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New dimeric, trimeric and supramolecular organotin(IV) dithiocarboxylates: Synthesis, structural characterization and biocidal activities

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ABSTRACT

Some new tri-, chlorodi- and diorganotin(IV) dithiocarboxylates (**1**–**10**) of 4-benzylpiperidine-1-carbodithioate ligand (L), with general formulae R_3SnL {R = *n*-C_4H_9 (**1**), C_6H_{11} (**2**), CH_3 (**3**) and C_6H_5 (**4**)}, R_2SnClL {R = *n*-C_4H_9 (**5**), C_2H_5 (**7**), CH_3 (**9**)} and R_2SnL_2 {R = *n*-C_4H_9 (**6**), C_2H_5 (**8**), CH_3 (**10**)}, have been synthesized by the reaction of organotin(IV) chlorides with the ligand-salt in the appropriate molar ratio. Elemental analysis, Raman, IR, multinuclear NMR (^1H, ^{13}C and ^{119}Sn) and X-ray crystallographic studies have been undertaken to elucidate the structures of the complexes, both in solution and in solid state. Single-crystal X-ray diffraction study indicate trimeric, dimeric, supramolecular cyclic and supramolecular zig–zag chain structures for complexes **2**, **4**, **6** and **9**, respectively. Square-pyramidal geometry is attributed to complex **9** on the basis of the τ value (0.4). A subsequent antimicrobial study indicates that the compounds are biologically active.

1. Introduction

Dithiocarboxylate anions are among the most well-known metal-coordinating agents. These anions are highly effective ligands for metals owing to the stability of the resulting metal dithiocarboxylates, due to a significant contribution of the resonance form shown in the Scheme 1 (structure IV) to the overall electronic structure. Underscoring the affinity of dithiocarboxylate ligands for metals, these ligands also play a significant role in medicine. For example, the diethyldithiocarbamate anion, $Et_2CNS_2^-$, has had extensive clinical use as antidote for copper poisoning, i.e., Wilson's disease [1] and ameliorating nephrotoxicity associated with platinum-based chemotherapy [2]. In addition to the medicinal uses, metal dithiocarboxylates are used in the vulcanization of rubber [3], as pesticides [4] and as synthetic precursors for the deposition of metal sulfide nanoparticles [5]. The synthesis of metal complexes with this type of active ligand is a research area of increased interest in inorganic, pharmaceutical and medicinal chemistry as a possible approach to the development of new drugs. A judicious choice of ligands can modulate the properties of complexes. Consequently, metal-based dithiocarboxylates such as *ziram* (zinc-dimethyldithiocarboxylate) and *zineb* (zinc ethylene-1,2-bis-dithiocarboxylate) are marketed as fungicides. Organotin(IV) dithiocarboxylates, in particular, are continuing to attract significant attention because of their structural diversity and variety of biological applications, e.g., fungicidal, bactericidal, insecticidal and antitumor activity [6–9]. These complexes exert their toxic effect owing to the non-covalent interactions with the cell constituents [10]. Encouraged by these findings and our interest in the field of organotin complexes [11], we decided to synthesize tin-based dithiocarboxylates with a new ligand, 4-benzylpiperidine-1-carbodithioate, and then screen them for fungicidal and bactericidal activity, thereby widening their scope in biological applications (Scheme 2a).

2. Experimental

2.1. Materials and methods

The reagents, triorganotin(IV) chlorides, diorganotin(IV) dichlorides and 4-benzylpiperidine were obtained from Aldrich Chemical CO., while CS_2 was purchased from Riedal-de Haën. Methanol was dried before use by the literature procedure [12]. Microanalyses were performed using a Leco CHNS 932 apparatus. IR spectra were recorded with KBr pellets in the range from 4000 to 400 cm^{-1}

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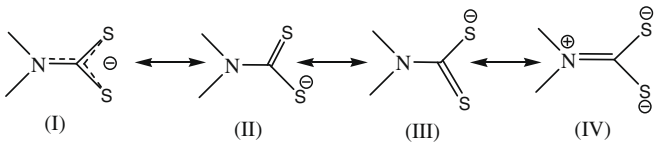


Scheme 1. Resonant forms of the $-NCSS^-$ moiety.

using a Bio-Rad Excaliber FT-IR, model FTS 300 MX spectrometer (USA). Raman spectra (±1 cm^{-1}) were measured with an InVia Renishaw spectrometer, using argon-ion (514.5 nm) and near-infrared diode (785 nm) lasers. WIRE 2.0 software was used for the data acquisition and spectra manipulations. The ^1H and ^{13}C NMR spectra were obtained by a Hg-300 MHz spectrometer and the ^{119}Sn NMR spectra were recorded on a Varian Unity 500-MHz instrument using Me_4Sn as external reference.

2.2. Syntheses

2.2.1. Synthesis of 4-benzylpiperidinium 4-benzylpiperidine-1-carbodithioate (L-salt)

Carbon disulfide (in excess) in methanol (50 mL) was added dropwise to 4-benzylpiperidine (5 g, 28.57 mmol) in methanol (50 mL) and the mixture was stirred for 4 h at 273 K. The solvent was evaporated under reduce pressure to yield a white product, which was recrystallized from methanol. (Yield: 4.68 g, 77%). M.p. 132–134 °C. *Anal.* Calc. for $C_{25}H_{34}N_2S_2$ (426.7): C, 70.37; H, 8.03; N, 6.57; S, 15.03. Found: C, 70.22; H, 7.97; N, 6.61; S, 14.91%. Raman (cm^{-1}): 644 ν(C–S), 1075 ν(C=S), 1455 ν(C–N). IR (cm^{-1}): 1017 ν(C–S), 1453 ν(C–N). ^1H NMR (ppm): 3.04–2.96, 2.60–2.58, 2.82–2.67, 2.60–2.58, 1.84–1.64, 1.35–1.27 (m, 18H, piperidine-H), 5.77, 3.79 (d, 4H, CH_2), 7.34–7.14 (m, 10H, Ar–H), 8.3 (s, 2H, NH_2). ^{13}C NMR (ppm): 208.8 (C-1), 51.2, 44.7, 38.2, 36.5, 32.4, 29.7, (piperidine-C), 42.9, 42.8 (CH_2), 140.1, 139.4, 129.1, 129.0, 128.4, 128.3, 126.3, 126.0 (Ar–C).

