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Investigation on the coordination modes: Syntheses, characterization and crystal structures of diorganotin (IV) dichloride with 4(5)-imidazoledithiocarboxylic acid

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Abstract

A series of diorganotin (IV) complexes of the types of $R_2SnCl(SSCC_3H_3N_2)$ (R = CH₃ 1, "Bu 2, C₆H₅ 3 and C₆H₅CH₂ 4), $R_2Sn(SSCC_3H_3N_2)_2$ (R = CH₃ 5, "Bu 6, C₆H₅ 7 and C₆H₅CH₂ 8) and $R_2Sn(SSCC_3H_2N_2)$ (R = CH₃ 9, "Bu 10, C₆H₅ 11 and C₆H₅CH₂ 12) have been obtained by reactions of 4(5)-imidazoledithiocarboxylic acid with diorganotin (IV) dichlorides in the presence of sodium ethoxide. All complexes are characterized by elemental, IR, ¹H, ¹³C and ¹¹⁹Sn NMR spectra analyses. Also, the complexes 1, 7 and 9 are characterized by X-ray crystallography diffraction analyses, which reveal that the complex 1 is monomeric structure with five-coordinate tin (IV) atom, the complex 7 is monomeric structure with six-coordinate tin (IV) atom and the complex 9 is one-dimensional chain with five-coordinate tin (IV) atom.

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1. Introduction

Increasing investigation of organotin (IV) complexes has been focused on acquiring well-defined solid-state structures to learn the nature of their versatile coordination chemistry [1–5]. Especially, organotin compounds react with the ligands with nitrogen atoms, yielding products characterized by Sn–N bonds [6]. The fact has led to considerable effort being devoted to characterizing model compounds obtained from the ligands that have other donor atoms or group, such as sulfur. A characteristic feature of these complexes in the solid state is that the ligands chelate the tin atom through S and N atoms. In our previous work, we have reported

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on the chemical, structural, and spectroscopic properties of a series of similar organotin (IV) compounds and characterized by different coordinating properties [7]. As an extension of this research program and in connection with our current interest in the coordination chemistry of organotin compounds with heterocyclic ligands, we chose another fascinating ligand: 4(5)-imidazoledithiocarboxylic acid.

This ligand is interesting because of its potential multipledentate coordinate possibilities. Owing to the existence of a deprotonated thiol and more than one coordinative active nitrogen atom, the coordination modes of these novel ligands might bond which takes place either from nitrogen atoms and the deprotonated thiol sulfur or from the dithiocarboxylic moiety. As exhibited in Scheme 1, at least five bonding modes between this ligand and tin are conceivable although nobody investigated its actual coordination mode until

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now. For example, organotin complexes with chelation by both N and S atoms (modes A and B) have been reported [8,9] and the S, S chelations (modes C and D) are commonly observed in organotin dithiocarboxylates [10,11]. In addition, bridging between different molecules via the heterocycles (modes B, D and E) rather than chelation is possible.

Therefore, we design a series of experiments of diorganotin (IV) dichlorides with 4(5)-imidazoledithiocarboxylic acid in the presence of sodium ethoxide. When using a 1:1:1 molar ratio of R₂SnCl₂:HSSCC₃H₃N₂: EtONa, we obtain four monomeric complexes **1–4** of the type of R₂SnCl(SSCC₃H₃N₂) (R = CH₃ **1**, "Bu **2**, C₆H₅ **3** and C₆H₅CH₂ **4**). Using a 1:2:2 molar ratio of R₂SnCl₂:HSSCC₃H₃N₂:EtONa, we obtain four monomeric complexes **5–8** and the general formula is R₂Sn(SSCC₃H₃N₂)₂ (R = CH₃ **5**, "Bu **6**, C₆H₅ **7** and C₆H₅CH₂ **8**). With 1:1:2 ratio of R₂SnCl₂:HSSCC₃-H₃N₂:EtONa, another four one-dimensional polymeric complexes **9–12** of the type of R₂Sn(SSCC₃H₂N₂) (R = CH₃ **9**, "Bu **10**, C₆H₅ **11** and C₆H₅CH₂ **12**) were obtained.

2. Experimental

2.1. Materials and measurements

Dimethyltin dichlorides, di-n-butyltin dichlorides, diphenyltin dichlorides and 4(5)-imidazoledithiocarboxylic acid are commercially available, and they are used without further purification. Dibenzyltin dichlorides were prepared by a standard method reported in the literature [12]. The melting points were obtained with Kofler micro-melting point apparatus and were uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ¹H, ¹³C and ¹¹⁹Sn NMR spectra were recorded on Varian Mercury Plus 400 spectrometer operating at 400, 100.6 and 149.2 MHz, respectively. The spectra were acquired at room temperature (298 K) unless otherwise specified; ¹³C spectra are broadband proton decoupled. The chemical shifts were reported in ppm with respect to the references and were stated relative to external tetramethylsilane (TMS) for ¹H and ¹³C NMR, and to neat tetramethyltin for ¹¹⁹Sn NMR. Elemental analyses (C, H, N) were performed with a PE-2400II apparatus.

