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Di- and tri-organotin(IV) complexes of the new bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand and the decarboxylated analogues

Maura Pellei [a,*], Simone Alidori [a], Franco Benetollo [b], Giancarlo Gioia Lobbia [a], Marilena Mancini [a], Gaia Emanuela Gioia Lobbia [c], Carlo Santini [a]

[a] *Dipartimento di Scienze Chimiche, Università di Camerino, via S. Agostino 1, 62032 Camerino (MC), Italy*
[b] *ICIS-C.N.R., Corso Stati Uniti 4, 35127 Padova, Italy*
[c] *Scuola di Specializzazione in Farmacia Ospedaliera, via Lili 55, Università di Camerino, Camerino (MC), Italy*

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Abstract

The new sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate, Na[(*S*-tim)$_2$CHCO$_2$], has been prepared in ethanol solution using 2-mercapto-1-methylimidazole, dibromoacetic acid and NaOH. New di- and tri-organotin(IV) derivatives have been synthesized from reaction between SnR_nCl_{4-n} (R = Ph, Cy and ^{n}Bu, $n = 2$–3) acceptors and Na[(*S*-tim)$_2$CHCO$_2$]. Complexes of the type {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]SnR_3} and related decarboxylated species {[κ^2*N*,*N*-(*S*-tim)$_2$CH$_2$]SnR_2Cl_2} have been obtained and characterized by elemental analyses, FT-IR, ESIMS and multinuclear (^{1}H, ^{13}C and ^{119}Sn) NMR spectral data. The adduct {κ^1*O*-[(*S*-tim)$_2$CHCO$_2$]Sn(H$_2$O)(C$_4$H$_9$)$_3$} was characterized by single crystal X-ray studies. The dichloromethane reaction solution of {κ^1*O*-[(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_5$)$_3$} was re-crystallized and the decarboxylated species {[(*S*-tim)$_2$CH$_2$]SnCl(H$_2$O)(C$_6$H$_5$)$_3$} was obtained as a crystalline solid and characterized by X-ray crystallography.

Keywords: Organotin(IV); Scorpionates; Methimazole; X-ray; Spectroscopy

1. Introduction

Organotin compounds occupy an important place in academic research, as well as in industrial chemistry; they are of interest in view of the considerable structural diversity that they possess. This aspect has been attracting the attention of a number of researchers and a multitude of structural types have been discovered [1–3]. Many organotin compounds have been tested for their *in vitro* activity against a large variety of tumor lines [4–6]. Recently organotin compounds have been used as reagents in reduction, transmetallation and coupling reactions or as extremely versatile catalysts in organic reactions [7–14]; the generally high selectivity of organotin reagents allows one to save time and to avoid product losses of protection–deprotection cycles. In industry, organotin compounds are utilized for esterification and transesterification reactions, for silicone curing, for the preparation of polyurethanes [15], but the stabilization of poly(vinyl chloride) (PVC) is their largest application so far [16]. Organotin have been known for their excellent biocidal properties and they are used in agricultural biocides and additives for antifouling paints for marine transport vessels [17]. In the investigation of the possible utility of triorganotin trichloroacetates as CX_2 transfer agents it was found that they decompose with carbon dioxide evolution in the presence of an olefin [18].

Recently, we have reported the synthesis and the spectroscopic characterization of new poly(pyrazolyl)borate

* Corresponding author. Tel./fax: +39 (0) 737 402213.
E-mail address: maura.pellei@unicam.it (M. Pellei).

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[19,20] and poly(imidazolyl)borate [21,22] 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 poly(azolyl)borate ligands to the tin atom and find a rationale related to the stability and structural motifs of this class of compounds [23]. As an extension of this research field, we have developed the chemistry of some new organotin carboxylates obtained by the interaction of a number of organotin(IV) halides with new polyfunctional S,N,O-ligands, containing two pyridine groups and other biologically relevant hydrophilic moieties, such as carboxylate groups [24].

In recent years, a number of authors [25–34] have synthesized S,N-ligands of the type $(CH_2)_n(SAz)_2$ based on a nitrogenated aromatic ring system such as benzimidazole or pyridine. These ligands are able to coordinate by both S and the neighbouring N atom, and hence to form stable chelate rings of five or more atoms [35–41]. In particular, Gardinier [42,43] and Casas [44] have recently reported the synthesis, the analytic, spectroscopic and structural characterization of the bis(thioimidazolyl)methane family of compounds. These compounds are attractive owing to both their potential biomedical applications [45,46] and their potential utility in fundamental coordination chemistry [44,47–51].

Bearing in mind the above, we have developed a strategy for producing a new class of monoanionic and polyfunctional N,O,S-ligands of possible considerable coordinative flexibility. Towards this end, we report now the synthesis and characterization of the new sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand, Na[(*S*-tim)$_2$CHCO$_2$] (Fig. 1) and its interaction with a number of di- and triorganotin(IV) halides. Complexes of the type {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]SnR$_3$} and related decarboxylated species {[κ^2*N*,*N*-(*S*-tim)$_2$CH$_2$]SnR$_2$Cl$_2$} have been obtained and characterized. Since carboxylic acid derivatives are ubiquitous synthetic building blocks, the ability to access reactive organometallic species via decarboxylation offers clear practical advantages [52–56].

2. Materials and methods

2.1. General procedures

All syntheses and handling were carried out under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques or a glove box. All solvents were dried, degassed and distilled prior to use. Elemental analyses (C,H,N,S) were performed in house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. Thermal Analysis was performed using a power compensation Differential Scanning Calorimeter (DSC Pyris1, Perkin–Elmer US Instrument Division, Norwalk, CT 06859 USA); the instrument was previously calibrated for melting enthalpy and temperature using high grade purity Indium as a standard. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT-IR instrument. IR annotations used: br = broad, m = medium, mbr = medium broad, s = strong, sbr = strong broad, sh = shoulder, w = weak. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Oxford-400 Varian spectrometer (400.4 MHz for ^{1}H, 100.1 MHz for ^{13}C and 149.3 MHz for ^{119}Sn). NMR annotations used: m = multiplet, s = singlet. Electrospray mass spectra (ESIMS) 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 μL min^{-1}, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 V 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 3.0 computer program.