2.2.2. General procedure for synthesis of complexes

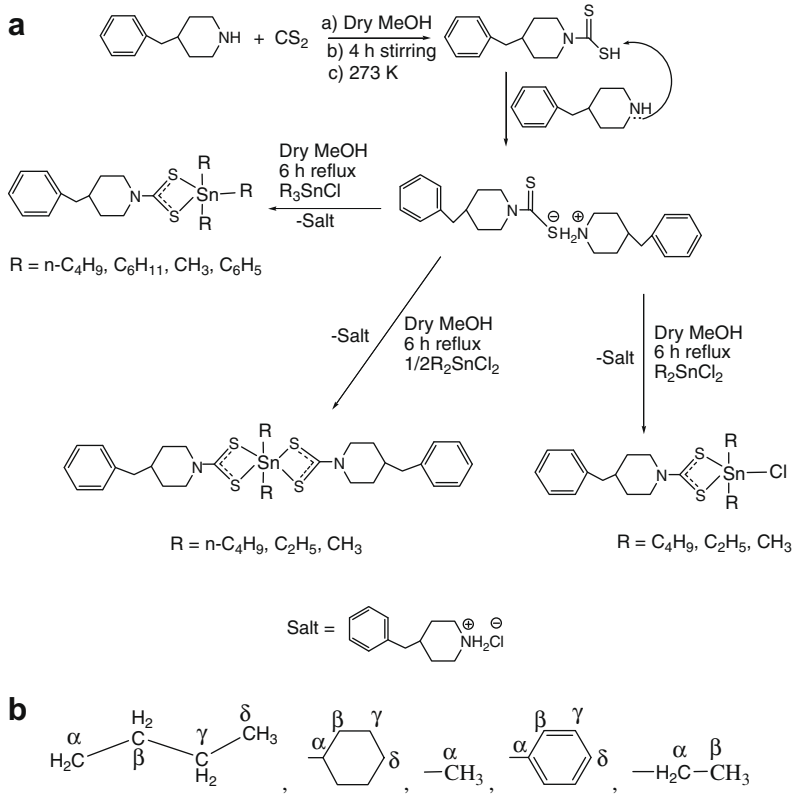
Triorganotin(IV) chloride and diorganotin(IV) dichloride in methanol (30 mL) was added dropwise to the ligand-salt in methanol (50 mL) in the appropriate molar ratio and the mixture was refluxed for 6 h with constant stirring. The salt was allowed to settle and was removed by filtration. The filtrate was rotary evaporated and the product thus obtained was recrystallized from chloroform–ethanol (4:1) mixture (Scheme 2a).

2.2.3. Tributyltin(IV) 4-benzylpiperidine-1-carbodithioate **(1)**

(Yield: 0.46 g, 74%). Sticky material. *Anal.* Calc. for $C_{25}H_{43}NS_2Sn$ (540.5): C, 55.56; H, 8.02; N, 2.59; S, 11.87. Found: C, 55.49; H, 7.93; N, 2.56; S, 11.81%. Raman (cm^{-1}): 587 ν(C–S), 1030 ν(C=S), 1440 ν(C–N), 504 ν(Sn–C), 380 ν(Sn–S). IR (cm^{-1}): 965 ν(C–S), 1467 ν(C–N). ^1H NMR (ppm): 1.38–1.28, 3.08–3.04, 1.85–1.78 (m, 9H, piperidine-H) 5.19 (d, $^3J_{H-H}$ = 12.9 Hz, 2H, CH_2), 7.33–7.12 (m, 5H, Ar–H), 1.65–1.20 (m, 18H, $H_{\alpha,\beta,\gamma}$, SnBu), 0.93 (t, $^3J_{H-H}$ = 7.3 Hz, 9H, H_δ, SnBu). ^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 197.2 (CS), 36.5, 42.6, 52.4 (piperidine-C), 31.9 (CH_2), 139.8, 129.1, 128.5, 126.3 (Ar–C), 17.5 {(C-α, SnBu), [341]}, 29.1 {(C-β, SnBu), [18]} 27.8 {(C-γ, SnBu), [68]}, 13.7 (C-δ, SnBu). ^{119}Sn NMR: δ −129.6.

2.2.4. Tricyclohexyltin(IV) 4-benzylpiperidine-1-carbodithioate **(2)**

(Yield: 0.51 g, 70%). M.p. 122–124 °C. *Anal.* Calc. for $C_{31}H_{49}NS_2Sn$ (618.6): C, 60.19; H, 7.98; N, 2.26; S, 10.37. Found: C, 60.07; H, 7.90; N, 2.23; S, 10.30%. Raman (cm^{-1}): 547 ν(C–S), 1077 ν(C=S), 1472 ν(C–N), 645 ν(Sn–C), 370 ν(Sn–S). IR (cm^{-1}): 963 ν(C–S), 1460 ν(C–N). ^1H NMR (ppm): 1.34–1.29, 1.82–1.75, 3.07–2.99 (m, 9H, piperidine-H) 5.19 (d, $^3J_{H-H}$ = 13.2 Hz, 2H, CH_2), 7.30–7.11 (m, 5H, Ar–H), 1.96–1.24 (m, 33H, $H_{\alpha,\beta,\gamma,\delta}$, SnC_6H_{11}). ^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 198.7 (CS), 37.7, 42.8, 52.8 (piperidine-



Scheme 2. (a) Synthesis of ligand-salt and complexes and (b) numbering scheme of organic groups attached to Sn atom.

C), 31.7 (CH_2), 140.1, 129.3, 128.5, 126.3 (Ar–C), 35.0 {(C-α, SnC_6H_{11}), [334]}, 32.2 {(C-β, SnC_6H_{11}), [16]} 29.5 {(C-γ, SnC_6H_{11}), [67]}, 27.2 (C-δ, SnC_6H_{11}). ^{119}Sn NMR: δ 82.3.

