 1-acetylimidazole, L^5 = imidazoline-2(1,3*H*)-thione, L^6 = 1-methyl-imidazoline-2(3*H*)-thione, L^7 = 1-benzylimidazole, L^8 = 4-phenylimidazole, L^9 = 1-methylimidazole, L^{10} = 4-methylimidazole, L^{11} = 2-methylimidazole, L^{12} = 2-isopropylimidazole, L^{13} = 2-chloroimidazole, L^{14} = 1-methyl-2-(methylsulfinyl)imidazole.

[b] Molecules of water in parentheses (); not. inv. = not investigated; N–CO break. = breaking of the N(1)–$COCH_3$ bond. [c] *Trans*-octahedral from Ref. [8].

[d] From Ref. [9]. [e] From Ref. [10]. [f] s From Ref. [11]. [g] From Ref. [30]. [h] Distorted bipyramid trigonal from Ref. [4]. [i] *Trans*-octahedral from Ref. [31].

[l] Distorted bipyramid trigonal from Ref. [6]. [m] *Trans*-octahedral from Ref. [28]. [n] Bipyramid trigonal from Ref. [29]. [o] Distorted octahedral from Ref. [29].

of 1:1 was found), all the derivatives obtained show a ligand to metal ratio of 2:1.

No adduct was obtained from the interaction of L^5 or L^6 and R_3SnCl or $Bu^n_2SnCl_2$.

From the interaction of L^5 with Me_nSnCl_{4-n} ($n=1$ or 2) analogous compounds to those reported in literature afforded [11].

It is interesting to observe that in diethyl ether from the reaction between L^6 and $RSnCl_3$ ($R=Bu^n$ or Me) a 2:1 adduct was obtained, whereas in dichloromethane a 1:1 adduct was previously synthesized [11].

All the diorgano- and triorgano-tin(IV) derivatives are moderately soluble in chlorinated solvents, acetone and DMSO, and generally insoluble in diethyl ether, ethanol and water. The monoorganotin(IV) adducts are generally less soluble in all the solvents commonly used. These compounds are stable also when exposed to moisture for a long time, whereas upon prolonged standing at 120°C, or in acetone and chloroform solutions, organotin(IV) oxides and hydroxides are often recovered.

The triorganotin(IV) adducts **1** and **2** are often unstable not only in solution but also in the solid state and when they exposed to moisture for many hours, they decompose in accordance with the following equation:

$$2[L_2R_3Sn]Cl \rightleftharpoons [(L)_2R_2SnCl_2] + R_4Sn + 2L. \quad (3)$$

The decomposition (3) is established by the presence in the ^{119}Sn NMR spectrum of compounds **1** and **2**, previously exposed to moisture for 2 days, of the signals due to $[(L)_2R_2SnCl_2]$ and R_4Sn species.

IR data

By comparison with the data reported for other organotin(IV) complexes containing N-donor ligands, we suggest the following assignments for adducts **1**–**27**.

Ligand absorptions In the 3200–2950 cm^{-1} region, the ligands exhibit weak bands typical of C–H stretching due to a pseudoaromatic ring, and in the region 1600–1500 cm^{-1} some more intense absorptions due to the ring breathing mode [12]. These bands do not shift markedly upon coordination to tin, suggesting a weak influence of the complexation on the absorptions within the donor.

In the 2800–2600 cm^{-1} region the ligands exhibit a broad band typical of N–H stretching. In the tin(IV) and organotin(IV) adducts this band shifts in the 3400–3100 cm^{-1} region suggesting an important influence of the coordination to tin. The position and the broadening of the N–H stretching band are consistent with the presence of a hydrogen bond between the N–H moiety and the halide groups [4, 13, 14].

Sn–C stretching frequencies. In the trimethyltin(IV) derivative **1** a strong absorption is observed at *ca.* 549 cm^{-1}. It is due to $\nu_{(asym)}$ Sn–C stretching vibration and is consistent with an essentially trigonal pyramidal arrangement of methyl groups (C_{3v}) [15–18]. In the derivatives **2** and **6** the $\nu_{(asym)}$ Sn–C stretching vibration is found at *ca.* 290 cm^{-1}: a trigonal pyramidal arrangement of aryl groups is likely.

Only a single Sn–C stretching vibration was observed in the spectra of the diorganotin(IV) derivatives **7**, **8**, **12**, **13**, **15**, **18**, **19**, **23** and **24** in accordance with a *trans*-octahedral configuration of the two alkyl groups [19, 20]. In the spectrum of derivatives **14** and **20** two medium or strong absorptions in the range 290–270 cm^{-1} were found. In this case the presence of the *cis*–isomer is likely.

