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# Synthesis, characterization and hydrolytic behavior of new bis(2-pyridylthio)acetate ligand and related organotin(IV) complexes

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**Abstract**

The new sodium bis(2-pyridylthio)acetate ligand, $Na[(pyS)_2CHCO_2]$, has been prepared in ethanol solution using 2-mercaptopyridine, dibromoacetic acid and NaOH. New mono- and di-organotin(IV) derivatives containing the anionic bis(2-pyridylthio)acetate have been synthesized from reaction between $SnR_nCl_{4-n}$ (R = Me, Ph and $^n$Bu, $n$ = 1–2) acceptors and $Na[(pyS)_2CHCO_2]$. Mono-nuclear complexes of the type $\{[(pyS)_2CHCO_2]R_nSnCl_{4-n-1}\}$ have been obtained and characterized by elemental analyses, FT-IR, ESI-MS, multinuclear ($^1$H and $^{119}$Sn) NMR spectral data and X-ray crystallography. ESI-MS spectra of methanol solution of the complexes show the existence of hydrolysed species. Attempts to crystallize the dimethyltin(IV) derivative (**3**), from acetonitrile solution yield the dimeric dicarboxylatotetramethyldistannoxane (**8**), which was characterized by single crystal diffraction analysis.


*Keywords:* Organotin(IV); bis(2-pyridylthio)acetate; 2-mercaptopyridine; Electrospray ionization mass spectroscopy; Crystal structure

## 1. Introduction

In recent years there has been considerable interest in organotin derivatives. This is because in the past organotin compounds have been accumulated in nature due to their various industrial [1] and agricultural applications [2]. The discovery of their dangerous impacts on living organisms has led to a significant decrease of usage from the late 1980s, however due to their high toxicity [3]. On the other hand, in recent years many organotin compounds have been tested for their in vitro activity against a large variety of tumor lines and have been found to be as effective or better than traditional heavy metal anticancer drugs, such as *cis*-platin [4]. In addition to the aforesaid applications organotin compounds are also 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 [5].

Recently, we have reported the synthesis and the spectroscopic characterization of new scorpionate ligands [6,7] 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 [8]. As an extension of this research field, we are now interested in the development of the chemistry of some new organotin carboxylates

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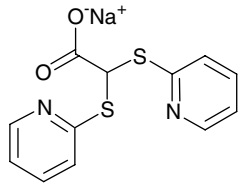


Fig. 1. Structure of the ligand, **1**.

obtained from the interaction of a number of organotin(IV) halides with new polyfunctional *S*,*N*,*O*-ligands, containing two pyridine groups which also incorporate other biologically relevant groups as well as the thioethers and carboxylates as hydrophilic moiety.

In recent years a number of authors [9] 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 coordination by both S and the neighbouring N atom, and hence to the formation of stable chelate rings of five or more atoms [10–13]. In particular the bis(2-pyridylthio)methane has a rich coordination chemistry as recently reported for Zn(II), Hg(II), Cu(I), Ag(I) [14], Cd(II) [15] and Cu(II) [16] complexes. Tris(2-pyridylthio)methane has also been synthesized by Kinoshita et al. [16] and they have shown that this ligand reacts with $[Cu(NCMe)_4]$ forming the first example of a compound containing a Cu(II)–C($sp^3$) bond.

Bearing in mind the above, we have developed a strategy for producing a new class of monoanionic and polyfunctional *N*,*O*,*S*-ligands of considerable co-ordinative flexibility. Toward this end, we report now 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 (Fig. 1).

X-ray crystal structure of the asymmetric distannoxane, obtained from re-crystallization of the dimethyltin(IV) derivative, was determined to probe the bonding behavior of the ligand and its implications on the hydrolytic behavior and stability of these compounds.

## 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 $^1H$, 75 MHz for $^{13}C$ and 111.9 MHz for $^{119}Sn$). Melting points were taken on an SMP3 Stuart Scientific Instrument. The electrical conductivity measurements ($\Lambda_m$, 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 (ESIMS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using a methanol mobile phase. The compounds were added to the reagent grade acetone to give solutions of approximate concentration 0.1 mM. These solutions were injected (1 μl) into the spectrometer via a HPLC HP 1090 Series II fitted with an autosampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 μl $min^{-1}$, and nitrogen was employed both as a drying and nebulizing gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion mode, respectively. Confirmation of all major species in this ESIMS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the IsoPro computer program [17].