2.2.5. Trimethyltin(IV) 4-benzylpiperidine-1-carbodithioate ***(3)***

(Yield: 0.34 g, 71%). M.p. 133–134 °C. *Anal.* Calc. for $C_{16}H_{25}NS_2Sn$ (414.2): C, 46.39; H, 6.08; N, 3.38; S, 15.48. Found: C, 46.33; H, 6.03; N, 3.35; S, 15.39%. Raman (cm^{-1}): 618 ν(C–S), 1030 ν(C=S), 1474 ν(C–N), 521 ν(Sn–C), 361 ν(Sn–S). IR (cm^{-1}): 970 ν(C–S), 1457 ν(C–N). ^{1}H NMR (ppm), [^2J(^{119}Sn, ^{1}H), Hz]: 1.39–1.27, 1.82–1.75, 3.07–3.03 (m, 9H, piperidine-H) 5.07 (d, $^3J_{H-H}$ = 12.6 Hz, 2H, CH_2), 7.34–7.14 (m, 5H, Ar–H), 1.56 {(s, 9H, $H_α$, $SnCH_3$), [57]}.^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 201.1 (CS), 36.5, 42.5, 51.8 (piperidine-C), 31.8 (CH_2), 126.2, 128.4, 129.1, 139.7 (Ar–C), 15.0 {(C-α, $SnCH_3$), [391]}. ^{119}Sn NMR: δ −49.8.

2.2.6. Triphenyltin(IV) 4-benzylpiperidine-1-carbodithioate ***(4)***

(Yield: 0.55 g, 79%). M.p. 138–139 °C. *Anal.* Calc. for $C_{31}H_{31}NS_2Sn$ (600.4): C, 62.01; H, 5.20; N, 2.33; S, 10.68. Found: C, 61.92; H, 5.17; N, 2.31; S, 10.62%. Raman (cm^{-1}): 617 ν(C–S), 1019 ν(C=S), 1488 ν(C–N), 264 ν(Sn–C), 370 ν(Sn–S). IR (cm^{-1}): 988 ν(C–S), 1470 ν(C–N). ^{1}H NMR (ppm): 1.37–1.33, 1.91–1.79, 3.29–3.21 (m, 9H, piperidine-H) 4.89 (d, $^3J_{H-H}$ = 12.3 Hz, 2H, CH_2), 7.32–7.17 (m, 5H, Ar–H), 7.71–7.41 (m, 15H, $H_{β, γ, δ}$, SnC_6H_5). ^{13}C NMR (ppm): 193.3 (CS), 36.6, 41.8, 53.2 (piperidine-C), 31.6 (CH_2), 125.9, 128.5, 129.0, 140.1 (Ar–C), 142.9 (C-α, SnC_6H_5), 136.4 (C-β, SnC_6H_5), 128.9 (C-γ, SnC_6H_5), 129.1 (C-δ, SnC_6H_5). ^{119}Sn NMR: δ −182.2.

2.2.7. Chlorodibutyltin(IV) 4-benzylpiperidine-1-carbodithioate ***(5)***

(Yield: 0.47 g, 77%). Sticky material. *Anal.* Calc. for $C_{21}H_{34}NS_2SnCl$ (518.8): C, 48.62; H, 6.61; N, 2.70; S, 12.36. Found: C, 48.53; H, 6.54; N, 2.67; S, 12.30%. Raman (cm^{-1}): 619 ν(C–S), 1031 ν(C=S), 1445 ν(C–N), 581 ν(Sn–C), 345 ν(Sn–S), 255 ν(Sn–Cl). IR (cm^{-1}): 968 ν(C–S), 1475 ν(C–N). ^{1}H NMR (ppm): 1.37–1.27, 1.86–1.78, 3.11–3.03 (m, 9H, piperidine-H) 4.72 (d, $^3J_{H-H}$ = 12.9 Hz, 2H, CH_2), 7.31–7.09 (m, 5H, Ar–H), 1.99–1.31 (m, 12H, $H_{α, β, γ}$, SnBu), 0.93 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, $H_δ$, SnBu). ^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 195.6 (CS), 36.4, 42.5, 52.7 (piperidine-C), 31.9 (CH_2), 139.2, 129.2, 127.5,126.6 (Ar–C), 26.5 {(C-α, SnBu), [590]}, 36.4 {(C-β, SnBu), [18]}, 28.7 {(C-γ, SnBu), [67]}, 13.9 (C-δ, SnBu). ^{119}Sn NMR: δ −175.0.

2.2.8. Dibutyltin(IV) bis[4-benzylpiperidine-1-carbodithioate] ***(6)***

(Yield: 0.33 g, 76%). M.p. 141–142 °C. *Anal.* Calc. for $C_{34}H_{50}N_2S_4Sn$ (733.7): C, 55.65; H, 6.87; N, 3.82; S, 17.48. Found: C, 55.56; H, 6.80; N, 3.78; S, 17.41%. Raman (cm^{-1}): 587 ν(C–S), 1028 ν(C=S), 1473 ν(C–N), 503 ν(Sn–C), 334 ν(Sn–S). IR (cm^{-1}): 969 ν(C–S), 1465 ν(C–N). ^{1}H NMR (ppm): 1.40–1.30, 1.86–1.78, 3.42–3.37 (m, 9H, piperidine-H) 4.89 (d, $^3J_{H-H}$ = 12.3 Hz, 2H, CH_2), 7.28–7.09 (m, 5H, Ar–H), 1.85–1.33 (m, 12H, $H_{α, β, γ}$, SnBu), 0.93 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, $H_δ$, SnBu). ^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 190.6 (CS), 36.7, 42.5, 52.5 (piperidine-C), 31.9 (CH_2), 139.4, 128.7, 127.5, 126.5 (Ar–C), 26.5 {(C-α, SnBu), [601]}, 36.7 {(C-β, SnBu), [19]}, 29.3 {(C-γ, SnBu), [68]}, 13.9 (C-δ, SnBu). ^{119}Sn NMR: δ −201.1.