2.2. Syntheses

2.2.1. $(CH_3)_2 SnCl(SSCC_3H_3N_2)$ (1)

The reaction is carried out under nitrogen atmosphere. The 4(5)-imidazoledithiocarboxylic acid (0.144 g, 1 mmol) and sodium ethoxide (0.068 g, 1 mmol) were added to the solution of dry benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. After the dimethyltin dichlorides (0.219 g, 1 mmol) were added to the reactor, the reaction mixture was stirred for 12 h at 40 °C and then filtrated. The solvent is gradually removed by evaporation under vacuum until solid product is obtained. The solid is then recrystallized from ethyl ether and the red crystal complex 1 is formed. Yield: 79%. M.p. 108–110 °C. Anal. Calc. for C₆H₉ClN₂S₂Sn: C, 22.01; H, 2.77; N, 8.56. Found: C, 22.25; H, 2.70; N, 8.52%. IR (KBr, cm⁻¹): 3256, 1614, 1258, 1020, 553, 448, 358. ¹H NMR (CDCl₃–D₂O, ppm): δ 0.97(s, 6H, ${}^{2}J_{\text{SnH}} = 87.2$), 7.03(d, 1H), 7.82(d, 1H), 13.20(d, 1H). ¹³C NMR (CDCl₃, ppm): δ 11.3(¹J¹¹⁹Sn⁻¹³C), 521 Hz), 122.1, 124.3, 136.3, 222.3. ¹¹⁹Sn NMR (CDCl₃, ppm): -141.9.

2.2.2. $({}^{n}Bu)_{2}SnCl(SSCC_{3}H_{3}N_{2})$ (2)

The solid is obtained from ethyl ether. Yield: 84%. M.p. 143–145 °C. *Anal.* Calc. for $C_{12}H_{21}ClN_2S_2Sn: C, 35.02; H, 5.14; N, 6.81. Found: C, 35.21; H, 5.31; N, 6.67%. IR (KBr, cm⁻¹): 3245, 1603, 1260, 1024, 560, 459, 371. ¹H NMR (CDCl₃–D₂O, ppm): <math>\delta$ 1.08(t, 6H), 1.50–1.79(m, 12H), 7.01(d, 1H), 7.36(d, 1H), 13.04(d, 1H). ¹³C NMR (CDCl₃, ppm): δ 27.2, 26.5, 26.1, 13.7, 122.4, 124.3, 135.7, 223.1. ¹¹⁹Sn NMR (CDCl₃, ppm): –137.2.

2.2.3. $(Ph)_2 SnCl(SSCC_3H_3N_2)$ (3)

The solid is obtained from ethyl ether. Yield: 82%. M.p. 171–173 °C. *Anal.* Calc. for $C_{16}H_{13}ClN_2S_2Sn$: C, 42.56; H, 2.90; N, 6.20. Found: C, 42.38; H, 3.04; N, 6.39%. IR (KBr, cm⁻¹): 3275, 1623, 1262, 1026, 561, 459, 382. ¹H NMR (CDCl₃–D₂O, ppm): δ 7.31–7.83(m, 10H), 7.18(d, 1H), 7.67(d, 1H), 13.23(d, 1H). ¹³C NMR (CDCl₃, ppm): δ 129.0, 129.3, 137.8, 122.4, 124.1, 135.9, 225.2. ¹¹⁹Sn NMR (CDCl₃, ppm): -176.9.

2.2.4. $(PhCH_2)_2SnCl(SSCC_3H_3N_2)$ (4)

The solid is obtained from ethyl ether. Yield: 79%. M.p. >220 °C (dec.). *Anal*. Calc. for $C_{18}H_{17}ClN_2S_2Sn$: C, 45.07; H, 3.57; N, 5.84. Found: C, 45.16; H, 3.71; N, 5.71%. IR (KBr, cm⁻¹): 3302, 1614, 1263, 1030, 574, 448, 360. ¹H NMR (CDCl₃–D₂O, ppm): δ 3.09(s, 4H), 7.21–7.64(m, 10H), 7.08(d, 1H), 7.81(d, 1H), 13.24 (d, 1H). ¹³C NMR (CDCl₃, ppm): δ 38.1, 127.4, 129.6, 141.5, 122.6, 123.1, 136.7, 225.2. ¹¹⁹Sn NMR (CDCl₃, ppm): –157.2.