3. Experimental

3.1. Synthesis

3.1.1. Na[(S-tim)$_2$CHCO$_2$] (1)

2-Mercapto-1-methylimidazole (5.000 g, 43.8 mmol) was added to a solution of NaOH (4.380 g, 109.5 mmol) in 100 mL of absolute ethanol. After 12 h stirring, a solution of dibromoacetic acid (4.770 g, 21.9 mmol) in 40 mL of absolute ethanol was added dropwise to the sodium salt so obtained, and this mixture was stirred at gentle reflux for 6 h to give an orange emulsion. The mixture was allowed to cool to rt, filtered and then concentrated

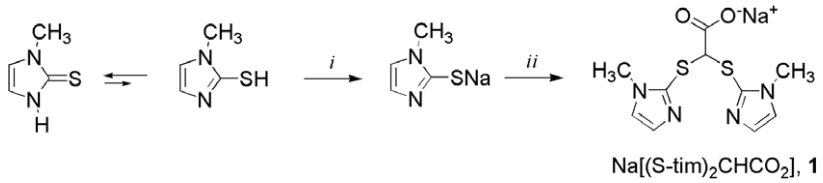

Fig. 1. Synthesis of the sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand, Na[(*S*-tim)$_2$CHCO$_2$], starting from 2-mercapto-1-methylimidazole. Conditions: (i) NaOH in ethanol solution, r.t., 12 h; (ii) dibromoacetic acid, reflux, 6 h.

affording an orange/yellow solid. The crude product was re-crystallized from chloroform/petroleum ether (1:4), yielding Na[(*S*-tim)$_2$CHCO$_2$] (**1**) as microcrystalline needles. Yield 75%. Mp. 110–120 °C dec. ^{1}H NMR (CDCl$_3$, 293 K): δ 3.52 (s, 6H, C*H*$_3$), 5.05 (s, 1H, C*H*COO), 6.90 (s, 2H, C*H*), 6.97 (s, 2H, C*H*). ^{1}H NMR (D$_2$O, 293 K): δ 3.47 (s, 6H, C*H*$_3$), 4.73 (s, 1H, C*H*COO), 6.85 (d, 2H, C*H*), 6.99 (d, 2H, C*H*). ^{1}H NMR (D$_2$O/DCl, 293 K): δ 3.45 (s, 6H, C*H*$_3$), 6.84 (d, 2H, C*H*), 6.97 (d, 2H, C*H*). ^{1}H NMR (CD$_3$OD, 293 K): δ 3.75 (s, 6H, C*H*$_3$), 4.89 (s, 1H, C*H*COO), 6.96 (d, 2H, C*H*), 7.15 (d, 2H, C*H*). ^{13}C NMR (CDCl$_3$, 293 K): δ 34.10 (*C*H$_3$), 62.23 (*C*HCOO), 123.42 (*C*H), 129.97 (*C*H), 139.88 (*C*S), 173.14 (CH*C*OO). ^{13}C NMR (D$_2$O, 293 K): δ 33.72 (*C*H$_3$), 60.79 (*C*HCOO), 125.14 (*C*H), 128.94 (*C*H), 137.80 (*C*S), 173.30 (CH*C*OO). ^{13}C NMR (D$_2$O/DCl, 293 K): δ 33.71 (*C*H$_3$), 60.52 (*C*HCOO), 125.13 (*C*H), 128.94 (*C*H), 137.79 (*C*S), 173.27 (CH*C*OO). IR (Nujol, cm^{-1}): 3091w (CH), 1615sbr (ν_{asym}C=O), 1506m (C=C + C=N), 1350sh (ν_{sym}C=O), 686s, 667m, 627w, 505s, 422sbr, 366m, 323w, 294m, 279w. ESIMS (major positive-ions, CH$_3$OH), *m*/*z* (%): 307 (100) [(*S*-tim)$_2$CHCO$_2$ + Na + H]$^+$, 329 (80) [(*S*-tim)$_2$CHCO$_2$ + 2Na]$^+$, 636 (45) [{(*S*-tim)$_2$CHCO$_2$}$_2$ + 3Na]$^+$, 942 (30) [{(*S*-tim)$_2$CHCO$_2$}$_3$ + 4Na]$^+$, 1248 (10) [{(*S*-tim)$_2$CHCO$_2$}$_4$ + 5Na]$^+$. ESIMS (major negative-ions, CH$_3$OH), *m*/*z* (%): 239 (100) [(*S*-tim)$_2$CHCO$_2$ − CO$_2$]$^-$, 283 (30) [(*S*-tim)$_2$CHCO$_2$]$^-$. ESIMS (major positive-ions, H$_2$O), *m*/*z* (%): 241 (15) [[(*S*-tim)$_2$CHCO$_2$] − CO$_2$ + 2H]$^+$, 285 (40) [(*S*-tim)$_2$CHCO$_2$ + 2H]$^+$, 307 (100) [(*S*-tim)$_2$CHCO$_2$ + Na + H]$^+$, 329 (15) [(*S*-tim)$_2$CHCO$_2$ + 2Na]$^+$, 636 (20) [{(*S*-tim)$_2$CHCO$_2$}$_2$ + 3Na]$^+$, 942 (20) [{(*S*-tim)$_2$CHCO$_2$}$_3$ + 4Na]$^+$. ESIMS (major negative-ions, H$_2$O), *m*/*z* (%): 239 (100) [(*S*-tim)$_2$CHCO$_2$ − CO$_2$]$^-$, 283 (25) [(*S*-tim)$_2$CHCO$_2$]$^-$. ESIMS (major positive-ions, H$_2$O/CH$_3$COOH), *m*/*z* (%): 241 (10) [[(*S*-tim)$_2$CHCO$_2$] − CO$_2$ + 2H]$^+$, 285 (100) [(*S*-tim)$_2$CHCO$_2$ + 2H]$^+$, 307 (20) [(*S*-tim)$_2$CHCO$_2$ + Na + H]$^+$. ESIMS (major negative-ions, H$_2$O/CH$_3$COOH), *m*/*z* (%): 239 (100) [(*S*-tim)$_2$CHCO$_2$ − CO$_2$]$^-$, 283 (30) [(*S*-tim)$_2$CHCO$_2$]$^-$. Calc. for C$_{10}$H$_{11}$N$_4$NaO$_2$S$_2$: C, 39.21; H, 3.62; N, 18.29; S, 20.93. Found: C, 39.04; H, 3.81; N, 18.03; S, 20.67%.