### 2.2. Synthesis

#### 2.2.1. Synthesis of $[(pyS)_2CHCO_2]Na$ (*1*)

2-Mercaptopyridine (5.56 g, 50.0 mmol) was added to a solution of NaOH (3.600 g, 90.0 mmol) in 40 ml of absolute ethanol. After 1 day stirring, a solution of dibromoacetic acid (5.45 g, 25.0 mmol) in 40 ml of absolute ethanol was added drop wise to the sodium salt so obtained, and this mixture was stirred for 2 days and then heated at gentle reflux for 6 h to give a pale yellow emulsion. The mixture was allowed to cool to r.t., concentrated and then filtered affording a pale yellow solid. The crude product was recrystallized in methanol/acetone (1:2) yielding $Na[(pyS)_2CHCO_2]$ (**1**) as pale yellow microcrystalline needles. Yield 86%; m.p. 212–215 °C. $^1H$ NMR ($D_2O$, 293 K): $\delta$ 5.78 (s, 1H, C*H*$CO_2$), 7.20 (m, 2H, 5-C*H*), 7.44 (m, 2H, 3-C*H*), 7.67 (m, 2H, 4-C*H*), 8.30 (m, 2H, 6-C*H*). $^1H$ NMR ($CD_3OD$, 293 K): $\delta$ 6.08 (s, 1H, C*H*$CO_2$), 7.08 (m, 2H, 5-C*H*), 7.45 (m, 2H, 3-C*H*), 7.62 (m, 2H, 4-C*H*), 8.33 (m, 2H, 6-C*H*). $^{13}C$ NMR ($CD_3OD$, 293 K): $\delta$ 5.44 (*C*HCOO), 121.49 (5-*C*H), 123.93 (3-*C*H), 138.19 (4-*C*H), 150.28 (6-*C*H), 160.40 (2-*C*H). IR (nujol, $cm^{-1}$): 3048w (CH), 1615s ($\nu_{asym}$ C=O), 1580m, 1555m (C=C + C=N), 1411m ($\nu_{sym}$ C=O), 1377m, 1132m, 747m. ESIMS (major positive-ions, $CH_3OH$), *m*/*z* (%): 301 (100) $[\{(pyS)_2CHCO_2H\} + Na^+]^+$, 579 (80) $[\{(pyS)_2CHCO_2H\}_2 + Na^+]^+$. ESIMS (major negative-ions, $CH_3OH$), *m*/*z* (%): 110 (100) $[(pyS)]^-$, 233 (30) $[\{(pyS)_2CHCO_2\} - CO_2]^-$, 577

(30) $[\{(pyS)_2CHCO_2\}_2 + Na^+]^-$. Calc. for $C_{12}H_9N_2NaO_2S_2$: C, 47.99; H, 3.02; N, 9.33; S, 21.35%. Found: C, 48.02; H, 3.08; N, 9.03, S, 21.40%.

#### 2.2.2. {[(pyS)$_2$CHCO$_2$]Sn(CH$_3$)Cl$_2$} (2)

To a $CH_2Cl_2$ solution (50 ml) of $MeSnCl_3$ (0.240 g, 1.0 mmol), Na[$(pyS)_2CHCO_2$] (0.300 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 chloroform was added (20 ml). The KCl was removed by filtration and the filtrate reduced to half volume. Then diethyl ether was added (40 ml) and a yellow precipitate afforded, which was filtered off, washed with *n*-hexane (10 ml) and dried to constant weight under reduced pressure. Yield: 71%. M.p.: 134–137 °C. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 1.41 (s, 3H, Sn–C*H*$_3$, $^2J$ (Sn–$^1$H) = 103 Hz), 6.38 (s, 1H, C*H*CO$_2$), 7.16 (m, 2H, 5-C*H*), 7.31 (m, 2H, 3-C*H*), 7.73 (m, 2H, 4-C*H*), 8.43 (m, 2H, 6-C*H*). $^{119}$Sn NMR ($CDCl_3$, 293K): −483.5 (sbr). IR (nujol, cm$^{-1}$): 3163w (CH), 1600sh ($\nu_{asym}$ C=O), 1580m (C=C + C=N), 1411m ($\nu_{sym}$ C=O), 545m (Sn–C), 480s (Sn–O), 281sbr (Sn–Cl). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 279 (80) $[\{(pyS)_2CHCO_2H\} + H^+]^+$, 301 (60) $[\{(pyS)_2CHCO_2H\} + Na^+]^+$, 579 (20) $[\{(pyS)_2CHCO_2H\}_2 + Na^+]^+$, 543 (20) $[(CH_3)SnCl_2\ \{(pyS)_2CHCO_2\}–H^+ + Na^+ + K^+]^+$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (80) $[(pyS)]^-$, 233 (30) $[\{(pyS)_2CHCO_2\} - CO_2]^-$, 487 (100) $[\{(pyS)_2CHCO_2\}_2 - 2CO_2 + Na^+]^-$. Anal. Calc. for $C_{13}H_{12}Cl_2N_2O_2S_2Sn$: C, 32.40; H, 2.51; N, 5.81; S, 13.30%. Found: C, 32.55; H, 2.70; N, 5.98; S, 13.58%.

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

Compound **3** was prepared similarly to compound **2**, by using $Me_2SnCl_2$ (0.220 g, 1.0 mmol) and Na[$(pyS)_2CHCO_2$] (0.300 g, 1.0 mmol) in dichloromethane solution (30 ml). Re-crystallization from petroleum ether gives complex **3** as a micro-crystalline solid (68% yield). M.p.: 130 °C dec. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 1.14 (s, 6H, Sn–C*H*$_3$, $^2J$(Sn–$^1$H) = 82.0 Hz), 6.40 (s, 1H, C*H*CO$_2$), 7.12 (m, 2H, 5-C*H*), 7.24 (m, 2H, 3-C*H*), 7.55 (m, 2H, 4-C*H*), 8.40 (m, 2H, 6-C*H*). $^{13}$C NMR ($CDCl_3$, 293 K): $\delta$ 31.11 (s, $^1J$(Sn–$^{13}$C): 660 Hz, Sn-*C*H$_3$), 49.98 (*C*HCOO), 119.91 (5-*C*H), 122.50 (3-*C*H), 136.21 (4-*C*H), 149.65 (6-*C*H), 157.85 (2-*C*H), 207.16 (*C*OO). $^{119}$Sn NMR ($CDCl_3$, 293K): −182.3 (s). IR (nujol, cm$^{-1}$): 3170w, 3080w (CH), 1601mbr ($\nu_{asym}$ C=O), 1571m, 1551m (C=C + C=N), 1413m ($\nu_{sym}$ C=O), 567s (Sn–C), 479s (Sn–O), 279s (Sn–Cl). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 301 (20) $[\{(pyS)_2CHCO_2H\} + Na^+]^+$, 426 (20) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}]^+$, 704 (20) $[(CH_3)_2Sn(pyS)_2CHCO_2\}_2 + H^+]^+$, 726 (40) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}_2 + Na^+]^+$, 801 (100) $[(CH_3)_2SnCl\{(pyS)_2CHCO_2\}_2 + K^+ + Na^+]^+$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (100) $[(pyS)]^-$, 233 (60) $[\{(pyS)_2CHCO_2\} - CO_2]^-$, 702 (20) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}_2 - H^+]^-$, 981 (60) $[(CH_3)_2Sn\ \{(pyS)_2CHCO_2\}_3]^-$. Anal. Calc. for $C_{14}H_{15}ClN_2O_2S_2Sn$: C, 36.43; H, 3.28; N, 6.07; S, 13.89%. Found: C, 36.45; H, 3.15; N, 6.12; S, 13.61%.