2.2.5. $(CH_3)_2 Sn(SSCC_3H_3N_2)_2$ (5)

The solid is obtained from ethyl ether. Yield: 81%. M.p. 176–178 °C. *Anal.* Calc. for $C_{10}H_{12}N_4S_4Sn$: C, 27.60; H, 2.78; N, 12.87. Found: C, 27.52; H, 2.61; N, 12.72%. IR (KBr, cm⁻¹): 3261, 1601, 1260, 1021, 551, 450, 359. ¹H NMR (CDCl₃–D₂O, ppm): δ 0.93(s, 6H), 7.01(d, 2H), 7.89(d, 2H), 13.24(d, 2H). ¹³C NMR (CDCl₃, ppm): δ 11.7, 122.5, 124.0, 136.2, 223.4. ¹¹⁹Sn NMR (CDCl₃, ppm): –201.7.

2.2.6. $({}^{n}Bu)_{2}Sn(SSCC_{3}H_{3}N_{2})_{2}$ (6)

The solid is obtained from ethyl ether. Yield: 90%. M.p. 141–143 °C. *Anal.* Calc. for C₁₆H₂₄N₄S₄Sn: C, 37.00; H, 4.66; N, 10.79. Found: C, 36.85; H, 4.51; N, 10.63%. IR (KBr, cm⁻¹): 3296, 1598, 1257, 1021, 561, 454, 370. ¹H NMR (CDCl₃–D₂O, ppm): δ 1.10(t, 6H), 1.51–1.82(m, 12H), 7.02(d, 2H), 7.80(d, 2H), 13.36(d, 2H). ¹³C NMR (CDCl₃, ppm): δ 27.0, 26.5, 25.8, 13.4, 122.1, 123.3, 136.8, 224.2. ¹¹⁹Sn NMR (CDCl₃, ppm): –198.3.

2.2.7. $(Ph)_2Sn(SSCC_3H_3N_2)_2$ (7)

The solid is recrystallized from ethyl ether and the red crystal complex 7 is formed. Yield: 84%. M.p. >220 °C (dec.). *Anal.* Calc. for C₂₀H₁₆N₄S₄Sn: C, 42.95; H, 2.88; N, 10.02. Found: C, 42.79; H, 3.01; N, 9.86%. IR (KBr, cm⁻¹): 3301, 1612, 1264, 1028, 562, 460 373. ¹H NMR (CDCl₃–D₂O, ppm): δ 7.34–7.81(m, 10H), 7.12(d, 2H), 7.76(d, 2H), 13.01(d, 2H). ¹³C NMR (CDCl₃, ppm): δ 128.1, 130.7, 137.2, 122.7, 123.5, 136.3, 225.9. ¹¹⁹Sn NMR (CDCl₃, ppm): –208.9.

2.2.8. $(PhCH_2)_2Sn(SSCC_3H_3N_2)_2$ (8)

The solid is obtained from ethyl ether. Yield: 76%. M.p. 182–184 °C. *Anal.* Calc. for $C_{22}H_{20}N_4S_4Sn$: C, 44.98; H, 3.43; N, 9.54. Found: C, 44.79; H, 3.58; N, 9.41%. IR (KBr, cm⁻¹): 3322, 1604, 1267, 1031, 572, 445, 361. ¹ H NMR (CDCl₃–D₂O, ppm): δ 3.11(s, 4H), 7.28–7.61(m, 10H), 7.03(d, 2H), 7.84(d, 2H), 13.34 (d, 2H). ¹³C NMR (CDCl₃, ppm): δ 38.1, 127.5, 129.4, 141.5, 143.6, 123.1, 124.0, 136.5, 225.2. ¹¹⁹Sn NMR (CDCl₃, ppm): –191.0.

2.2.9. $(CH_3)_2 Sn(SSCC_3H_2N_2)$ (9)

The solid is recrystallized from ethyl ether and the red crystal complex **9** is formed. Yield: 78%. M.p. >220 °C (dec.). *Anal.* Calc. for C₆H₈N₂S₂Sn: C, 24.77; H, 2.77; N, 9.63. Found: C, 24.65; H, 2.70; N, 9.52%. IR (KBr, cm⁻¹): 1607, 1266, 1022, 558, 457, 361. ¹H NMR (CDCl₃, ppm): δ 0.89(s, 6H, ²J_{SnH} = 64.6), 7.06(s, 1H),

7.73(s, 1H). ¹³C NMR (CDCl₃, ppm): δ 10.2(¹*J*¹¹⁹Sn–¹³C), 467 Hz), 122.5, 124.1, 136.2, 220.5. ¹¹⁹Sn NMR (CDCl₃, ppm): -77.4.