3.1.2. {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_5$)$_3$} (**2**)

To a chloroform solution (50 mL) of (C$_6$H$_5$)$_3$SnCl (0.385 g, 1.0 mmol), Na[(*S*-tim)$_2$CHCO$_2$] (0.306 g, 1.0 mmol) was added at room temperature. After addition, the reaction mixture was stirred for 4 h and then filtered; the solvent was removed under vacuum and the residue was washed with chloroform/*n*-hexane (1:5). The yellow product was re-crystallized from chloroform/*n*-hexane. Yield: 43%. ^{1}H NMR (CDCl$_3$, 293 K): δ 3.50 (s, 6H, C*H*$_3$), 5.32 (s, 1H, C*H*COO), 6.83 (s, 2H, C*H*), 7.03 (s, 2H, C*H*), 7.44–7.71 (m, 15H, Sn–C$_6$*H*$_5$). ^{119}Sn NMR (CDCl$_3$, 293 K): −95.83 (s). IR (Nujol, cm^{-1}): 3116w (CH), 1656s (ν_{asym}C=O), 1508m (C=C + C=N), 1308s (ν_{sym}C=O), 456s (Ph), 444m, 429m (Sn–O), 278s, 245s (Sn–C). ESIMS (major positive-ions, CH$_3$OH), *m*/*z* (%): 241 (80) [(*S*-tim)$_2$CHCO$_2$ − CO$_2$ + 2H]$^+$, 634 (100) [{[(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_5$)$_3$} + H]$^+$. ESIMS (major negative-ions, CH$_3$OH), *m*/*z* (%): 421 (100) [Sn(C$_6$H$_5$)$_3$Cl + Cl]$^-$. Calc. for C$_{28}$H$_{26}$N$_4$O$_2$S$_2$Sn: C, 53.10; H, 4.14; N, 8.85; S, 10.13. Found: C, 52.90; H, 4.28; N, 8.69; S, 9.80%. The dichloromethane reaction solution of **2** was re-crystallized and the decarboxylated species {[(*S*-tim)$_2$CH$_2$]SnCl(H$_2$O)(C$_6$H$_5$)$_3$} (**5**) was obtained as a crystalline solid and characterized by X-ray crystallography.

3.1.3. {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]Sn(C$_4$H$_9$)$_3$} (**3**)

Complex **3** was prepared analogously to compound **2** by using (C$_4$H$_9$)$_3$SnCl (0.325 g, 1.0 mmol) and Na[(*S*-tim)$_2$CHCO$_2$] (0.306 g, 1.0 mmol) in chloroform solution (50 mL). The yellow product was re-crystallized from chloroform/*n*-hexane (1/3), in 85% yield. ^{1}H NMR (CDCl$_3$, 293 K): δ 0.85–1.58 (m, 27H, Sn C$_4$*H*$_9$), 3.67 (s, 6H, C*H*$_3$), 5.34 (s, 1H, C*H*COO), 6.92 (s, 2H, C*H*), 7.04 (s, 2H, C*H*). ^{119}Sn NMR (CDCl$_3$, 293 K): 127.96 (s). IR (Nujol, cm^{-1}): 3136w, 3106w (CH), 1642s (ν_{asym}C=O), 1511m (C=C + C=N), 1335m (ν_{sym}C=O), 573s (Sn–C), 455s (Sn–O). ESIMS (major positive-ions, CH$_3$OH), *m*/*z* (%): 574 (100) [{[(*S*-tim)$_2$CHCO$_2$]Sn(C$_4$H$_9$)$_3$} + H]$^+$, 863 (30) [{[(*S*-tim)$_2$CHCO$_2$][Sn(C$_4$H$_9$)$_3$]$_2$}]$^+$. ESIMS (major negative-ions, CH$_3$OH), *m*/*z* (%): 379 (100) [Sn(C$_4$H$_9$)$_3$Cl(H$_2$O) + Cl]$^-$, 239 (40) [(*S*-tim)$_2$CH]$^-$, 857 (40) [{[(*S*-tim)$_2$CHCO$_2$]$_2$[Sn(C$_4$H$_9$)$_3$]}]$^-$. Calc. for C$_{22}$H$_{38}$N$_4$O$_2$S$_2$Sn: C, 46.08; H, 6.68; N, 9.77; S, 11.18. Found: C, 45.89; H, 6.82; N, 9.59; S, 10.98%. Re-crystallization of the crude product from chloroform/diethyl ether (1:1) gave the species {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]Sn(H$_2$O)(C$_4$H$_9$)$_3$} (**3** · **H$_2$O**) as a crystalline solid suitable for X-ray crystallographic study.

3.1.4. {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_{11}$)$_3$} (**4**)

Compound **4** was prepared analogously to compound **2**, by using (C$_6$H$_{11}$)$_3$SnCl (0.404 g, 1.0 mmol) and Na[(*S*-tim)$_2$CHCO$_2$] (0.306 g, 1.0 mmol) in chloroform solution (50 mL). The product was re-crystallized from chloroform/*n*-hexane. Yield: 55%. ^{1}H NMR (CDCl$_3$, 293 K): δ 1.32–1.93 (m, 33H, Sn–C$_6$*H*$_{11}$), 3.70 (s, 6H, C*H*$_3$), 5.42 (s, 1H, C*H*COO), 6.93 (s, 2H, C*H*), 7.06 (s, 2H, C*H*). ^{119}Sn NMR (CDCl$_3$, 293 K): 37.76 (s). IR (Nujol, cm^{-1}): 3136w (CH), 1639s (ν_{asym}C=O), 1511m (C=C + C=N), 1328s (ν_{sym}C=O), 603s; 505m (Sn–C), 420mbr (Sn–O), 336m, 325s, 304m, 252m. ESIMS (major positive-ions, CH$_3$OH), *m*/*z* (%): 241 (70) [[(*S*-tim)$_2$CHCO$_2$] − CO$_2$ + 2H]$^+$, 285 (60) [(*S*-tim)$_2$CHCO$_2$ + 2H]$^+$, 653 (100) [{[(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_{11}$)$_3$} + H]$^+$. ESIMS (major negative-ions, CH$_3$OH), *m*/*z* (%): 239 (60) [(*S*-tim)$_2$CHCO$_2$ − CO$_2$]$^-$, 283 (10) [(*S*-tim)$_2$CHCO$_2$]$^-$, 590 (60) [{(*S*-tim)$_2$CHCO$_2$}$_2$ + Na]$^-$, 687 (100) [{[(*S*-tim)$_2$CHCO$_2$]$_2$Sn(C$_6$H$_{11}$)$_3$ + Cl}]$^-$. Anal. Calc. for C$_{28}$H$_{44}$N$_4$O$_2$S$_2$Sn: C, 51.62; H, 6.81; N, 8.60; S, 9.84. Found: C, 51.16; H, 7.01; N, 8.75; S, 10.02%.