#### 2.2.4. {[(pyS)$_2$CHCO$_2$]Sn(C$_4$H$_9$)Cl$_2$} (4)

Compound **4** was prepared similarly to compound **2**, by using $(C_4H_9)SnCl_3$ (0.282 g, 1.0 mmol) and Na[$(pyS)_2CHCO_2$] (0.300 g, 1.0 mmol) in dichloromethane solution (30 ml). Re-crystallization from petroleum ether gives complex **4** as a micro-crystalline solid (52% yield). Mp: 92 °C dec. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 0.90 (t, 3H, C*H*$_3$ of Sn–Bu$^n$), 1.22–2.15 (mbr, 6H, C*H*$_2$ of Sn–Bu$^n$), 6.36 (s, 1H, C*H*CO$_2$), 7.14 (m, 2H, 5-C*H*), 7.24 (m, 2H, 3-C*H*), 7.62 (m, 2H, 4-C*H*), 8.42 (m, 2H, 6-C*H*). $^{119}$Sn NMR ($CDCl_3$, 293K): −499.8 (sbr). IR (nujol, cm$^{-1}$): 3085w (CH), 1600sh ($\nu_{asym}$ C=O), 1574m, 1558m (C=C + C=N), 1416m ($\nu_{sym}$ C=O), 619m (Sn–C), 483s (Sn–O), 302s, 285s (Sn–Cl). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 279 (40) $[\{(pyS)_2CHCO_2H\} + H^+]^+$, 489 (20) $[(C_4H_9)SnCl\ \{(pyS)_2CHCO_2\}_2]^+$, 976 (100) $[\{(C_4H_9)SnCl\}_2\ \{(pyS)_2\ CHCO_2\}_2 - H^+]^+$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (20) $[(pyS)]^-$, 233 (40) $[\{(pyS)_2\ CHCO_2\} - CO_2]^-$. Anal. Calc. for $C_{16}H_{18}Cl_2N_2O_2S_2Sn$: C, 36.67; H, 3.46; N, 5.35; S, 12.24%. Found: C, 36.39; H, 3.39; N, 5.09; S, 12.01%.

#### 2.2.5. {[(pyS)$_2$CHCO$_2$]Sn(C$_4$H$_9$)$_2$Cl} (5)

Compound **5** was prepared similarly to compound **2**, by using $(C_4H_9)_2SnCl_2$ (0.304 g, 1.0 mmol) and Na[$(pyS)_2CHCO_2$] (0.300 g, 1.0 mmol) in dichloromethane solution (30 ml). Re-crystallization from petroleum ether gives complex **5** as a micro-crystalline solid (63% yield). Mp: oil. $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 0.91 (t, 6H, C*H*$_3$ of Sn–Bu$^n$), 1.20–1.78 (mbr, 12H, C*H*$_2$ of Sn–Bu$^n$), 6.44 (s, 1H, C*H*CO$_2$), 7.15 (m, 2H, 5-C*H*), 7.26 (m, 2H, 3-C*H*), 7.59 (m, 2H, 4-C*H*), 8.43 (m, 2H, 6-C*H*). $^{119}$Sn NMR ($CDCl_3$, 293 K): −205.8 (s). IR (nujol, cm$^{-1}$): 3176w, 3046w (CH), 1606m ($\nu_{asym}$ C=O), 1574m, 1550m (C=C + C=N), 1413m ($\nu_{sym}$ C=O), 616s, 579s (Sn–C), 479s (Sn–O), 296s, 276s (Sn–Cl). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 1056 (100) $[\{(C_4H_9)_2Sn\}_2Cl\ \{(pyS)_2CHCO_2\}_2]^+$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (40) $[(pyS)]^-$, 233 (30) $[\{(pyS)_2CHCO_2\} - CO_2]^-$, 339 (100) $[(C_4H_9)_2SnCl_2 + Cl^-]^-$, 581 (30) $[(C_4H_9)_2SnCl_2\{(pyS)_2\ CHCO_2H\}]^-$. Anal. Calc. for $C_{20}H_{27}ClN_2O_2S_2Sn$: C, 44.02; H, 4.99; N, 5.13; S, 11.75%. Found: C, 43.95; H, 5.12; N, 5.03; S, 12.00%.