2.2.10. $({}^{n}Bu)_{2}Sn(SSCC_{3}H_{2}N_{2})$ (10)

The solid is obtained from ethyl ether. Yield: 85%. M.p. 152–154 °C. *Anal.* Calc. for $C_{12}H_{20}N_2S_2Sn$: C, 38.42; H, 5.37; N, 7.47. Found: C, 38.31; H, 5.41; N, 7.38%. IR (KBr, cm⁻¹): 1611, 1253, 1020, 547, 451, 365. ¹H NMR (CDCl₃, ppm): δ 1.15(t, 6H), 1.56–1.78(m, 12H), 7.01(s, 1H), 7.80(s, 1H). ¹³C NMR (CDCl₃, ppm): δ 27.5, 26.8, 26.3, 13.6, 122.9, 124.2, 135.8, 223.3. ¹¹⁹Sn NMR (CDCl₃, ppm): -72.1.

2.2.11. $(Ph)_2Sn(SSCC_3H_2N_2)$ (11)

The solid is obtained from ethyl ether. Yield: 82%. M.p. >220 °C (dec.). *Anal.* Calc. for $C_{16}H_{12}N_2S_2S_1$: C, 46.29; H, 2.91; N, 6.75. Found: C, 46.18; H, 3.04; N, 6.59%. IR (KBr, cm⁻¹): 1608, 1257, 1024, 551, 449, 380. ¹H NMR (CDCl₃, ppm): δ 7.35–7.78(m, 10H), 7.18(s, 1H), 7.81(s, 1H). ¹³C NMR (CDCl₃, ppm): δ 129.1, 129.7, 137.5, 122.7, 123.5, 135.9, 225.0. ¹¹⁹Sn NMR (CDCl₃, ppm): -85.7.

2.2.12. $(PhCH_2)_2Sn(SSCC_3H_2N_2)$ (12)

The solid is obtained from ethyl ether. Yield: 86%. M.p. >220 °C (dec.). *Anal.* Calc. for $C_{18}H_{16}N_2S_2Sn$: C, 48.78; H, 3.64; N, 6.32. Found: C, 48.66; H, 3.71; N, 6.21%. IR (KBr, cm⁻¹): 1606, 1263, 1021, 561, 447, 369. ¹ H NMR (CDCl₃, ppm): δ 3.15(s, 4H), 7.30–7.58(m, 10H), 7.07(s, 1H), 7.79(s, 1H). ¹³C NMR (CDCl₃, ppm): δ 38.3, 127.2, 129.7, 141.0, 122.1, 122.9, 136.4, 224.5. ¹¹⁹Sn NMR (CDCl₃, ppm): -79.2.

2.3. X-ray crystallographic studies

Diffraction data were collected on a Smart CCD areadetector with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A semiempirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full matrix least-squares using SHELXL-97. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

3. Results and discussion

3.1. Syntheses

Reactions of diorganotin (IV) dichlorides with 4(5)imidazoledithiocarboxylic acid in 1:1 or 1:2 stoichiometry depending on the nature of the starting acceptor and reaction condition afford air-stable complexes in good yields. The syntheses procedures are shown in Scheme 2.

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Table 1 Crystal, data collection and structure refinement parameters for complexes 1, 7 and 9

Complex	1	7	9
Empirical formula	$C_6H_9N_2S_2Sn$	$C_{20}H_{16}N_4S_4S_n$	$C_6H_8N_2S_2Sn$
Formula weight	327.41	559.30	290.95
Temperature	298(2)	298(2)	298(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	P2(1)/c	C2/c	Fdd2
Unit cell dimension			
a (Å)	12.757(5)	22.94(3)	20.434(10)
b (Å)	13.162(5)	17.46(2)	17.937(9)
<i>c</i> (Å)	14.247(5)	16.22(19)	19.299(9)
β (°)	103.057(5)	135.00(2)	90
Ζ	8	8	16
Absorption coefficient (mm ⁻¹)	2.735	1.490	1.648
Crystal size (mm)	$0.45 \times 0.41 \times 0.22$	$0.36 \times 0.19 \times 0.16$	$0.17 \times 0.15 \times 0.10$
θ Range for data collection (°)	2.13-25.03	2.33-25.03	3.70-25.03
Index ranges	$-15 \leqslant h \leqslant 15;$	$-25 \leqslant h \leqslant 27;$	$-17 \leq h \leq 24;$
	$-15 \leqslant k \leqslant 15;$	$-20 \leqslant k \leqslant 20;$	$-20 \leqslant k \leqslant 21;$
	$-15 \leqslant l \leqslant 16$	$-19 \leqslant l \leqslant 12$	$-22 \leqslant l \leqslant 22$
Reflections collected	11743	11 201	8472
Unique reflections $[R_{int}]$	4026 [0.0328]	3984 [0.0980]	3001 [0.1248]
Data/restraints/parameters	4026/0/217	3984/0/263	3001/1/100
S (goodness-of-fit) on F^2	1.000	0.903	0.728
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0347, wR_2 = 0.0917$	$R_1 = 0.0599, wR_2 = 0.1289$	$R_1 = 0.0492, wR_2 = 0.0788$
R indices (all data)	$R_1 = 0.0618, wR_2 = 0.1144$	$R_1 = 0.1100, wR_2 = 0.1518$	$R_1 = 0.1669, wR_2 = 0.0993$