2.2.9. Chlorodiethyltin(IV) 4-benzylpiperidine-1-carbodithioate ***(7)***

(Yield: 0.43 g, 79%). M.p. 125–126 °C. *Anal.* Calc. for $C_{17}H_{26}NS_2SnCl$ (462.7): C, 44.13; H, 5.66; N, 3.03; S, 13.86. Found: C, 44.05; H, 5.59; N, 3.00; S, 13.79%. Raman (cm^{-1}): 620 ν(C–S), 1031 ν(C=S), 1446 ν(C–N), 476 ν(Sn–C), 370 ν(Sn–S), 271 ν(Sn–Cl). IR (cm^{-1}): 963 ν(C–S), 1463 ν(C–N). ^{1}H NMR (ppm): 1.32–1.19, 1.82–1.75, 3.11–3.02 (m, 9H, piperidine-H) 4.72 (d, $^3J_{H-H}$ = 13.2 Hz, 2H, CH_2), 7.30–7.08 (m, 5H, Ar–H), 1.81 {(q, $^3J_{H-H}$ = 7.5 Hz, 4H, $H_α$, SnEt), 1.46 {(t, $^3J_{H-H}$ = 7.5 Hz, 6H, $H_β$, SnEt) .^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 195.5 (CS), 36.4, 42.5, 51.7 (piperidine-C), 31.9 (CH_2), 126.6, 128.7, 129.2, 139.1 (Ar–C), 21.3 {(C-α, SnEt), [534]}, 10.4 (C-β, SnEt). ^{119}Sn NMR: δ −180.2.

2.2.10. Diethyltin(IV) bis[4-benzylpiperidine-1-carbodithioate] ***(8)***

(Yield: 0.29 g, 74%). Sticky material. *Anal.* Calc. for $C_{30}H_{42}N_2S_4Sn$ (677.6): C, 53.17; H, 6.25; N, 4.13; S, 18.93. Found: C, 53.03; H, 6.11; N, 4.10; S, 18.85%. Raman (cm^{-1}): 619 ν(C–S), 1028 ν(C=S), 1455 ν(C–N), 493 ν(Sn–C), 372 ν(Sn–S). IR (cm^{-1}): 961 ν(C–S), 1459 ν(C–N). ^{1}H NMR (ppm): 1.32–1.19, 1.82–1.75, 3.11–3.02 (m, 9H, piperidine-H) 4.74 (d, $^3J_{H-H}$ = 13.2 Hz, 2H, CH_2), 7.28–7.08 (m, 5H, Ar–H), 1.81 {(q, $^3J_{H-H}$ = 7.5 Hz, 4H, $H_α$, SnEt), 1.43 {(t, $^3J_{H-H}$ = 7.5 Hz, 6H, $H_β$, SnEt) .^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 191.6 (CS), 36.6, 42.6, 52.6 (piperidine-C), 31.9 (CH_2), 126.6, 128.7, 129.2, 139.3 (Ar–C), 29.3 {(C-α, SnEt), [578]}, 10.5 (C-β, SnEt). ^{119}Sn NMR: δ −184.6.

2.2.11. Chlorodimethyltin(IV) 4-benzylpiperidine-1-carbodithioate ***(9)***

(Yield: 0.39 g, 77%). M.p. 161–163 °C. *Anal.* Calc. for $C_{15}H_{22}NS_2SnCl$ (434.6): C, 41.45; H, 5.10; N, 3.22; S, 14.75. Found: C, 41.35; H, 5.04; N, 3.19; S, 14.69%. Raman (cm^{-1}): 621 ν(C–S), 1024 ν(C=S), 1500 ν(C–N), 514 ν(Sn–C), 368 ν(Sn–S), 249 ν(Sn–Cl). IR (cm^{-1}): 961 ν(C–S), 1459 ν(C–N). ^{1}H NMR (ppm), [^2J(^{119}Sn, ^{1}H), Hz]: 1.39–1.36, 1.82–1.78, 3.10–3.02 (m, 9H, piperidine-H) 4.66 (d, $^3J_{H-H}$ = 13.2 Hz, 2H, CH_2), 7.30–7.10 (m, 5H, Ar–H), 1.36 {(s, 6H, SnMe), [82]}. ^{13}C NMR (ppm), [^nJ(^{119}Sn, ^{13}C), Hz]: 194.9 (CS), 36.9, 42.4, 52.7 (piperidine-C), 31.8 (CH_2), 126.6, 128.7, 129.2, 139.5 (Ar–C), 10.2 (C-α, SnMe), [571]}. ^{119}Sn NMR: δ −201.2.

2.2.12. Dimethyltin(IV) bis[4-benzylpiperidine-1-carbodithioate] ***(10)***

(Yield: 0.30 g, 80%). M.p. 180–184 °C. *Anal.* Calc. for $C_{28}H_{38}N_2S_4Sn$ (649.6): C, 51.77; H, 5.90; N, 4.31; S, 19.74. C, 51.67; H, 5.82; N, 4.28; S, 19.66%. Raman (cm^{-1}): 622 ν(C–S), 1030 ν(C=S), 1474 ν(C–N), 511 ν(Sn–C), 364 ν(Sn–S). IR (cm^{-1}): 971 ν (C–S), 1451 ν(C–N). ^{1}H NMR (ppm), [^2J(^{119}Sn, ^{1}H), Hz]: 1.39–1.28, 1.80–1.78, 3.04–2.95 (m, 9H, piperidine-H) 4.66 (d, $^3J_{H-H}$ = 13.2 Hz, 2H, CH_2), 7.30–7.10 (m, 5H, Ar–H), 1.36 {(s, 6H, SnMe), [90]}. ^{13}C NMR (ppm): 195.1 (CS), 36.9, 42.1, 52.7 (piperidine-C), 31.6 (CH_2), 126.6, 128.7, 129.2, 139.3 (Ar–C), 10.5 (C-α, SnMe). ^{119}Sn NMR: δ −337.0.

2.3. X-ray crystallographic studies

A crystal fragment, cut to size to fit in the homogeneous part of the X-ray beam, was mounted on top of a glass fiber and aligned on a Bruker SMART APEX CCD diffractometer (platform with full three-circle goniometer). The crystal was cooled to 100(1) K using the Bruker KRYOFLEX low-temperature device. Intensity measurements were performed using graphite monochromatized Mo Kα radiation from a sealed ceramic diffraction tube (SIEMENS). X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer which was equipped with a 4 K CCD detector set 60.0 mm from the crystal. Data integration and global cell refinement was performed with the program SAINT. The program suite SAINTPLUS was used for space group determination (XPREP). The structure was solved by Patterson method; extension of the model was accomplished by direct methods and applied to different structure factors using the program DIRDIF. All refinement calculations and graphics were performed with the program PLUTO and PLATON package.