#### 2.2.6. {[(pyS)$_2$CHCO$_2$]Sn(C$_6$H$_5$)Cl$_2$} (6)

Compound **6** was prepared similarly to compound **2**, by using $(C_6H_5)SnCl_3$ (0.302 g, 1.0 mmol) and

$Na[(pyS)_2CHCO_2]$ (0.300 g, 1.0 mmol) in dichloromethane solution (30 ml). Re-crystallization from *n*-hexane gives complex **6** as a micro-crystalline solid (63% yield). Mp: 105–107 °C. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ 6.36 (s, 1H, C*H*$CO_2$), 7.14 (t, 2H, 5-C*H*), 7.26 (d, 2H, 3-C*H*), 7.46–7.60 (m, 5H, $C_6H_5$), 7.75 (m, 2H, 4-C*H*), 8.40 (d, 2H, 6-C*H*). $^{119}Sn$ NMR ($CDCl_3$, 293K): −480.3 (br). IR (nujol, $cm^{-1}$): 3176w, 3046w (CH), 1589sbr ($\nu_{asym}$ C=O), 1574m, 1558m (C=C + C=N), 1417m ($\nu_{sym}$ C=O), 483s, 452s (Sn–O), 400m, 301sbr (Sn–Cl), 224w (Sn–C). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 262 (100) $[\{(pyS)_2CHCO\}]^+$, 545 (30) $[(C_6H_5)SnCl_2\{(pyS)_2\ CHCO_2H\}]^+$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (50) $[(pyS)]^-$, 233 (30) $[\{(pyS)_2CHCO_2\} - CO_2]^-$. Anal. Calc. for $C_{18}H_{14}Cl_2N_2O_2S_2Sn$: C, 39.94; H, 2.59; N, 5.15; S, 11.79%. Found: C, 40.25; H, 2.82; N, 5.03; S, 11.60%.

### 2.2.7. {[(pyS)$_2$CHCO$_2$]Sn(C$_6$H$_5$)$_2$Cl} (7)

Compound **7** was prepared similarly to compound **2**, by using $(C_6H_5)_2SnCl_2$ (0.344 g, 1.0 mmol) and $Na[(pyS)_2CHCO_2]$ (0.300 g, 1.0 mmol) in dichloromethane solution (30 ml). Re-crystallization from petroleum ether gives complex **7** as a micro-crystalline solid (52% yield). Mp: 87–89 °C. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ 6.50 (s, 1H, C*H*$CO_2$), 7.20 (t, 2H, 5-C*H*), 7.26 (d, 2H, 3-C*H*), 7.45–7.60 (m, 10H, $C_6H_5$), 7.78 (m, 2H, 4-C*H*), 8.25 (d, 2H, 6-C*H*). $^{119}Sn$ NMR ($CDCl_3$, 293K): −310.0 (s). IR (nujol, $cm^{-1}$): 3046w (CH), 1574s ($\nu_{as}$ C=O), 1557m (C=C + C=N), 1414m ($\nu_{sym}$ C=O), 481m, 452m (Sn–O), 306s (Sn–Cl), 237m (Sn–C). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 150 (100) $[(pySH) + K^+]^+$, 383 (40) $[(C_6H_5)_2Sn(pyS)]^+$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (100) $[(pyS)]^-$, 233 (30) $[\{(pyS)_2CHCO_2\} - CO_2]^-$. Anal. Calc. for $C_{24}H_{19}ClN_2O_2S_2Sn$: C, 49.22; H, 3.27; N, 4.78; S, 10.95%. Found: C, 49.43; H, 3.30; N, 4.67; S, 10.78%.

### 2.2.8. {(CH$_3$)$_2$[(pyS)$_2$CHCO$_2$]-SnOSn[(pyS)$_2$CHCO$_2$](CH$_3$)$_2$}$_2$ (8)

$\{[(pyS)_2CHCO_2]Sn(CH_3)_2Cl\}$, **3**, (0.462 g, 1.00 mmol) was dissolved in 50 ml of moist acetonitrile (95:5 v/v acetonitrile/water), and the clear solution was stirred at room temperature for 24 h. Thereafter, solvent was stripped off under vacuum. To the resulting viscous mass was added *n*-hexane with constant stirring. A white solid thus obtained was filtered and dried under vacuo. Recrystallization of the crude product from acetonitrile afforded **8** in analytically pure form. Yield: 80%. M.p.: 115 °C dec. $^1H$ NMR ($CDCl_3$, 293 K): $\delta$ 0.75 (s, 12H, Sn–C*H*$_3$, $^2J(Sn-^1H) = 88$ Hz), 0.69 (s, 12H, Sn–C*H*$_3$, $^2J(Sn-^1H) = 87$ Hz), 6.42 (s, 4H, C*H*$CO_2$), 6.98 (m, 8H, 5-C*H*), 7.25 (m, 8H, 3-C*H*), 7.50 (m, 8H, 4-C*H*), 8.39 (m, 8H, 6-C*H*). $^{13}C$ NMR ($CDCl_3$, 293 K): $\delta$ 12.66 (s, $^1J(Sn-^{13}C)$: 741 Hz, Sn-*C*H$_3$), 13.91 (s, $^1J(Sn-^{13}C)$: 731 Hz, Sn-*C*H$_3$), 49.00 (*C*HCOO), 119.94 (5-*C*H), 122.44 (3-*C*H), 136.23 (4-*C*H), 149.84 (6-*C*H), 156.01 (2-*C*H). $^{119}Sn$ NMR ($CDCl_3$, 293K): −173.2 (sbr), −182.5 (sbr). IR (nujol, $cm^{-1}$): 3168w, 3076w (CH), 1610mbr ($\nu_{asym}$ C=O), 1571m, 1551m (C=C + C=N), 1410m ($\nu_{sym}$ C=O), 580s, 530s (Sn–C), 490s, 461m ($SnO_2$), 228m, 203m (Sn–O)(COO). ESIMS (major positive-ions, $CH_3OH$), *m/z* (%): 301 (20) $[\{(pyS)_2CHCO_2H\} + Na^+]^+$, 426 (10) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}]^+$, 704 (20) $[\{(CH_3)_2Sn\}(pyS)_2CHCO_2\}_2 + H^+]^+$, 726 (30) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}_2 + Na^+]^+$, 807 (100) $[\{(CH_3)_2SnO\}_2(CH_3)_2Sn\{(pyS)_2CHCO_2\}_4 + Na^+ + H^+]^{++}$. ESIMS (major negative-ions, $CH_3OH$), *m/z* (%): 110 (100) $[(pyS)]^-$, 233 (60) $[\{(pyS)_2CHCO_2\} - CO_2]^-$, 702 (20) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}_2 - H^+]^-$, 981 (60) $[(CH_3)_2Sn\{(pyS)_2CHCO_2\}_3]^-$. Anal. Calc. for $C_{56}H_{60}N_8O_{10}S_8Sn_4$: C, 38.73; H, 3.48; N, 6.45; S, 14.77%. Found: C, 38.45; H, 3.55; N, 6.12; S, 14.61%.