3.2. Spectroscopic studies

3.2.1. IR spectra

The stretching frequencies of interest are those associated with the acid CSS, Sn–C, Sn–S and Sn–N groups. In the infrared spectra of all complexes the absence of the band at about 2590 cm⁻¹, which appears in the free-ligand as the v(S–H) vibration, indicates metal–ligand bond formation through this site. While strong absorption appearing in the region 350–400 cm⁻¹, which is absent in the free ligand, is assigned to the Sn–S stretching mode of vibration. All these values are consistent with that detected in a number of organotin (IV) derivatives [13,14]. The v(C=N) band, occurring at about 1604 cm⁻¹, is considerably shifted towards lower frequencies with respect to that of the free ligand, confirming the coordination of the heterocyclic N to the tin. The stretching frequency is



(when A: B: C= 1: 1: 1, complexes1-4; A:B:C= 1: 2: 2, complexes 5-8; A: B: C= 1: 1:2, complexes 9-12)

lowered owing to the displacement of electron density from N to Sn atom, thus resulting in the weakening of the C=N bond as reported in the literature [15]. So that the weak- or medium-intensity bands in the region $445-470 \text{ cm}^{-1}$ are assigned to Sn–N stretching vibrations.

3.2.2. NMR spectroscopic

¹H NMR spectroscopy of the free ligand, single resonance is observed at 1.61 ppm, which is absent in the spectra of the complexes, indicating the replacement of the dithiocarboxylic acid proton by a diorganotin moiety. In addition, the presence of the N–H proton signal in the complexes 1–8 reveals that the other N atom does not coordinate to Sn, which further testifies their formations. The ${}^{2}J_{\text{SnH}}$ of dimethyltin derivatives 1 and 9 has a value of 87.2, falling in the range for five coordinated trigonal bipyramidal tin (IV) adducts [16].

The ¹³C NMR spectra of all complexes show a significant downfield shift of all dithiocarboxylic resonances, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor. The ${}^{1}J_{\rm SnC}$ value for 1 is 521 Hz, similar to that of the five-coordinate compound, and the calculated θ (C–Sn–C) by the Holeček and Lyčka equation [16] are 122.5°, which are close to the angles observed in the solid state for 1. So it can be reasonably assumed that the structure in solution of all these complexes is likely similar to that observed in the solid state.

The ¹¹⁹Sn NMR data show 1 only one signal, typical of a five-coordinate species, which have been found in accordance with the structure of solid state [17]. The chemical shift for 7 shows -208.9 ppm, which is almost within the range corresponding to coordination number 6, -210 to -400 ppm [18]. However, the chemical shift for 9 shows -77.4 ppm within the range corresponding to coordination number 4, -60 to +200 ppm [18]. So it can be reasonably assumed that the structure in solution of 9 is likely different from that observed in the solid state.

4. Crystal structures

4.1. Crystal structure of $(CH_3)_2 SnCl(SSCC_3H_2N_2)$ (1)

For complex 1, the asymmetric unit contains two monomers A and B (Fig. 1), which are different from a crystallographic point of view. The conformations of the two independent molecules A and B are almost the same, with only small differences in bond lengths and bond angles (Table 1). Tin forms four primary bonds: two to the methyl groups, and one each to sulfur and chlorine atoms. In addition, there exists a coordination interaction between tin and nitrogen atoms. The Sn-N bond lengths are 2.357(5) Å [Sn(1)–N(1)] and 2.319(5) Å [Sn(2)–N(3)]. All these values lie in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [19], but are considerably less than the van der waal's radii of the two atoms (3.74 Å) [20], thus providing five-membered chelate rings with bite angles of 76.70(13)° for N(1)-Sn(1)-S(1) and of 76.69(14)° for N(3)-Sn(2)-S(3). Including the tin-nitrogen interaction, the geometry at tin becomes distorted *cis*-trigonal bipyramidal with the nitrogen and chlorine atoms in axial sites (Cl(1)–Sn(1)–N(1), 160.48(13)° and Cl(2)–Sn(2)–N(3),



Fig. 2. The unit cell of complex 1.



Fig. 1. The molecular structure of complex 1.