3. Results and discussion

3.1. Syntheses of ligand-salt and complexes 1–10

The new organotin(IV) 4-benzylpiperidine-1-carbodithioate complexes were prepared by the reaction of the ligand-salt (L-salt)

with the selected triorganotin(IV) chlorides and diorganotin(IV) dichlorides in the appropriate mole ratio in dry methanol (Scheme 2a). The numbering system for the organic groups attached to Sn is given in scheme 2b. The compounds **1**–**10** are quite stable in moist-air and are soluble in common organic solvents.

3.2. Vibrational spectra

The assignment of the Raman bands of the complexes has been made by comparison with the Raman spectra of their related precursors. In the complexes, the appearance of a new peak in the region 334–380 cm^{-1} owing to a Sn–S vibration indicated the formation of complexes. In addition, all the complexes displayed a sharp Sn–C peak in the range 476–645 cm^{-1}, except for the triphenyltin(IV) derivative where a weak vibration appeared at 263 cm^{-1} due to Sn–C stretching. A peak associated with ν(Sn–Cl) was observed in the chlorodiorganotin(IV) derivatives only, which indicates the substitution of one chloride in the diorganotin salt during the reaction.

With respect to the dithiocarboxylate moiety, two main regions of the IR are of particular interest. First, the 1450–1580 cm^{-1} region, which is primarily associated with the 'thioureide' band due to the ν(N–CSS) vibration; second, the 940–1060 cm^{-1} region, which is associated with ν(C–S) stretching. The stretching vibration peak due to ν(N–CSS), in the complexes studied here were located in the range 1457–1475 cm^{-1}. These values lie between the range reported for C–N single bond (1250–1360 cm^{-1}) and C=N double bond (1640–1690 cm^{-1}), and is an indication of partial double bond character in C–N bond [13]. The presence of a band in the above-mentioned range for ν(N–CSS) is due to the four possible resonance structures (Scheme 1). On passing from the ligand-salt to the complexes, the ν(N–CSS) mode is shifted to higher energies, showing an increase of C–N double bond character [14]. Regarding the chlorodiorganotin(IV) derivatives, the ν(N–CSS) band is shifted to higher energy as compared to diorganotin(IV) complexes owing to the presence of electron-withdrawing effect of chloride in the complexes, thus promoting a higher positive charge on nitrogen atom. A single band for C–S in the region of 900–1060 cm^{-1}, in complexes, is in accord with bidentate bonding of 1,1-dithiolate moiety with Sn [15].

3.3. NMR spectra

The ^{1}H NMR spectra were recorded for the compounds **1**–**10** in DMSO-d_6. The characteristic chemical shifts were identified by their intensity and multiplicity patterns. The total number of protons, calculated from the integration curves, is in agreement with the expected molecular composition of the compounds. For the ligand, the piperidine protons demonstrate three triplets (1.78–1.85, 1.27–1.39 and 3.04–3.08 ppm) in the aliphatic region as expected for the structure. The protons of the benzyl part resonate in two regions; a doublet (~5.07 ppm) due to CH_2 protons and a multiplet (7.12–7.33 ppm) because of phenyl moiety. The proton chemical shifts assignment of the organic groups attached to Sn exhibited a singlet at ~1.53 ppm for compounds **3**, **9** and **10** and appeared as multiplets in the aliphatic region in case of compounds **1**, **2**, **5** and **6**. The protons of the ethyltin(IV) derivatives appeared as a quartet and a triplet as expected, while the aromatic protons of the triphenyltin(IV) complex resonate as multiplets in the range 7.42–7.71 ppm. The ^2J [^{119}Sn, ^{1}H] coupling constant value for complex **3** was 57 Hz, in the range normally expected for four-coordinate Sn and consistent with CSnC angle of 110.9° while the angle calculated (Table 1) from ^2J [^{119}Sn, ^{1}H] coupling constant certify the 5- and six-coordinate environment around Sn for compounds **9** and **10**, respectively [16]. However, the coupling constants, ^2J [^{119}Sn, ^{1}H] for *n*-butyl-, cyclohexyl-, ethyl- and triphenyltin(IV) derivatives could not be calculated due to their complex peak pattern. In case of compound **4**, the difference in chemical shift resonances of *ortho* to *meta* and *para* protons (0.3 ppm) is an indication of anisobidentate bonding of 1,1-dithiolate moiety in solution [17].

The ^{13}C NMR chemical shifts due to organic groups, attached to Sn atom, were observed at positions comparable to the other similar compounds [18]. The disappearance of duplicate peak pattern and a small shift in the position of CS carbon confirmed the coordination of ligand to the Sn center via CSS moiety. In organotin compounds, the ^1J(^{119}Sn, ^{13}C) coupling constant can be used to assess the coordination number of the Sn atom. The coupling constants were calculated and found to be in the order of 341 Hz for tributhyltin **1**, 334 Hz for tricyclohexyltin **2** and 391 Hz for trimethyltin **3** compounds which are the typical values for tetrahedral compounds [19] as given in Table 1. A characteristic feature for triphenyltin derivative is the observance of ^{13}C chemical shift of the *ipso*-carbon at about 142.9 ppm which is attributed to a five-coordinated Sn atom [20]. The calculated value of the ^1J(^{119}Sn, ^{13}C) coupling constant for **5**, **6**, **7**, **8** and **9** are 590, 601, 534, 578 and 571 Hz, respectively which described the penta-coordinated environment about the Sn atom in these compounds.

The ^{119}Sn chemical shift values obtained for triorganotin(IV) complexes lie in the range expected for tetrahedral geometry, except for the Ph_3Sn(IV) complex which gave a ^{119}Sn peak corresponding to a five-coordinated Sn atom. The ^{119}Sn NMR data for the chlorodi- and diorganotin(IV) compounds are in conformity with five coordination around the Sn atom. Among the diorganotin(IV) derivatives, only complex **10** furnished a ^{119}Sn peak associated with the octahedral geometry in solution [21].