## 2.3. X-ray measurements and structure determination

Crystal data for $\{(CH_3)_2[(pyS)_2CHCO_2]SnOSn[(pyS)_2CHCO_2](CH_3)_2\}_2$, (**8**): $C_{56}H_{60}N_8O_{10}S_8Sn_4$, $M_r = 1736.36$, triclinic, space group $P\bar{1}$, with $a = 9.996(2)$, $b = 13.463(2)$, $c = 14.336(3)$ Å, $\alpha = 110.02(3)$, $\beta = 106.19(3)$, $\gamma = 90.91(3)°$, $V = 1727.5(6)$ Å$^3$, $Z = 1$, $\rho_{calc} = 1.669$ mg/m$^3$, $F(000) = 860$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $\mu$ (Mo K$\alpha$) = 1.728 mm$^{-1}$, crystal size $0.20 \times 0.26 \times .032$ mm.

A prismatic pale yellow crystal was centered on a four-circle Philips PW1100 (Febo System) diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated MoK$\alpha$ radiation ($\lambda = 0.71073$ Å), following standard procedures at room temperature. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-Polarization effects and for absorption, as described by North et al. [18].

The structure was solved by direct methods SIR-97 [19]. Refinement was carried out by full-matrix least-squares procedures using anisotropic temperature factors for all non-hydrogen atoms. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 Uequiv of the parent carbon atom). For a total of 394 parameters and for 6141 reflections having ($I \geqslant 2\sigma(I)$), $wR'([\sum w(F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}) = 0.143$, $S = 1.170$ and conventional $R = 0.054$; min/max residual electron density −0.964/0.674 e Å$^{-3}$.

Structure refinement and final geometrical calculations were carried out with SHELXL-97 [20] and PARST [21] programs, drawings were produced using ORTEP II [22]. Significant geometric parameters are in Table 1.

## 3. Results and discussion

Complexes **2**–**7** have been synthesized by methathetic reaction of $Na[(pyS)_2CHCO_2]$ with $SnR_nX_{4-n}$ acceptors in $CH_2Cl_2$.

$$Na[(pyS)_2CHCO_2] + SnR_nCl_{4-n} \rightarrow [(pyS)_2CHCO_2]R_nSnCl_{4-n-1}] + NaCl \quad \mathbf{2-7} \quad (1)$$

| | | |
|---|---|---|
| **2** | $R = CH_3$ | $n = 1$ |
| **3** | $R = CH_3$ | $n = 2$ |
| **4** | $R = {}^nBu$ | $n = 1$ |
| **5** | $R = {}^nBu$ | $n = 2$ |
| **6** | $R = Ph$ | $n = 1$ |
| **7** | $R = Ph$ | $n = 2$ |

The derivatives **1**–**7** are stable in air. Compound **1** shows a good solubility only in water and methanol solution. Derivatives **2**–**7** are stable in alcohols, acetone, acetonitrile and chlorinated solvents, and they are non-electrolytes in $CH_2Cl_2$ solution. The identity of these compounds has been established by ESI-MS, IR, and multinuclear ($^1H$, $^{13}C$, $^{119}Sn$) 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 pz ring C–H stretching and medium to strong absorptions in the range 1550–1580 $cm^{-1}$ are related to ring "breathing" vibrations.

The presence of COO moiety is detected by an intense absorption in the range 1574–1606 $cm^{-1}$, due to the asymmetric $CO_2^-$ stretching mode, the shift to red with respect to free neutral ligands ($\nu_{asym}CO_2^- = 1615\ cm^{-1}$), being observed upon complex formation. This is in accordance with electronic flow from the ligand toward the tin moiety, with consequent decreasing C=O bond order.

In the far-IR region medium to strong absorptions appear upon coordination, due to stretching modes of Sn–O, Sn–R and Sn–Cl [23]. Frequency of Sn–Cl mode undergoes a decrease on going from mono- to di-alkyl or di-phenyl derivatives. In fact, the Sn–Cl stretching frequencies in the dichloride- and monochloride-tin(IV) derivatives fall as strong or medium broad bands in the range 276–306 $cm^{-1}$. In the far-IR spectra the Sn–C stretching frequencies fall as strong or medium broad bands in the range 545–619 $cm^{-1}$ for alkyl derivatives **2**–**5**, and in the range 224–237 $cm^{-1}$ for phenyl complexes **6** and **7**; these absorptions agree well with the trend previously observed in similar N-donor complexes [24].