159.11(14)°) and one sulfur and two methyl carbon atoms occupying the equatorial plane (C(5)-Sn(1)-C(6), 126.8(3)° and C(11)–Sn(2)–C(12), 125.7(3)°). The sum of the angles subtended at the tin atom in the trigonal plane is 358.6° for A and 359.5° for B, so that the atoms Sn(1), C(5), C(6) and S(1) for A and Sn(2), C(11), C(12) and S(3) for B are almost in the same plane. The Sn-Cl bond length (Sn(1)-Cl(1), 2.484(2) Å and Sn(2)–Cl(2), 2.480(2) Å) lies in the range of the normal covalent radii (2.37–2.60 Å) [19]. The Sn–S bond length (Sn(1)-S(2), 2.4798(18) Å and Sn(2)-S(3), 2.4892(17) Å)is well within the range of 2.478-2.541 Å reported for dimethyltin dithiocarboxyl complexes [21,22], it is shorter than that of $Me_2Sn[(S_2CN(CH_2)_4) 2.518(1)]$ Å [23] and it is almost equal to that of $Me_2Sn(S_2CNEt_2)_2$ Me₂Sn(S₂CNMe₂)₂ 2.47(1) Å [24] and 2.488(1) Å [25]. Finally, the Sn–C bond lengths are approximately equal (from 2.104(6) and 2.113(9) Å), similar to the average value of 2.13 Å [20].

4.2. Crystal structure of $(Ph)_2Sn(SSCC_3H_3N_2)_2$ (7)

The molecular structure and unit cell are shown in Figs. 3 and 4. Selected bond lengths (Å) and angles (°) are listed in Table 3. For the complex 7, similar to the complex 1, there exist two monomers in the asymmetric unit. Both ligands chelate to one tin, bonding through one dithiocarboxylate sulfur and the nitrogen atom. The complex contains a hexa-coordinated tin atom and has a distorted octahedral environment. Two carbons of phenyl and two sulfur atoms of the two ligands are covalently linked to the tin. The valence extension is preformed via two nitrogen atoms. The carbons are situated in a *cis* position to each other C(17)–Sn(1)–C(18) 102.4(4)° and C(15)–Sn(2)–C(15)#2 102.7(4)°. Distortions from strict

octahedral coordination are partly because of the bonding variety. The two sulfur atoms occupy *trans* positions S(1)-Sn(1)-S(1)#1 157.42(1)° and S(3)#2-Sn(2)-S(3) 157.35(11)°, while the cases for the nitrogen bonding vary and they occupy *cis* positions (N(1)-Sn(1)-N(1)#1, 76.6(3)°. Besides, on each side of the tin atom, the S and N equatorial ligating atoms belong to the same moiety (N(1)-Sn(1)-S(1) 75.43(18)°, N(1)-Sn(1)-S(1)#1 86.81(18)°, N(1)#1-Sn(1)-S(1) 86.81(18)° and N(1)#1-Sn(1)-S(1)#1 75.43(18)° for A and N(3)-Sn(2)-S(3) 75.45(17)°, N(3)#2-Sn(2)-S(3) 86.78(18)°, S(3)#2-Sn(2)-S(3) 157.35(11)° and N(3)#2-Sn(2)-S(3)#2



Fig. 4. The unit cell of complex 7.



Fig. 3. The molecular structure of complex 7.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex 1

Molecule A		Molecule B	
Sn(1)–C(5)	2.104(6)	Sn(2)–C(11)	2.109(7)
Sn(1)–C(6)	2.108(7)	Sn(2)-C(12)	2.113(9)
Sn(1)-N(1)	2.357(5)	Sn(2)–N(3)	2.319(5)
Sn(1)-S(1)	2.4798(18)	Sn(2)–Cl(2)	2.480(2)
Sn(1)-Cl(1)	2.484(2)	Sn(2)–S(3)	2.4892(17)
Sn(1)–Cl(2)	3.922(3)	Sn(2)-Cl(1)#1	4.243(2)
C(5)-Sn(21)-C(6)	126.8(3)	C(11)-Sn(2)-C(12)	125.7(3)
C(5)-Sn(1)-N(1)	88.4(2)	C(11)-Sn(2)-N(3)	94.7(3)
C(6)-Sn(1)-N(1)	91.9(3)	C(12)-Sn(2)-N(3)	90.8(3)
C(5)-Sn(1)-S(1)	116.8(2)	C(11)-Sn(2)-Cl(2)	97.3(2)
C(6)–Sn(1)–S(1)	115.0(2)	C(12)-Sn(2)-Cl(2)	96.1(3)
N(1)-Sn(1)-S(1)	76.70(13)	N(3)-Sn(2)-Cl(2)	159.11(14)
C(5)–Sn(1)–Cl(1)	98.3(2)	C(11)-Sn(2)-S(3)	110.8(2)
C(6)-Sn(1)-Cl(1)	98.6(3)	C(12)-Sn(2)-S(3)	123.0(2)
N(1)-Sn(1)-Cl(1)	160.48(13)	N(3)-Sn(2)-S(3)	76.69(14)
S(1)-Sn(1)-Cl(1)	83.94(6)	Cl(2)-Sn(2)-S(3)	83.06(7)
C(5)–Sn(1)–Cl(2)	63.30(19)	C(11)-Sn(2)-Cl(1)#1	62.0(2)
C(6)–Sn(1)–Cl(2)	75.8(3)	C(12)-Sn(2)-Cl(1)#1	64.2(2)
N(1)-Sn(1)-Cl(2)	128.37(13)	N(3)-Sn(2)-Cl(1)#1	103.58(13)
S(1)–Sn(1)–Cl(2)	153.79(6)	Cl(2)-Sn(2)-Cl(1)#1	97.15(7)
Cl(1)–Sn(1)–Cl(2)	70.53(6)	S(3)-Sn(2)-Cl(1)#1	172.83(6)