3.1.5. {[κ^2N,N-(S-tim)$_2$ CH$_2$]Sn(C$_6$H$_5$)$_2$ Cl$_2$} (6)

To a chloroform solution (50 mL) of $(C_6H_5)_2SnCl_2$ (0.344 g, 1.0 mmol), Na[(*S*-tim)$_2$CHCO$_2$] (0.306 g, 1.0 mmol) was added at room temperature. After addition, the reaction mixture was stirred for 4 h and then filtered; the solvent was removed under vacuum and the residue was washed with chloroform/*n*-hexane (1:5). The product was re-crystallized from chloroform/diethyl ether (1:1), to give the decarboxylate complex **6** in 44% yield. ^{1}H NMR ($CDCl_3$, 293 K): δ 3.62 (s, 6H, C*H*$_3$), 4.44 (s, 2H, C*H*$_2$), 6.95 (s, 2H, C*H*), 7.10 (s, 2H, C*H*), 7.44–7.88 (m, 10H, C$_6$*H*$_5$). ^{119}Sn NMR ($CDCl_3$, 293 K): −200.26 (s). IR (Nujol, cm^{-1}): 3116w, 3043w (CH), 1513m (C=C + C=N), 456s (Ph), 275s (Sn–C), 229br (Sn–Cl). ESIMS (major positive-ions, CH_3OH), *m*/*z* (%): 241 (100) [(*S*-tim)$_2$CH$_2$ + H]$^+$, 585 (40) [{[(*S*-tim)$_2$CH$_2$]Sn(C$_6$H$_5$)$_2$Cl$_2$} + H]$^+$. ESIMS (major negative-ions, CH_3OH), *m*/*z* (%): 379 (100) [(C$_6$H$_5$)$_2$SnCl$_2$ + Cl]$^-$. Calc. for $C_{21}H_{22}Cl_2N_4S_2Sn$: C, 43.18; H, 3.80; N, 9.59; S, 10.98. Found: C, 42.97; H, 3.78; N, 9.23; S, 10.63%.

3.1.6. {[κ^2N,N-(S-tim)$_2$ CH$_2$]Sn(C$_4$H$_9$)$_2$Cl$_2$} (7)

Complex **7** was prepared analogously to compound **6** by using $(C_4H_9)_2SnCl_2$ (0.304 g, 1.0 mmol) and Na[(*S*-tim)$_2$CHCO$_2$] (0.306 g, 1.0 mmol) in chloroform solution (50 mL). The product was re-crystallized from dichloromethane/*n*-hexane/petroleum ether, in 41% yield. Re-crystallization of the crude product from dichloromethane/*n*-hexane gave the complex **7** as a crystalline solid. ^{1}H NMR ($CDCl_3$, 293 K): δ 0.90–1.84 (m, 18H, Sn–C$_4$*H*$_9$), 3.67 (s, 6H, C*H*$_3$), 4.65 (s, 2H, C*H*$_2$), 6.98 (s, 2H, C*H*), 7.13 (s, 2H, C*H*). IR (Nujol, cm^{-1}): 3111w (CH), 1512m (C=C + C=N), 590m (Sn–C), 235br (Sn–Cl). ESIMS (major positive-ions, CH_3OH), *m*/*z* (%): 241 (100) [(*S*-tim)$_2$CH$_2$ + H]$^+$, 263 (20) [(*S*-tim)$_2$CH$_2$ + Na]$^+$. ESIMS (major negative-ions, CH_3OH), *m*/*z* (%): 339 (100) [(C$_4$H$_9$)$_2$SnCl$_2$ + Cl]$^-$, 883 (30) [{[(*S*-tim)$_2$CH$_2$]-[Sn(C$_4$H$_9$)$_2$Cl$_2$]$_2$} + Cl]$^-$. Calc. for $C_{17}H_{30}Cl_2N_4S_2Sn$: C, 37.52; H, 5.56; N, 10.30; S, 11.78. Found: C, 37.49; H, 5.52; N, 10.19; S, 11.60%.

3.2. X-ray measurements and structure determination for {[(S-tim)$_2$CH$_2$]SnCl(H$_2$O)(C$_6$H$_5$)$_3$} (5), {[κ^1O-(S-tim)$_2$CHCO$_2$]Sn(H$_2$O)(C$_4$H$_9$)$_3$} (3 · H$_2$O)

The Intensities data were collected at room temperature using Philips PW1100 diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å), following the standard procedures at room temperature. There were no significant fluctuations of intensities other than those expected from Poisson statistics. All intensities were corrected for Lorentz polarization and absorption [57]. The structures were solved by standard direct methods [58]. Refinement was carried out by full-matrix least-squares procedures (based on F_o^2) using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 U_{equiv} of the parent carbon atom). The calculations were performed with the SHELXL-97 [59] program, implemented in the WinGX package [60]. Crystallographic and experimental details for the structure are summarized in Table 1.

4. Results and discussion

4.1. Synthesis

The sodium salt of bis(1-methyl-1*H*-imidazol-2-ylthio)acetate, **1**, has been prepared in absolute ethanol solution using 2-mercapto-1-methylimidazole, dibromoacetic acid and sodium hydroxide by the multiple routes as summarized in Fig. 1. While it has been reported that 2-mercapto-1-methylimidazole exists as predominantly the NH rather than SH tautomer in solution, [43] the greater acidity of the thiol moiety results in the formation of thiolate species on reaction with Brønsted bases. Compound **1** is an air-stable orange/yellow semi-crystalline solid; it is soluble in methanol, water, acetonitrile, and chlorinated solvents. The ligand Na[(*S*-tim)$_2$CHCO$_2$] was analysed by Thermal Analysis at 2 °C/min and 10 °C/min in a range of temperature between 20 °C and 130 °C; then heating/cooling/heating cycle at 10, 30 and 50 °C was performed between −45 °C and 90 °C. Results show a degradation at around 110–120 °C, without loss of mass detected before the degradation.