In the IR spectra of **2**–**7** always one absorption assigned to Sn–O has been detected between 452 and 483 $cm^{-1}$.

The room-temperature $^1H$ NMR spectra of derivatives **2**–**7**, in $CDCl_3$ solution (see Section 2), exhibit only one set of signals for the protons of the pyridyl rings of the $[(pyS)_2CHCO_2]^-$ ligand, resulting from dynamic exchange processes [25].

Upon interaction of ligand **1** with organotin(IV) acceptors, for all complexes studied, no significantly large shifts were evident for the proton atoms of the pyridyl rings: this observation implies a lack of direct bond involvement of these rings with the metal. In contrast, in the $^1H$ NMR spectra of complexes **2**–**7** the signals due to the C*H*COO group exhibit significant downfield shift (from 5.78 ppm in the free ligand to 6.36–6.50 ppm in the complexes): this is suggestive of a strong bonding of the tin atom to the carboxylate group of complexes.

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 the coordination number of tin [26]. In the dimethyltin(IV) derivative **3** the tin-proton coupling constant $^2J(Sn,^1H)$ is 82.0 Hz, falling in the range for five-coordinated dimethyltin(IV) species [27]. The tin-carbon coupling constant $^1J(Sn,^{13}C)$ is 660 Hz; on the basis of Lockarts's equation [26], the Me–Sn–Me angle is estimated to 134°, suggesting a skewed penta-coordination around the tin atom. The $^{119}Sn$ chemical shifts of diorganotin(IV) derivatives **3**, **5** and **7**, at −182.3, −205.8 and −310.0 ppm, respectively, are in accordance

Table 1
Selected interatomic bond lenghts (Å) and angles (°) for $\{(CH_3)_2[(pyS)_2CHCO_2]SnOSn\ [(pyS)_2CHCO_2](CH_3)_2\}_2$, **8**

| | | | |
|---|---|---|---|
| Sn(1)–O(1) | 2.250(5) | Sn(2)–O(1) | 2.479(5) |
| Sn(1)–O(3) | 2.044(6) | Sn(2)–O(3) | 2.003(5) |
| Sn(1)–C(1) | 2.102(7) | Sn(2)–C(3) | 2.098(9) |
| Sn(1)–C(2) | 2.100(7) | Sn(2)–C(4) | 2.094(7) |
| Sn(1)–O(3)′ | 2.129(5) | Sn(2)–O(4) | 2.116(6) |
| O(1)–C(5) | 1.278(5) | O(2)–C(5) | 1.216(9) |
| O(4)–C(17) | 1.300(8) | O(5)–C(17) | 1.216(9) |
| S(1)–C(6) | 1.811(8) | S(1)–C(7) | 1.758(9) |
| S(2)–C(6) | 1.817(8) | S(2)–C(12) | 1.779(8) |
| S(4)–C(18) | 1.800(7) | S(4)–C(24) | 1.774(8) |
| S(3)–C(18) | 1.794(7) | S(3)–C(19) | 1.771(8) |
| Sn(1)–Sn(1)′ | 3.334(1) | Sn(1)–Sn(2) | 3.523(1) |
| Sn(1)–O(1)–Sn(2) | 96.2(2) | Sn(1)–O(3)–Sn(2) | 121.0(3) |
| Sn(1)–O(3)–Sn(1)′ | 106.1(2) | Sn(2)–O(3)–Sn(1)′ | 132.5(2) |
| O(3)–Sn(1)–O(1) | 73.4(2) | O(3)–Sn(2)–O(1) | 69.1(2) |
| C(2)–Sn(1)–O(1) | 94.1(3) | C(3)–Sn(2)–O(1) | 89.9(3) |
| C(1)–Sn(1)–O(1) | 95.2(3) | C(4)–Sn(2)–O(1) | 89.1(3) |
| O(1)–Sn(1)–O(3)′ | 147.3(2) | O(4)–Sn(2)–O(1) | 150.6(1) |
| O(3)–Sn(1)–C(2) | 112.1(3) | O(3)–Sn(2)–C(3) | 107.7(3) |
| O(3)–Sn(1)–C(1) | 109.9(4) | O(3)–Sn(2)–C(4) | 108.6(3) |
| C(2)–Sn(1)–C(1) | 137.9(4) | C(3)–Sn(2)–C(4) | 140.6(3) |
| O(3)–Sn(1)–O(3)′ | 74.0(2) | O(3)–Sn(2)–O(4) | 81.5(2) |
| C(2)–Sn(1)–O(3)′ | 96.6(3) | C(3)–Sn(2)–O(4) | 101.2(3) |
| C(1)–Sn(1)–O(3)′ | 97.2(3) | C(4)–Sn(2)–O(4) | 98.7(3) |
| Sn(1)–O(1)–C(5) | 114.7(4) | Sn(2)–O(1)–C(5) | 148.7(4) |
| Sn(2)–O(4)–C(17) | 111.6(5) | | |

with those of five-coordinated diorganotin(IV)halides complexes involving S-, O- or N-donors [28–30]. The $^{119}$Sn chemical shifts of the monoorganotin(IV) derivatives **2**, **4** and **6**, at −483.5, −499.8 and −480.3, respectively, provide an additional support for five-coordinated tin atoms.