Sn-halide stretching frequencies. In the triorganotin(IV) derivative **6**, we observed the tin–chloride stretching frequency as medium absorption at 226 cm^{-1}. This indicates the non-ionic nature of this compound. The absorption is markedly shifted with respect to that indicated for the starting triorganotin(IV) chloride [21].

In the other triorganotin(IV) derivatives **1** and **2** the tin–chloride stretching frequency is absent. On the basis of previous reports [22] on triorganotin(IV) complexes and in accordance with the X-ray crystal structure determination of [bis(4-phenylimidazole)trimethyltin(IV)]chloride [4] we have hypothesized an ionic formulation of the type $[(L)_2R_3Sn]^+[Cl]^-$.

The tin(IV) chloride stretching frequencies in the di- and tri-halidetin(IV) derivatives fall as strong or medium broad bands in the range 220–320 cm^{-1}. These bands are lowered by 90–130 cm^{-1} with respect to those found in the starting tin(IV) reagents [23].

Behavior in solution

The conductivity measurements were carried out in acetone solution for all the soluble compounds whereas the molecular weight determinations were performed in chloroform solution only on selected sufficiently soluble and stable adducts.

The conductivity data show that triorganotin(IV) halide adduct **1**, **2** and **6** are not electrolytes in acetone and dissociate in $CHCl_3$ solution to a large extent (r = ratio between the vaporimetric molecular weight and formula weight lying in the range 0.30–0.55), in accordance with eq. (4), which indicates ligand loss in solution.

$$(L)_xR_3SnCl \rightleftharpoons (L)_{x-1}R_3SnCl + L \rightleftharpoons R_3SnCl + xL. \quad (4)$$

The conductance values for the diorganotin adducts of L^1, L^2, L^4, L^5 and L^6 are in the range 2.0–36 $\Omega^{-1}\,cm^{-2}\,mol^{-1}$ and also suggest a not electrolytic nature in acetone. The vaporimetric molecular weight determinations indicate extensive dissociation in chloroform solution for the soluble adducts. Some of the trichlorotin(IV) adducts and derivatives con-

taining the donor L^3 are partly ionized. The conductivity values for these complexes are in the range 44–95 $\Omega^{-1}\,cm^{-2}\,mol^{-1}$: they are lower with respect to those reported for 1:1 electrolytes in this solvent (the typical 1:1 electrolyte tetra-*n*-butylammonium bromide has a specific conductivity of 137 $\Omega^{-1}\,cm^2\,mol^{-1}$) in accordance with a partial ionic dissociation, but they are also greater with respect to those found in analogous imidazole organotin(IV) adducts [3–6].

^{1}H *NMR data*

The ^{1}H NMR spectra of the donors and of the organotin(IV) complexes **1**–**27** were recorded in $CDCl_3$ or in acetone-d_6 due to poor solubility in the former solvent.

The spectrum of the trimethyltin(IV) complex **1** indicates a nearly complete dissociation into the starting reagents. In fact, the Δ value (difference in chemical shift for the same type of proton in the free base and in its organotin(IV) complexes) is in the range 0.04–0.01 ppm and the tin–proton coupling constants are of the same order of magnitude as those reported for the starting triorganotin(IV) acceptors [24].

Instead, in the spectra of the triphenyltin(IV) complexes **2** and **6**, the signals of the ligand are displaced upfield and the Δ value is in the range (−0.26)–(−0.06) ppm. This peculiarity can be explained by considering the shielding effect exerted on H2, H4 and H5 protons by aromatic protons of the phenyl rings linked to tin(IV).

In the spectra of the mono- and di-organotin(IV) complexes of L^1, L^2, L^3 and L^4, the signals of the ligands are generally displaced to lower field. The deshielding observed is attenuated at a position remote from the metal. The Δ observed is likely due to a σ-charge donation from the N-donor to tin(IV) acceptor and is evidence of the existence of the complexes in solution. The Δ is greater for the trihalo- with respect to for dihalo-tin(IV) adducts in accordance with a stronger Sn–N bonding interaction in the former compounds.

The magnitudes of the tin(IV)–proton coupling constants for these diorganotin(IV) complexes are different from those reported in literature for the starting tetracoordinate diorganotin(IV) halides [25], but they are smaller with respect to that indicated for hexacoordinate undissociated organotin(IV) complexes containing N-donor ligands [26, 27]: this suggests a partial dissociation of our complexes in acetone or in chloroform solution in accordance with the data derived from molecular weight measurements.