Table 1
Experimental data for the crystallographic analyses

	5	**3 · H$_2$O**
Compound	{[(*S*-tim)$_2$CH$_2$]SnCl-(H$_2$O)(C$_6$H$_5$)$_3$}	{[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]-Sn(H$_2$O)(C$_4$H$_9$)$_3$}
Empirical formula	$C_{27}H_{29}ClN_4OS_2Sn$	$C_{22}H_{38}N_4O_3S_2Sn$
Formula weight	643.80	589.37
Temperature (K)	293(2)	293(2)
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$I2/a$
a (Å)	10.232(2)	18.454(3)
b (Å)	11.528(2)	15.761(3)
c (Å)	13.474(2)	21.945(4)
α (°)	107.54(2)	
β (°)	108.63(3)	110.92(3)
γ (°)	90.13(2)	
Volume (Å^3)	1427.5(4)	5962(2)
Z	2	8
D_{calc} (g cm^{-3})	1.498	1.313
F(000)	652	2432
θ Range (°)	3–28	3–26
μ (cm^{-1})	11.62	10.23
No. reflections collected	7176	6280
No. observed [$I \geqslant 2\sigma(I)$]	5546	4099
R (F_o)[a]	0.040	0.051
R_w (F_o^2)[b]	0.094	0.143
Goodness of fit	1.060	1.040

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $R_w = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Complexes **2**–**4** have been synthesized by metathetic reaction of Na[(*S*-tim)$_2$CHCO$_2$] with R$_3$SnCl acceptors (R = C$_6$H$_5$, C$_4$H$_9$ or C$_6$H$_{11}$) in chloroform solution at room temperature (Eq. (1)).

$$\underset{\mathbf{1}}{\text{Na[(}S\text{-tim)}_2\text{CHCO}_2\text{]}} + \text{R}_3\text{SnCl} \xrightarrow{\text{CHCl}_3\,/\,\text{r.t.}} \underset{\begin{array}{l}\mathbf{2}\text{: R} = \text{C}_6\text{H}_5\\ \mathbf{3}\text{: R} = \text{C}_4\text{H}_9\\ \mathbf{4}\text{: R} = \text{C}_6\text{H}_{11}\end{array}}{\{[\kappa^1 O\text{-(}S\text{-tim)}_2\text{CHCO}_2\text{]SnR}_3\}} + \text{NaCl} \qquad (1)$$

The derivatives **2**–**4** are stable under inert atmosphere; they show a good solubility in methanol, acetone, acetonitrile and chlorinated solvents, and they are insoluble in water, diethyl ether and *n*-hexane. Re-crystallization of the crude product **3** from chloroform/diethyl ether (1:1) gave the Lewis adduct with water {[$\kappa^1 O$-(*S*-tim)$_2$CHCO$_2$]Sn(H$_2$O)-(C$_4$H$_9$)$_3$}, **3** · **H$_2$O**, as a crystalline solid suitable for X-ray crystallographic study (Eq. (2)).

$$\underset{\mathbf{3}}{\{[\kappa^1 O\text{-(}S\text{-tim)}_2\text{CHCO}_2\text{]Sn(C}_4\text{H}_9)_3\}} + \text{H}_2\text{O} \rightarrow \underset{\mathbf{3}\cdot\mathbf{H_2O}}{\{[\kappa^1 O\text{-(}S\text{-tim)}_2\text{CHCO}_2\text{]Sn(C}_4\text{H}_9)_3\}\cdot\text{H}_2\text{O}} \qquad (2)$$

Complexes **6** and **7** have been obtained by reaction of Na[(*S*-tim)$_2$CHCO$_2$] with R$_2$SnCl$_2$ acceptors (R = C$_6$H$_5$ or C$_4$H$_9$) in chloroform solution at room temperature (Fig. 2). The decarboxylation of the ligand likely occurs in presence of traces of moisture, that can be introduced into the system with the reagents. In fact in water solution the decarboxylation of the ligand occurs yielding the [(*S*-tim)$_2$CH$_2$] species.

This may not necessarily interfere with the initial formation of the complexes, but then causes the decomposition of the diorganotin derivatives due to their hygroscopic nature via decarboxylation of the ligand [19]. Analogously, from the reaction of Na[(*S*-tim)$_2$CHCO$_2$] with (C$_6$H$_5$)$_3$SnCl the main product {[$\kappa^1 O$-(*S*-tim)$_2$CHCO$_2$]Sn(C$_6$H$_5$)$_3$}, **2**, was obtained together with the decarboxylated species {[(*S*-tim)$_2$CH$_2$]SnCl(H$_2$O)(C$_6$H$_5$)$_3$}, **5**, obtained as a crystalline solid from the crystallization by slow evaporation of the reaction solution.

The derivatives {[$\kappa^2 N,N$-(*S*-tim)$_2$CH$_2$]Sn(C$_6$H$_5$)$_2$Cl$_2$}, **6** and {[$\kappa^2 N,N$-(*S*-tim)$_2$CH$_2$]Sn(C$_4$H$_9$)$_2$Cl$_2$}, **7**, are reasonably stable in air; they show a good solubility in methanol, acetone, acetonitrile and chlorinated solvents, and they are insoluble in water, diethyl ether and *n*-hexane. Re-crystallization of the crude product **7** from dichloromethane/*n*-hexane gave the complex {[$\kappa^2 N,N$-(*S*-tim)$_2$CH$_2$]Sn(C$_4$H$_9$)$_2$Cl$_2$} (Fig. 2), as a crystalline solid. The same compound was obtained using as starting material the neutral bis(1-methyl-2-imidazolylthio)methane ligand, [(*S*-tim)$_2$CH$_2$], and the crystal structure of compound **7** has been already reported by Casas et al. [44].