Attempts to crystallize the mixed-ligand tin compound **3**, {[(pyS)$_2$CHCO$_2$]Sn(CH$_3$)$_2$Cl}, from acetonitrile solution did not yield the desired product. Instead, tetraorganodistannoxane {(CH$_3$)$_2$[(pyS)$_2$CHCO$_2$]SnOSn[(pyS)$_2$CHCO$_2$](CH$_3$)$_2$}$_2$, **8**, was obtained as colourless crystals, presumably due to the hydrolysis of **3** in the presence of traces of moisture in the solvent (Fig. 2). Treatment of **3** with moist acetonitrile (95:5 v/v CH$_3$CN/H$_2$O) also gave the distannoxane in 80% isolable yield. It is believed that {(CH$_3$)$_2$Sn(OH)[(pyS)$_2$CHCO$_2$]} is the key intermediate during hydrolysis pathway of **3** and subsequently undergo condensation to afford the distannoxane; a similar mechanistic proposition has been suggested for the hydrolysis of other diorganotin dihalides [31] and diorganotin diacetate [32].

The identity of **8** has been established by elemental analysis, IR, NMR spectroscopy, and X-ray crystallography. The IR spectrum of **8** reveals strong absorptions at 1610 and 1410 cm$^{-1}$ due to $\nu_{asym}$ (COO) and $\nu_{sym}$ (COO) bands, respectively. The difference between these bands, $\Delta$ [$\Delta = \nu_{asym}$ (COO) − $\nu_{sym}$ (COO)], is 200 cm$^{-1}$ and it is close to the value found for sodium bis(2-pyridylthio)acetate (204 cm$^{-1}$) and for the unidentate carboxylate groups [23]. Two bands at 490 and 461 cm$^{-1}$, assigned to $\nu_{asym,sym}$(SnO)$_2$ are observed, indicating non-linear Sn–O moieties, while the bands at 228 and 203 cm$^{-1}$ can be assigned to the tin–oxygen (COO) bridging and unidentate stretching modes, respectively [23].

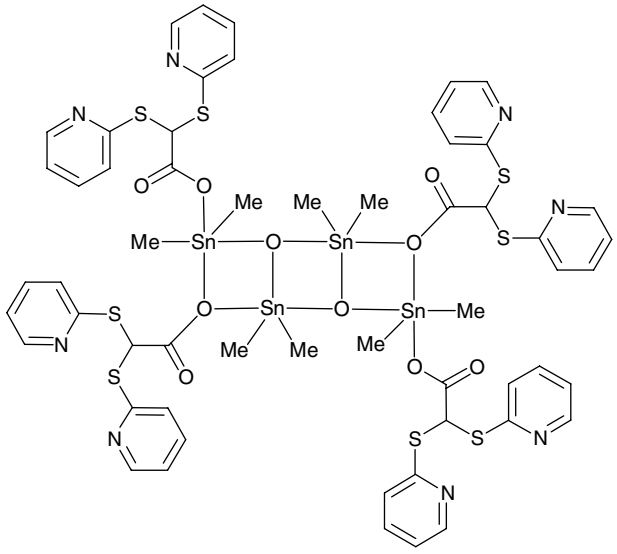


Fig. 2. Structure of dimeric dicarboxylatotetramethyldistannoxane, **8**.

The $^{119}$Sn NMR spectrum shows two resonances of equal intensity at $\delta$ −173.2 and −182.5 due to endocyclic and exocyclic tin atoms, respectively, and suggests the retention of dimeric structure in solution. In this respect, derivative **8** bears a close analogy with symmetric distannoxanes [5d,33] in contrast to asymmetric analogues in which different oxo–tin species are known to exist in dynamic equilibrium in solution [34].

As expected from the crystallographic data of complex **8**, and in accordance with the $^1$H NMR spectrum, two distinct peaks appear in the $^{13}$C NMR spectrum for the alkyltin carbon atoms, reflecting the existence of two differently coordinated tin atoms. The $^1J$(Sn–$^{13}$C) values for [Me$_2$SnLOLSnMe$_2$]$_2$ (**8**), were found to be 741 and 731 Hz, respectively; using the Lockhart and Manders equation [26,27], the C–Sn–C angles in solution, were calculated as 142° and 141°, respectively.

Electrospray ionization is considered a 'soft' ionization technique and is particularly suitable for 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.

For the ligand **1** significant fragments at *m*/*z* 301 and 579 in the positive- and at *m*/*z* 577 in the negative-ion spectra have been attributable to aggregates of the ligand with Na$^+$; peaks at *m*/*z* 110 and 233, respectively due to the fragments [(pyS)]$^-$ and [{(pyS)$_2$CHCO$_2$}-CO$_2$]$^-$, are present in the negative-ion spectrum of **1**. Peaks at *m*/*z* 110, 150, 233, 279, 301 and 579, due to the free O-donor ligand or its decomposition fragments, are present in the spectra of all derivatives **2**–**8**.

The cationic spectra of mono-organotin derivatives **2**, **4** and **6** show peaks, at *m*/*z* 543, 489 and 545, due to the mononuclear complexes [(CH$_3$)SnCl$_2${(pyS)$_2$CHCO$_2$} − H$^+$ + Na$^+$ + K$^+$]$^+$, [(C$_4$H$_9$)SnCl{(pyS)$_2$CHCO$_2$}$_2$]$^+$ and [(C$_6$H$_5$)SnCl$_2${(pyS)$_2$CHCO$_2$H}]$^+$, respectively, index of a great stability of mono-organotin complexes in methanol solution.