75.45(17)° for B, so their positions are fixed and the S–Sn– N angles can only admit very little deformation.

Due to the symmetry operation, two Sn–S and Sn–N bonds are identical, respectively. Both the Sn–S bond lengths 2.596(3) Å are greater than that in $[Ph_2Sn(S_2CO'Pr)_2]$ (Sn–S 2.482(1) Å) [26] and $[Ph_2Sn(S_2CC_6H_4CH_3-4)_2]$ (Sn–S 2.482(7) Å) [27], but

Table 3 Selected bond lengths (Å) and bond angles (°) for complex 7

within the sum of the van der Waals radii of 4.05 Å for tin and sulfur atom [28]. The Sn–N distances Sn(1)-N(1) are longer than the sum of the covalent radii of Sn and N (2.15 Å), but all these values lie in the range recorded in the Cambridge Crystallographic Database from 2.27 to 2.58 Å [19].

4.3. Crystal structure of $(CH_3)_2Sn(SSCC_3H_2N_2)$ (9)

The molecule structure is connected in polymeric structures as shown in Fig. 5. Selected bond lengths (Å) and angles (°) are listed in Table 4. Intermolecular tin-nitrogen bonds (2.311(11) Å) that are comparable in strength to the intramolecular tin–nitrogen bonds and close in length to the sum of the covalent radii of tin and nitrogen, 2.15 Å [20], create a continuous polymeric chain.

For the complex, the ligand chelates to one tin, bonding through one dithiocarboxylate sulfur and the nitrogen atom, an additional intermolecular Sn–N interaction between the other nitrogen atom of the 4(5)-imidazoledithiocarboxylic acid and the tin atom of a neighboring molecule gives rise to the polymeric structure. Therefore, the ligand is tridentate in the complex. The overall configuration at tin is best described as distorted trigonal bipyramidal: tin and the bonded sulfur and carbon atoms are nearly coplanar and deviate only slightly from regular distorted geometry, mean deviation from plane is 0.0176 Å with N(1) and N(2)#1 (-x + 1/4, y + 1/4, z + 1/4) occupying the axial sites, the axial-Sn-axial, N(1)–Sn–N(2)#1 is

Selected bolid lengths (11) and boli	a angles () for complex /		
Sn(1)–C(5)	2.155(8)	Sn(2)–C(15)	2.177(8)
Sn(1)-C(5)#1	2.155(8)	Sn(2)-C(15)#2	2.177(8)
Sn(1)–N(1)#1	2.323(7)	Sn(2)–N(3)#2	2.339(6)
Sn(1)–N(1)	2.323(6)	Sn(2)–N(3)	2.339(6)
Sn(1)–S(1)#1	2.596(3)	Sn(2)–S(3)#2	2.596(3)
Sn(1)–S(1)	2.596(3)	Sn(2)–S(3)	2.596(3)
C(1)–S(1)	1.729(8)	C(11)–S(3)	1.722(8)
C(1)–S(2)	1.674(8)	C(11)–S(4)	1.667(8)
C(5)-Sn(1)-C(5)#1	102.4(4)	C(15)-Sn(2)-C(15)#2	102.7(4)
C(5)-Sn(1)-N(1)#1	161.1(2)	C(15)-Sn(2)-N(3)#2	91.6(3)
C(5)#1-Sn(1)-N(1)#1	92.1(3)	C(15)#2-Sn(2)-N(3)#2	161.7(2)
C(5)–Sn(1)–N(1)	92.1(3)	C(15)–Sn(2)–N(3)	161.7(2)
C(5)#1-Sn(1)-N(1)	161.1(2)	C(15)#2–Sn(2)–N(3)	91.6(3)
N(1)#1-Sn(1)-N(1)	76.6(3)	N(3)#2–Sn(2)–N(3)	77.0(3)
C(5)-Sn(1)-S(1)#1	89.0(2)	C(15)–Sn(2)–S(3)#2	104.4(2)
C(5)#1-Sn(1)-S(1)#1	105.2(2)	C(15)#2-Sn(2)-S(3)#2	89.8(2)
N(1)#1-Sn(1)-S(1)#1	75.43(18)	N(3)#2-Sn(2)-S(3)#2	75.45(17)
N(1)-Sn(1)-S(1)#1	86.81(18)	N(3)-Sn(2)-S(3)#2	86.78(18)
C(5)-Sn(1)-S(1)	105.2(2)	C(15)–Sn(2)–S(3)	89.8(2)
C(5)#1-Sn(1)-S(1)	89.0(2)	C(15)#2–Sn(2)–S(3)	104.4(2)
N(1)#1-Sn(1)-S(1)	86.81(18)	N(3)#2–Sn(2)–S(3)	86.78(18)
N(1)-Sn(1)-S(1)	75.43(18)	N(3)–Sn(2)–S(3)	75.45(17)
S(1)#1-Sn(1)-S(1)	157.42(11)	S(3)#2–Sn(2)–S(3)	157.35(11)
S(1)-C(1)-S(2)	120.8(5)	S(3)-C(11)-S(4)	121.5(5)