4.2. Spectroscopy

The ligand **1** and the derivatives **2**–**6** have been characterized by analytical and spectral data. Infrared spectroscopy carried out on the solid samples (Nujol mull) showed all the expected bands for the ligand and the tin moieties: weak absorptions in the range 3043–3136 cm^{-1} are due to the azolyl ring C–H stretchings and medium to strong absorptions near 1510 cm^{-1} are related to ring "breathing" vibrations. The presence of the COO moiety in derivatives **2**–**4** is detected by an intense broad absorption in the range 1639–1656 cm^{-1} and 1308–1335 cm^{-1}, due to the asymmetric and symmetric stretching modes,

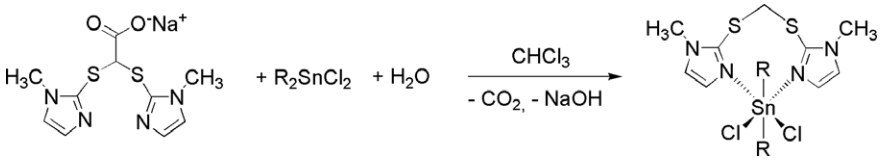

Fig. 2. Proposed synthesis of the diorganotin(IV) derivatives **6** and **7**, {[$\kappa^2 N,N$-(*S*-tim)$_2$CH$_2$]SnR$_2$Cl$_2$} (R = C$_6$H$_5$ and C$_4$H$_9$).

respectively; the shift to blue with respect to the sodium salt of the ligand ($\nu_{asym}C{=}O = 1615\ cm^{-1}$), being observed upon complex formation. The magnitude of $\nu_{asym}CO_2 - \nu_{sym}CO_2$ ($\Delta\nu$) separation can be used to explain the type of carboxylate structure present in the solid state [61,62]. $\Delta\nu$ values for **2**–**4** are of about 300 cm^{-1}, characteristic of monodentate coordination compounds. The absence of strong absorptions in the range at 1600–1700 cm^{-1} in the IR spectra of derivatives **6** and **7** confirms the decarboxylation of the ligand in these complexes. In the far-IR region medium to strong absorptions appear upon coordination, due to stretching modes of Sn–O, Sn–Cl, Sn–C [63]. The absence of Sn–Cl stretching vibrations in the spectra of the triorganotin(IV) derivatives **2**–**4** confirms the substitution of the chloride in the complexes formation. The Sn–Cl stretching vibrations fall as broad absorptions near 229–235 cm^{-1} in the diorganotin(IV) derivatives **6** and **7**. The Sn–C stretching frequencies fall as medium or strong absorptions in the range 245–275 cm^{-1} for the aryl derivatives **2** and **6**; similar stretching vibrations are detected in the range 505–590 cm^{-1} for the alkyl derivatives **3**, **4** and **7**. These absorptions agree well with the trends previously observed in similar N-donor complexes [64]. In the far-IR spectra absorptions tentatively assigned to Sn–O have been detected in the range 420–455 cm^{-1} in the triorganotin(IV) derivatives.

The ^1H and ^{13}C NMR spectra of a $CDCl_3$, D_2O and D_2O/DCl solution of Na[(*S*-tim)$_2$CHCO$_2$], **1**, agrees with the proposed formula. It is important to note that the resonance for C*H*COO group hydrogens occurs at 5.05 and 4.73 ppm, in $CDCl_3$ and D_2O solution, respectively, downfield with respect to the decarboxylate analogues [(*S*-tim)$_2$CH$_2$] [44]. In the ^1H NMR spectra of complexes **2**–**6**, in $CDCl_3$ solution (see Section 3), the signals due to the 2-mercapto-1-methylimidazolyl rings are always deshielded with respect to those in the spectra of the free donor, confirming the existence of the complexes in solution; the signals due to the C*H*COO group exhibit significant downfield shift (from 5.05 ppm in the free ligand to 5.32–5.42 ppm in the complexes **2**–**4**): this is suggestive of a strong bonding of the tin atom to the carboxylate group of the complexes. In the ^1H NMR spectra at room temperature of the decarboxylated derivatives **6** and **7**, the resonances due to the bridging methylene protons of the [(*S*-tim)$_2$CH$_2$] ligand appear as singlets at 4.44 and 4.65 ppm, respectively, probably as a result of averaging arising from rapid ring inversion of the puckered eight-membered ring containing the central Sn atom.

The room temperature ^1H NMR spectra of derivatives **2**–**6** exhibit only one set of signals for the protons of the imidazolyl rings of the ligands. The ^{119}Sn chemical shifts of the triorganotin(IV) derivatives **2**–**4**, at −95.83, 127.96 and 37.76 ppm, respectively, are in accordance with those of penta-coordinate triorganotin(IV)complexes involving S-, O- or N-donors [65–67].

Electrospray ionization is considered a 'soft' ionization technique. Consequently, few ions are produced, usually the molecular ion plus some adduct ion from the mobile phase solutions [68,69]. ESIMS is particularly suitable for study of labile organotin systems in solution. In the discussion of the mass spectra of the ligand and the di- and triorganotin(IV) derivatives, only the most abundant ion of the isotope cluster will be mentioned. In the positive-ion spectrum of the ligand **1**, dissolved in methanol solution and detected at fragmentation voltage of 30V, significant fragments at *m*/*z* 307 (100%), *m*/*z* 329 (80%), *m*/*z* 636 (45%), *m*/*z* 942 (30%) and *m*/*z* 1248 (10%) have been attributable to the species $[(S\text{-tim})_2CHCO_2 + Na + H]^+$, $[(S\text{-tim})_2CHCO_2 + 2Na]^+$, $[\{(S\text{-tim})_2CHCO_2\}_2 + 3Na]^+$, $[\{(S\text{-tim})_2CHCO_2\}_3 + 4Na]^+$ and $[\{(S\text{-tim})_2CHCO_2\}_4 + 5Na]^+$, respectively. In the negative-ion spectrum a fragment at *m*/*z* 283 (20%) is due to the free ligand $[(S\text{-tim})_2CHCO_2]^-$ and of a major peak at *m*/*z* 239 (100%) is attributable to the decarboxylated specie $[(S\text{-tim})_2CHCO_2 - CO_2]^-$. A similar pattern has been observed in the positive- and negative-ion spectra of the ligand **1**, dissolved in water or water/acetic acid solution.

In the positive-ion spectra of the triorganotin(IV) derivatives **2**–**4** significant fragments at *m*/*z* 634 (100%), 574 (100%) and 653 (100%) have been attributable to the complexes $[\{[(S\text{-tim})_2CHCO_2]SnR_3\} + H]^+$. The instability of the triorganotin(IV) derivatives in methanol solution is demonstrated by the presence in the positive- and negative-ion spectra of fragments at *m*/*z* 241 and *m*/*z* 239 due to the decarboxylated ligand, $[(S\text{-tim})_2CHCO_2 - CO_2 + 2H]^+$ and $[(S\text{-tim})_2CHCO_2 - CO_2]^-$, respectively; moreover in the negative-ion spectra the main fragments at *m*/*z* 421 (100%) and *m*/*z* 379 (100%) have been attributable to the free organotin(IV) acceptors $[\{Sn(C_6H_5)_3Cl\} + Cl]^-$ and $[Sn(C_4H_9)_3Cl(H_2O) + Cl]^-$. In the positive- and negative-ion spectra of the diorganotin(IV) derivatives **6** and **7** the main fragments have been attributable to the free ligand $[(S\text{-tim})_2CH_2 + H]^-$ at *m*/*z* 241 (100%) and to the free organotin acceptors $[(C_6H_5)_2SnCl_2 + Cl]^-$ and $[(C_4H_9)_2SnCl_2 + Cl]^-$, at *m*/*z* 379 (100%) and *m*/*z* 339 (100%), respectively.