The ^{1}H NMR spectra of the diorganotin(IV) adducts of 1-methyl-imidazoline-2(3*H*)thione (L^5) and imidazoline-2(1,3*H*)-thione (L^6) exhibit Δ values in the range 0.001–0.02 suggesting a nearly complete dissociation into starting reagents.

^{119}Sn *NMR data*

The ^{119}Sn NMR data are reported in acetone-d_6 for only some adducts, because the quality of the spectra is sometimes poor owing to the low solubility. The ^{119}Sn NMR chemical shift of compounds is comparable with that of the corresponding organotin(IV) acceptor in the same solvent [24] and clearly indicate that these adducts are extensively dissociated in acetone solution. Whereas the $\delta(^{119}Sn)$ chemical shifts for derivatives of imidazoline-2(1,3*H*)-thione (L^5) and 1-methyl-imidazoline-2(3*H*)thione (L^6) are sensibly different from those reported for the corresponding Lewis acid: also on the basis of literature data [24] and vaporimetric molecular weight determinations we suggest that these complexes are not completely dissociated in acetone solution.

Comparison with other imidazole organotin(IV) adducts

Table 1 shows a summary of the interactions of imidazoles with some organotin(IV) derivatives [3–11, 28–31].

In the adducts reported the ligand to metal ratio *n* goes from 1:1, for example in $[(L^2)Ph_3SnCl]$, to 3:1 in $[(L^{10})_3PhSnCl_3]$. When the ratio is 3:2, as in $[(L^8)_3(BuSnCl_3)_2]$, a dinuclear structure with the bridging chloride group is likely.

The solubility of the adducts reported in Table 1 is limited to a few polar solvent, such as acetone, *N*,*N*-dimethylformamide or DMSO. The adducts of L^7, L^8, L^9 and L^{10} are generally also soluble in chlorinated solvents due to the presence of methyl and aryl substituents in the azole ring. The derivatives of L^5 and L^6 show appreciable solubility also in water.

In no cases was the imidazole ring metallated or did basic salts result, whereas only in the interaction between 1-acetylimidazole (L^4) and organotin(IV) acceptors did breaking of the N(1)–C bond and coordination of the unsubstituted imidazole L^1 formed occur.

In most of cases mono and di-organotin(IV) chlorides adducts containing N-donor imidazole ligands have a perfect octahedral environment with all-*trans* coordination.

The triorganotin adducts prefer a distorted trigonal bipyramid geometry with the organic groups always in equatorial positions. If the imidazole was able to involve a chloride group in a hydrogen bonding network, a 2:1 adduct was obtained, whereas if the imidazole possess an alkyl or an aryl group in the N(1) position only 1:1 adducts were obtained. The reaction between imidazoles and tributyltin(IV)chloride was often unsuccessful, no simple adduct but intractable material being formed with the exception of derivatives $[(L^9)Bu_3SnCl](H_2O)$ and $[(L^{10})_2Bu_3Sn]Cl$, likely obtained owing to the greater basicity of these donors with respect to those so far employed.

The donating ability of this family of ligands can be correlated to the ratio *n* and to the stability of the complexes in solution. On the basis of this systematic study L^1, L^9 and L^{10} seem to be the better donors (L^{10} is the only able to give a 3:1 ligand to metal ratio) also due to the minor dissociation of the organotin(IV) complexes in chloroform and acetone solution. L^3, L^{11} and L^{12} are weaker donors probably due to the steric hindrance of phenyl, methyl and isopropyl group, respectively, in the C(2) position, whereas the lower donating ability of L^5 and L^6 is due to the fact that they coordinate throughout the S-atom, which has a lower affinity for the organotin(IV) acceptors with respect to the N-atom. With the latter donors, it is also possible to obtain a 1:1 adduct not only with triorgano- but also with di- and mono-organotin(IV) acceptors.

1:1 adducts are also obtained if the donor is able to coordinate in a bidentate fashion as 1-methyl-2-(methylsulfinyl)imidazole (L^{14}).

If hydroxideorganotin(IV) acceptors were used, substitution of the OH group and coordination of the deprotonated ligand occurred as in [Ph_3Sn(2-mercapto-1-methylimidazolato)tin(IV) [30].

Various degrees of hydration were found from 1/3 in [(L^{10})Ph_3SnCl]·1/3H_2O to 6 in [(L^{10})$MeSnCl_3$]·6H_2O.

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