3.4. X-ray structures

3.4.1. Crystal structures of compound *2*, *4*, *6* and *9*

An ORTEP view of compound **2** together with atomic numbering scheme is depicted in Fig. 1. Pertinent crystallographic parameters, relevant bond lengths and bond angles are given in Tables 2 and 3. The Sn atom is five-coordinate, being chelated by asymmetrically coordinating 4-benzylpiperidine-1-carbodithioate ligand and three cyclohexyl substituents. The Sn–S1 [3.160 Å] bond distance approximately *trans*- to the C26 is longer than the other Sn–S2 [2.4756(9) Å] bond distance. According to Addison et al., the geometry around the Sn atom can be characterized by the value of $\tau = (\beta - \alpha)/60$ [22], where β is the largest of the basal angles around the Sn atom. The angle $\alpha = \beta = 180°$ correspond to a square-pyramidal geometry, and the value of $\alpha = 120°$ corresponds to perfectly trigonal-bipyramidal geometry. Thus, the τ value is equal to zero for a perfect square-pyramidal and unity for a perfect trigonal-bipyramidal. For compound **2**, β is S1–Sn–C26 = 157.39°. The second largest of the basal angles around the Sn atom, α for compound **2** is S2–Sn–C20 = 116.84(8)°. The calculated τ value for the **2** is 0.67, and is an indicative of highly distorted trigonal-bipyramidal

Table 1
(C–Sn–C) angles (°) based on NMR parameters of selected compounds.

Compound Number	^1J(^{119}Sn, ^{13}C) (Hz)	^2J(^{119}Sn, ^{1}H) (Hz)	Angle (°)	
			^1J	^2J
1	341		106.6	
2	334		106.0	
3	391	57	111.0	110.9
5	590		128.5	
6	601		129.5	
7	534		123.6	
8	578		127.4	
9	571	82	126.8	127.5
10		90		135.5

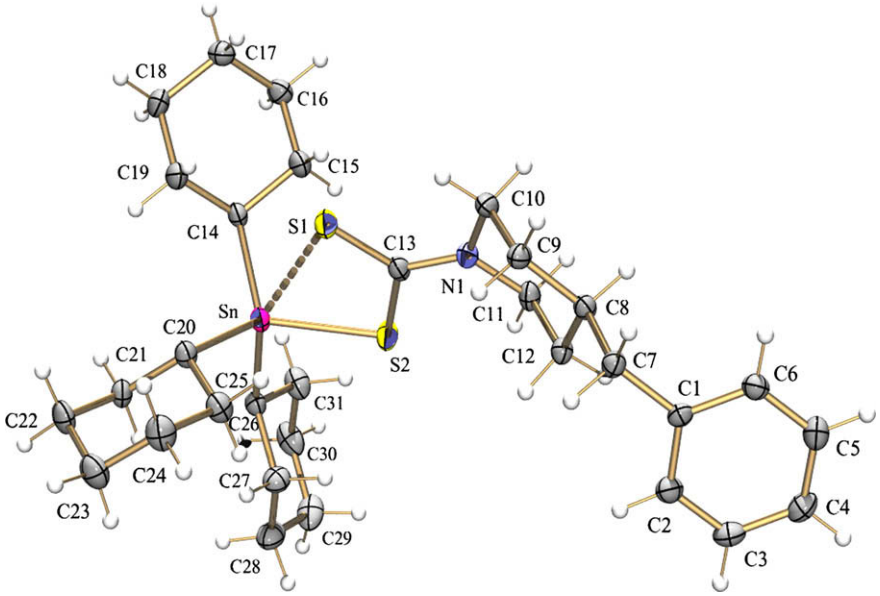


Fig. 1. ORTEP drawing of compound **2** with atomic numbering scheme.

Table 2
Crystal data and structure refinement parameters for compounds **2**, **4**, **6** and **9**.

	2	**4**	**6**	**9**
Empirical formula	$C_{31}H_{46}NS_2Sn$	$C_{31}H_{31}NS_2Sn$	$C_{34}H_{50}N_2S_4Sn$	$C_{15}H_{22}NS_2SnCl$
Formula mass	615.55	600.38	733.75	434.64
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a (Å)	10.5063(10)	9.2531(8)	9.7767(13)	13.2495(12)
b (Å)	10.6281(10)	10.7273(9)	10.9801(15)	9.7868(9)
c (Å)	15.0438(15)	14.4044(12)	17.105(2)	13.6949(12)
α (°)	109.3918(12)	95.313(10)	89.8273(19)	
β (°)	103.1745(12)	101.880(10)	79.0265(18)	90.7045(11)
γ (°)	92.5424(13)	94.328(10)	80.4534(19)	
V (Å^3)	1529.6(3)	1386.6(2)	1776.9(4)	1775.7(3)
Z	2	2	2	4
Crystal size (mm)	0.44 × 0.37 × 0.17	0.50 × 0.45 × 0.40	0.25 × 0.35 × 0.47	0.55 × 0.50 × 0.42
Total reflections	13801	10780	20874	14351
Independent reflections				
All	7234	4936	10225	8608
For $F_o \geqslant 4.0\sigma(F_o)$	6477		7585	8251
$R(F) = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$ for $F_o > 4.0\sigma(F_o)$	0.0401	0.0299	0.0528	0.0302
$wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$	0.1180		0.1302	0.0780
R indices (all data)		$R_1 = 0.0278$, $wR_2 = 0.0750$		
Final R indices [$I > 2\sigma(I)$]		$R_1 = 0.0228$, $wR_2 = 0.0530$		
Goodness-of-fit (GOF)	1.037	1.197	1.034	1.026
θ range for data collections (°)	2.68–28.28	2.41–25.93	2.51–25.68	2.56–28.28
Data/restraints/parameters	7234/0/316	4936/0/316	10225/0/581	8608/0/365

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **2**.