4.3. X-ray crystallography

The ORTEP representation and the numbering scheme of the complexes $\{[(S\text{-tim})_2CH_2]SnCl(H_2O)(C_6H_5)_3\}$, **5**, and $\{[\kappa^1O\text{-}(S\text{-tim})_2CHCO_2]Sn(H_2O)(C_4H_9)_3\}$, **3** · **H$_2$O**, are shown in Figs. 3 and 4; selected bond lengths and angles are listed in Table 2.

Several structures of $(C_6H_5)_3SnCl(H_2O)$ co-crystallized with other molecules have been determined, for example 3-[2-(1,10-phenanthrolyl)]-5,6-diphenyl-1,2,4-triazine [70], 3,4,7,8-tetramethyl-1,10-phenanthroline [71], [*N*,*N*′-bis-(3-methoxysalicylidene)propane-1,3-diamine]nickel(II) [72], di-2-pyridylketone 2-aminobenzoylhydrazone [73], *o*-phenanthroline [71], 2,20:60,200-terpyridyl [74], 18-crown-6 [75], 8-methoxyquinoline [76], di-2-pyridyl-2-thenoylhydrazone [77] and pyridine [78]. In these structures, there is hydrogen bonding between the coordinated water molecule

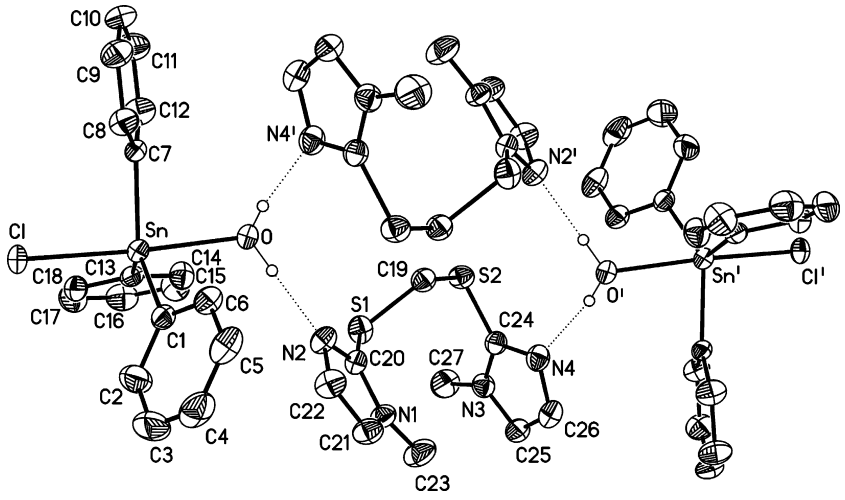

Fig. 3. View of the structure of $\{[(S\text{-tim})_2CH_2]SnCl(H_2O)(C_6H_5)_3\}$, **5**, showing the hydrogen bonding between the coordinated water molecule of $(C_6H_5)_3SnCl(H_2O)$ and the atoms of $(S\text{-tim})_2CH_2$ co-crystallized molecules in the structure (at $1-x$, $1-y$, $-z$).

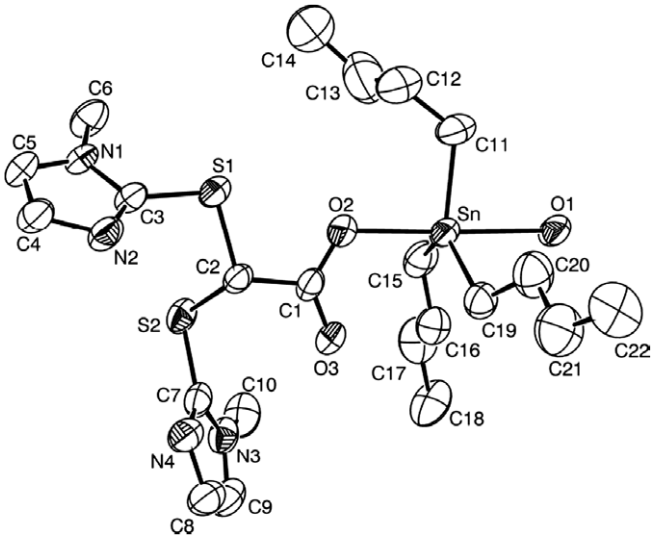

Fig. 4. The molecular structure of $\{[\kappa^1O\text{-}(S\text{-tim})_2CHCO_2]Sn(H_2O)(C_4H_9)_3\}$, $\mathbf{3}\cdot\mathbf{H_2O}$.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **5** and $\mathbf{3}\cdot\mathbf{H_2O}$