More complex fragmentation pattern has been detected in the positive- and negative-ion spectra of dimethyltin derivative **3**; the fragmentation is similar to that found in the spectra of **8**. However, in the positive-ion spectrum of derivative **8**, the major peak at *m*/*z* 807 is attributable to the formation of the stable the tetramethyldistannoxane species.

### 3.1. X-ray structural studies

The solid-state structure of {(CH$_3$)$_2$[(pyS)$_2$CHCO$_2$]-SnOSn[(pyS)$_2$CHCO$_2$](CH$_3$)$_2$}$_2$, (**8**) is shown in Fig. 3 with the atom-numbering scheme. It reflects the

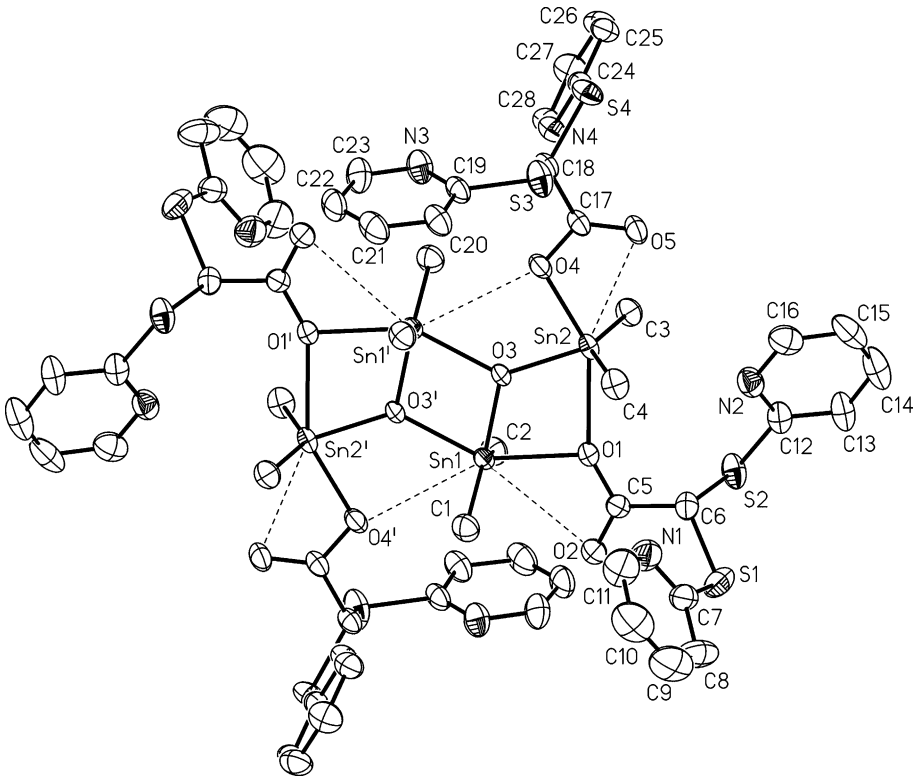


Fig. 3. An ORTEP drawing of a molecular structure of $\{(CH_3)_2[(pyS)_2CHCO_2]SnOSn[(pyS)_2CHCO_2](CH_3)_2\}_2$, **8** (Symmetry codes: at $-x$, $1-y$, $-z$). The Sn–O interactions are shown as dashed lines.

well-known property of organotin units association by oxygen bridges and consists of a ladder-type centrosymmetric dimer were the distannoxane oxygen atoms bonded to the metal atoms form a planar, central, four membered $Sn_2O_2$ ring [10c]. The tin atoms of the asymmetric unit, Sn(1) and Sn(2), are bridged by one carboxylate oxygen of the $(pyS)_2CHCO_2$ ligand, while the second bis(2-pyridylthio)acetate is monodentate on Sn(2) via the oxygen atom O(4). Two methyl groups completed the five coordination to the metal ion with a distorted trigonal bipyramidal geometry; the equatorial positions are occupied by two methyl carbons (C(1) and C(2)) and one oxygen (O(3)) and the axial positions O(1) and O(3)′ for Sn(1) and for Sn(2) by C(3), C(4) and O(3) in the equator, while in axial positions are O(1) and O(4).

The greatest deviations within the trigonal plane are seen in the C–Sn–C angles (C(1)–Sn(1)–C(2) 137.9(4), C(3)–Sn(2)–C(4) 140.6(3)°) and in the *axial* O–Sn–O angles (O(1)–Sn(1)–(O3)′ 147.3(2), O(1)–Sn(2)–O(4) 150.6(1)°). The bridging bis(2-pyridylthio)acetate anions are strongly asymmetric with Sn(1)–O(1) 2.250(4) and Sn(2)–O(1) 2.479(5)Å bond lengths, respectively, as found for the *axial* Sn–O bonds of the stannasiloxanes ($\{[R_2(Me_3SiO)Sn]_2O\}_2$ (R=Me, Et)) derivatives [35].

The tin–carbon distances (mean value 2.098(8)) and the other distances and angles in the molecule are in the expected value. The ligands have weak interactions with the Sn atoms (Sn(1)···O(2) 3.080(5), Sn(1)···O(4)′ 3.179(6) and Sn(2)···O(5) 2.881(7) see Fig. 3) as it has been observed in $[(Me_2SnO_2CC_6H_4\text{-}o\text{-}NH_2)_2]_2$ and $[(Me_2SnO_2CC_6H_4\text{-}p\text{-}NH_2)_2]_2$ [36].

## 4. Supplementary material

Crystallographic data for the structures here reported have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 253974. Copies of the available material can be obtained, free of charge from CCDC, 12 Unino Road, Cambridge, CH2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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