Sn–S2	2.4756(9)	Sn–C14	2.170(3)
Sn–C20	2.181(3)	Sn–C26	2.184(3)
S1–C13	1.691(3)	S2–C13	1.768(3)
Sn–S1	3.160		
S2–Sn–C14	112.09(8)	S1–Sn–C14	86.33
S2–Sn–C20	116.84(8)	S1–Sn–C20	80.78
S2–Sn–C26	95.35(8)	S1–Sn–C26	157.39
C14–Sn–C20	115.11(12)	S1–Sn–S2	62.80
C14–Sn–C26	108.77(11)	Sn–S2–C13	98.97(1)
C20–Sn–C26	106.30(12)	Sn–S1–C13	78.00
Sn–C14–C15	114.36(19)	Sn–C14–C19	109.9(2)
Sn–C20–C21	109.4(2)	Sn–C20–C25	113.4(2)
Sn–C26–C27	112.2(2)	Sn–C26–C31	112.4(2)

geometry. The C26 atom occupies one of the apical positions of the trigonal-bipyramid with the C26–Sn–S2 angle of 95.35(8)°. The quasi-axial S1 atom cannot occupy exactly the position *trans* to C26 and C26–Sn–S1 angle is 157.39°. Thus, ligand chelates the Sn atom via its two sulfur atoms in anisobidentate fashion, forming a four-membered ring with S1–Sn–S2 bond angle of 62.80°. The S–C bond lengths [S1–C13 = 1.691(3) Å and S2–C13 = 1.768(3) Å] also demonstrate the asymmetric nature of the ligand. The packing diagram confirmed trimeric structure for compound **2**, formed as the result of intermolecular H···H interactions (Fig. 2).

The molecular structure of compound **4** is shown in Fig. 3, while crystal data and selected bond lengths and bond angles are given in Tables 2 and 4, respectively. The geometry around Sn is almost a midway between square-pyramidal and trigonal-bipyramidal as evident from the τ value (0.66). The value indicates a highly

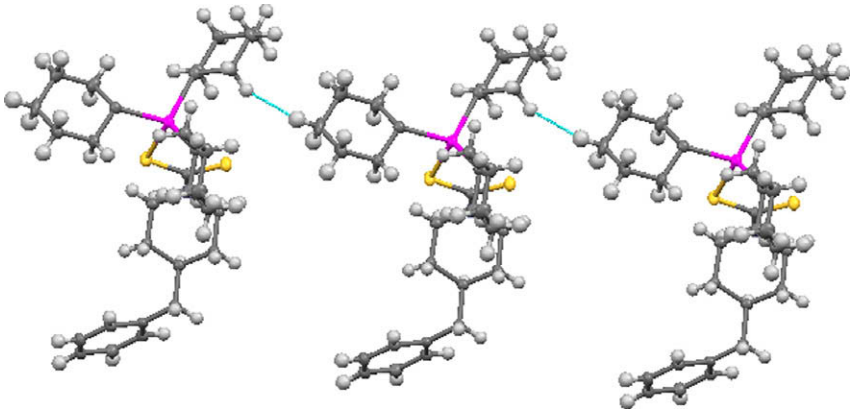


Fig. 2. Loosely associated trimer in compound **2**, connected through weak intermolecular cyclohexyl H···H interactions.

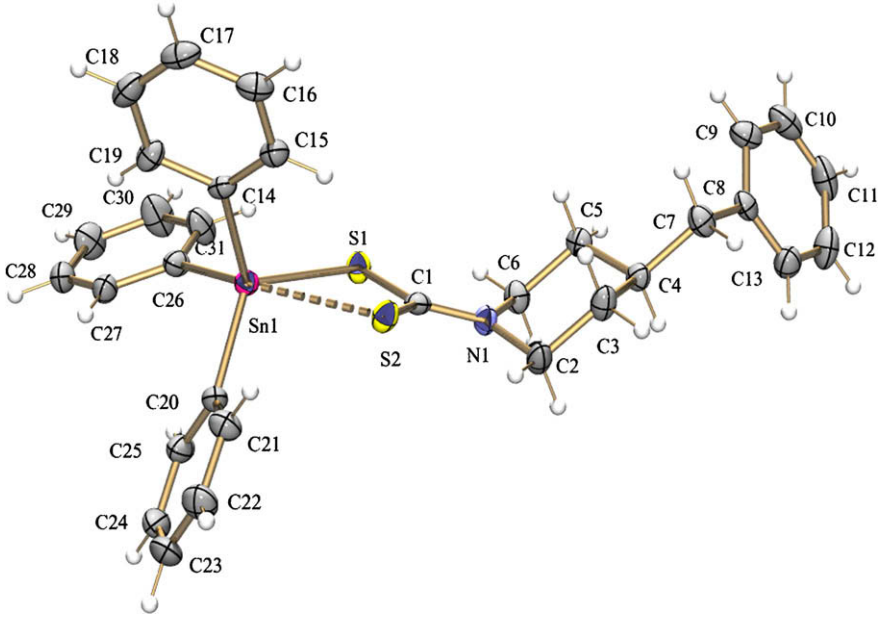


Fig. 3. ORTEP drawing of compound **4** with atomic numbering scheme.

distorted trigonal-bipyramidal arrangement around the Sn1 atom with C26 from a phenyl group and the S2 from the dithiocarboxylate ligand at the axial positions while C14 and C20 from two phenyl groups and S1 in the plane positions. The sum of the equatorial angles is 350° instead of the ideal value of 360°. Being a part of chelate, the angle S2–Sn1–S1 is not 90° but only 65.70°, so the S2 cannot occupy exactly the corresponding *trans* apical position of C26 and the angle between the apical groups is 158.88°. Finally, the C–S bond lengths are characteristic of the 1,1-dithiolate moiety and are intermediate between the values expected for single and double bonds [23]. The packing diagram indicated π···H interactions that gave rise to a dimeric structure (Fig. 4).

Table 4
Selected bond lengths (Å) and bond angles (°) for compound (**4**).