Symmetry codes: #1 -x + 1, y, -z + 3/2; #2 -x + 1, y, -z + 1/2.



Fig. 5. The molecular structure of complex 9.

 $157.8(4)^{\circ}$. In such structures, the sum of angles between the tin atom and the equatorial ligating atoms (two C and one S in each case) is 359.9° , compared with the ideal octahedral value of 360° .

The average Sn–C bond lengths are 2.155 Å, in good agreement with the published values [19]. These values also correspond well with the sum of the covalent radii (2.15 Å) of tin and carbon [29]. The Sn–N distances, 2.260(9) and 2.311(11) Å, are slightly greater than the sum of the covalent radii of tin and nitrogen, 2.15 Å [20], but in keeping with those reported in Sn–N compounds Me₂SnCl(2-Pic) [30], Me₂Sn(2-Pic)₂ [31] and {["Bu₂Sn(2-Pic)]₂O}₂ [32]. Concerning the Sn–S bond lengths, we may note that the complex 1 is slightly longer than the sum of the atomic radii (2.44 Å) [33], as the case is 2.454(3) Å, similar to that reported in penta-coordinated organotin complexes (2.47 Å) [34].

In summary,the 4(5)-imidazoledithiocarboxylic acid has been shown to be able to form monomeric and one-dimensional supramolecular complexes. The nuclearity and stoichiometry are found to depend on the nature of the starting acceptor and reaction condition. When using a 1:1:2 molar ratio of R_2SnCl_2 :HSSCC₃H₃-N₂:EtONa, four one-dimensional chain complexes were obtained. The ligand chelates to the tin, bonding through

Table 4					
Selected bond	lengths (Å) and bond	angles (°) for complex 9	

-			
Sn(1)–C(6)	2.092(16)	Sn(1)-S(1)	2.454(3)
Sn(1)-C(5)	2.219(13)	Sn(1)#2-N(2)	2.311(11)
Sn(1)-N(1)	2.260(9)	C(1) - S(1)	1.743(12)
Sn(1)-N(2)#1	2.311(11)	C(1)–S(2)	1.671(14)
C(5)-Sn(1)-C(6)	123.7(7)	C(6)-Sn(1)-S(1)	118.0(5)
C(6)-Sn(1)-N(1)	100.4(5)	C(5)-Sn(1)-S(1)	118.2(5)
C(5)-Sn(1)-N(1)	94.8(4)	N(1)-Sn(1)-S(1)	77.5(3)
C(6)-Sn(1)-N(2)#1	93.2(5)	N(2)#1-Sn(1)-S(1)	80.7(3)
C(5)–Sn(1)–N(2)#1	92.0(5)	S(1)-C(1)-S(2)	118.0(8)
N(1)-Sn(1)-N(2)#1	157.8(4)		

Symmetry codes: #1 -x + 1/4, y + 1/4, z + 1/4; #2 -x + 1, y - 1/4, z - 1/4.

the sulfur of dithiocarboxylate and two nitrogen atoms. The Sn–N bond lengths 2.206–2.260 Å approach the sum of the covalent radii of Sn and N (2.15 Å). So the ligand is tridentate and the coordinated number of tin atom is five. However, monomeric complexes possess five- or six-coordinate tin atoms and the ligand is bidentate. The Sn–N bond lengths are 2.323 Å. All these are also confirmed by IR and ¹H NMR spectra analyses. See (Fig. 2 and Table 2).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis of complexes 1, 7 and 9 have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 248294 1, 228114 7 and 223778 9. Copies of these information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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