Compound ***5***			
Sn–Cl	2.538(1)	Sn–O	2.351(3)
Sn–C(7)	2.130(4)	Sn–C(1)	2.132(4)
Sn–C(13)	2.147(4)	S(2)–C(24)	1.758(4)
S(2)–C(19)	1.797(4)	S(1)–C(20)	1.744(4)
S(1)–C(19)	1.821(4)	N(1)–C(21)	1.350(6)
N(1)–C(20)	1.356(4)	N(1)–C(23)	1.459(6)
N(2)–C(20)	1.319(5)	N(2)–C(22)	1.369(5)
N(3)–C(24)	1.350(4)	N(3)–C(25)	1.368(5)
N(3)–C(27)	1.465(6)	N(4)–C(24)	1.320(5)
N(4)–C(26)	1.372(6)		
O–Sn–Cl	172.2(1)	C(7)–Sn–C(1)	121.3(2)
C(7)–Sn–C(13)	113.9(1)	C(1)–Sn–C(13)	124.0 (2)
C(7)–Sn–O	85.0(1)	C(1)–Sn–O	85.7(1)
C(13)–Sn–O	89.5(1)	C(7)–Sn–Cl	90.6(1)
C(1)–Sn–Cl	91.1(1)	C(13)–Sn–Cl	98.1(1)
C(24)–S(2)–C(19)	99.0(2)	C(20)–S(1)–C(19)	102.6(2)
S(1)–C(19)–S(2)	112.0(2)		
Compound $\mathbf{3}\cdot\boldsymbol{H_2O}$			
Sn–O(1)	2.386(4)	Sn–O(2)	2.196(4)
Sn–C(11)	2.144(6)	Sn–C(15)	2.111(6)
Sn–C(19)	2.139(5)	C(1)–C(2)	1.529(6)
S(1)–C(2)	1.807(4)	S(1)–C(3)	1.746(6)
S(2)–C(2)	1.824(6)	S(2)–C(7)	1.755(7)
O(1)–Sn–O(2)	177.4(2)	C(11)–Sn–C(15)	118.1(4)
C(11)–Sn–C(19)	117.3(4)	C(15)–Sn–C(19)	123.4(3)
C(11)–Sn–O(1)	87.1(3)	C(15)–Sn–O(1)	87.5(3)
C(19)–Sn–O(1)	84.2(2)	C(11)–Sn–O(2)	90.8(3)
C(15)–Sn–O(2)	94.9(3)	C(19)–Sn–O(2)	95.4(2)
C(2)–S(1)–C(3)	101.1(3)	C(2)–S(2)–C(7)	100.5(3)
S(1)–C(2)–S(2)	107.6(3)	C(1)–C(2)–S(1)	110.6(3)
C(1)–C(2)–S(2)	112.0(3)		

of $(C_6H_5)_3SnCl(H_2O)$ and the N2 and N4 nitrogen atoms of co-crystallized molecules in the structure. In this paper, we report a structure in which the bis(1-methyl-1*H*-imidazol-2-ylthio)methane species is hydrogen bonded to $Ph_3SnCl(H_2O)$ (Fig. 3). In the molecular structure of compound **5**, the tin atom is five-coordinated in a slightly distorted trigonal-bipyramidal geometry by three carbon atoms of three phenyl groups in the equatorial plane, and by one chlorine anion and one water molecule in the axial positions. The slight distortion from the ideal trigonal-bipyramidal geometry is reflected in the O–Sn–Cl angle of 172.2(1)°, and the three C–Sn–C angles of 121.3(2)°, 113.9(1)° and 124.0(2)°. The two thioimidazolyl moieties are connected to the coordinated water molecule through O–H···N hydrogen bonds. The O–H(1)···N(2) and O–H(2)···N(4)′ (at $1-x$, $1-y$, $-z$) contact distances are 1.65(6) Å and 1.92(5) Å, with angles of 172° and 175°, respectively. These values are comparable to those found in similar pyridine ligand adducts [78].

X-ray quality crystals of $\mathbf{3}\cdot\mathbf{H_2O}$ were obtained from a $CHCl_3$/diethyl ether (1:2) solution. The structure consists

of discrete {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]Sn(H$_2$O)(C$_4$H$_9$)$_3$]} molecules and the labeling for the atoms are shown in Fig. 4. The tin atom is five-coordinated, being bonded to two oxygen atoms and three butyl groups, respectively. The coordination sphere is distorted trigonal bipyramid with the three equatorial positions being taken up by the carbon of the *n*-butyl substituents and the axial positions being occupied by an oxygen atom of a monodentate carboxylate ligand and a water molecule (O(1)–Sn–O(2) 177.4(2)°). The Sn–O(2)$_{(carboxylate)}$ bond distance is significantly shorter (2.196(4) Å) compared with the Sn–O(1)$_{(water)}$ (2.386(4) Å), thus the R–CO$_2$ moiety does not function as a symmetric bridging ligand. Because of the variation of the bond distances the tin atom is 0.15(1) Å out of the equatorial plane towards the more strongly bound O(2) atom. The O(3) oxygen atom of the carboxylic residue does not significantly interact with the tin atom, the Sn···O(3) separation being 3.200(5) Å. The water molecule forms hydrogen bonding contacts with the N(2) and N(4) of the 1*H*-imidazolyl rings of the symmetry-related molecule (O(1)···N(2)′ 2.803(5), O(1)···N(4)′ 2.725(6) Å, symmetry operation: at $-x$, $y-0.5$, $-z+0.5$) which allows for the formation of layers parallel to the crystallographic *ac* plane. The three Sn–C bond distances fall within the experimental error (Sn–C(11) 2.144(6), Sn–C(15) 2.111(6), Sn–C(19) 2.139(5) Å) and are also in agreement with the corresponding values found in [^{n}Bu$_3$Sn(*N*-phataloylglycinate)(OH$_2$)] [77]. The bond distances and angles within the co-crystallized bis(1-methyl-1*H*-imidazol-2-ylthio)acetate molecule have usual values and require no comment.

5. Summary and conclusion

Overall we describe the synthesis and isolation of a new monoanionic and polyfunctional *N,O,S*-ligand of possible considerable coordinative flexibility, the sodium bis(1-methyl-1*H*-imidazol-2-ylthio)acetate ligand. From the interaction of Na[(*S*-tim)$_2$CHCO$_2$] with di- and tri-organotin(IV) halides SnR$_n$Cl$_{4-n}$ (R = Ph, Cy and ^{n}Bu, n = 2–3), complexes of the type {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]SnR$_3$} and related decarboxylated species {[κ^2*N*,*N*-(*S*-tim)$_2$CH$_2$]-SnR$_2$Cl$_2$} have been obtained and characterized. Crystal structure of {[κ^1*O*-(*S*-tim)$_2$CHCO$_2$]Sn(H$_2$O)(C$_4$H$_9$)$_3$} revealed a distorted trigonal bipyramid coordination sphere, with the three equatorial positions being taken up by the carbon of the *n*-butyl substituents and the axial positions being occupied by an oxygen atom of a monodentate carboxylate ligand and a water molecule. In the molecular structure of {[(*S*-tim)$_2$CH$_2$]SnCl(H$_2$O)(C$_6$H$_5$)$_3$} the tin atom is five-coordinated in a slightly distorted trigonal-bipyramidal geometry by three carbon atoms of three phenyl groups in the equatorial plane, and by one chlorine anion and one water molecule in the axial positions, being the bis(1-methyl-1*H*-imidazol-2-ylthio)methane ligand hydrogen bonded to Ph$_3$SnCl(H$_2$O).

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Appendix A. Supplementary material

CCDC 660930 and 660931 contain the supplementary crystallographic data for **5** and **3** · **H$_2$O**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.021.

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