S1–Sn1	2.4892(8)	Sn1–S2	2.935
C14–Sn1	2.144(3)	C20–Sn1	2.156(3)
C26–Sn1	2.173(3)	C1–S2	1.696(3)
C1–S1	1.758(3)		
C14–Sn1–S1			
	115.38(8)	C20–Sn1–S1	119.21(9)
C26–Sn1–S1	93.88(9)	C14–Sn1–S2	89.50
C20–Sn1–S2	83.72	C26–Sn1–S2	158.88
C14–Sn1–C20			
	115.43(11)	C14–Sn1–C26	104.96(11)
C20–Sn1–C26	103.11(11)	C1–S1–Sn1	94.00(10)
C1–S2–Sn1	80.75	S2–C1–S1	118.35(18)
S1–Sn–S2	65.70		

Crystal data and selected interatomic parameters for compound **6** are collected in Tables 2 and 5, respectively. An ORTEP view of the molecule including numbering scheme is shown in Fig. 5. The Sn atom in **6** is coordinated by two butyl groups and two 4-benzylpiperidine-1-carbodithioate ligands, with the latter adopting different asymmetric coordination modes. The first dithiocarboxylate ligand is chelating but forms asymmetric Sn–S bond distances of 2.5315(14) Å and 2.9574(15) Å, respectively, while for the second ligand, Sn–S bond lengths are 2.5470(14) Å and 2.8970 (16) Å. The weaker Sn–S distances are well within the sum of the van der Waals radii for the Sn and S atoms (4.0 Å). The overall geometry at Sn is, however, highly distorted from the *trans* octahedral: the C27–Sn–C31 angle is only 137.3(2)° which is intermediate between *cis* and *trans*, the Sn and the four S atoms of the ligands are nearly coplanar but distorted from square-planar geometry, so that the *cis* S2-Sn–S4 angle is only 83.89(4)° and the *cis* S1-

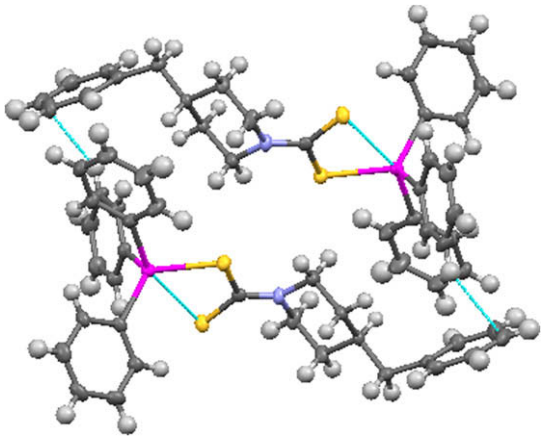


Fig. 4. Loosely associated dimer in compound **4**, connected through weak intermolecular π···H interactions.

Table 5
Selected bond lengths (Å) and bond angles (°) for compound (**6**).

Sn–S1	2.9574(15)	Sn–S2	2.5315(14)
Sn–S3	2.8970(16)	Sn–S4	2.5470(14)
Sn–C27	2.141(7)	Sn–C31	2.135(5)
S1–C13	1.701(5)	S2–C13	1.743(5)
S3–C26	1.695(6)	S4–C26	1.731(5)
S1–Sn–S2	64.95(4)	S1–Sn–S3	145.29(4)
S1–Sn–S4	148.84(4)	S1–Sn–C27	84.57(18)
S1–Sn–C31	84.61(14)	S2–Sn–S3	149.76(5)
S2–Sn–S4	83.89(4)	S2–Sn–C27	107.05(18)
S2–Sn–C31	105.35(15)	S3–Sn–S4	65.87(4)
S3–Sn–C27	82.93(18)	S3–Sn–C31	82.95(14)
S4–Sn–C27	106.03(19)	S4–Sn–C31	104.45(14)
C27–Sn–C31	137.3(2)	Sn–S1–C13	81.33(18)
Sn–S2–C13	94.39(16)	Sn–S3–C26	81.43(18)
Sn–S4–C26	92.06(18)	S1–C13–S2	119.1(3)
S3–C26–S4	120.5(3)		

Sn–S3 angle is 145.29(4)°. In both anisobidentate ligands, each shorter Sn–S bond is associated with a longer C–S bond and vice versa; this is in consonance with the bonding asymmetry of the ligands. The bond angles subtended at the Sn atom by the methylene carbons and S2 and S4 atoms range from 104.45(14)° to 107.05(18)° demonstrating that the Sn–C bonds are bent toward the longer Sn–S bonds. This situation must be a consequence of repulsion between the bonding electron pairs around the central Sn atom. Electronic and steric arguments have also been invoked to account the distortion of the similar structures from the regular octahedral geometry. Thus, the coordination geometry about the Sn atom in compound **6** is best described as being distorted skew trapezoidal-bipyramidal. Secondary π···H and H···H interactions, in compound **6**, result in a supramolecular cyclic structure as shown in Fig. 6.

The asymmetric unit of complex **9** contains two different molecules. An ORTEP diagram for one of the two independent molecules, together with an example of the atom numbering scheme used here is shown in Fig. 7. Crystal data and selected interatomic parameters are collected in Tables 2 and 6, respectively. The configuration about the tin atom is five-coordinate. The sum of the equatorial angles involving the two α-carbons of the methyl groups and a S atom [S11, S22]: 358.7°, show little deviation from the ideal angle of 360°. The coordination geometry, for both molecules, is almost intermediate between square-pyramidal and trigonal-bipyramidal with a slight bias towards the former, based on the τ value (0.40 and 0.44). A concrete explanation is available for the deviation of the coordination geometries towards square-pyramidal. In complex **9**, a secondary Sn···S interaction is responsible for lowering the τ value, which leads to the formation of a supramolecular zig–zag chain structure (Fig 8). For each molecule, the Cl atom occupies one of the apical positions of the highly distorted trigonal-bipyramid with the Cl1–Sn1–S11 and Cl2–Sn2–S22 angles of 86.57(3)° and 86.49(3)°, respectively. The quasi-axial S12 and S21 atoms cannot occupy exactly the position *trans* to Cl and Cl1–Sn1–S12 and Cl2–Sn2–S21 angles are 155.58(3)° and 155.38(3)°. Thus, the dithiocarboxylate group in both molecules is asymmetrically coordinated, and in each molecule Sn–S [Sn1–S12 = 2.6765(11) Å, Sn2–S21 = 2.6961(11) Å] bond length approximately *trans* to the chloride is longer than the other Sn–S [Sn1–S11 = 2.4908(9) Å and Sn2–S22 = 2.4866(9) Å] bond distance. The S–C bond lengths [(Sx1–Cx13 = 1.745(5) Å and 1.706(3) Å) and (Sx2–Cx13 = 1.711(3) Å and 1.763(5) Å)] also illustrate the asymmetric nature of the dithiocarboxylate group in each molecule.

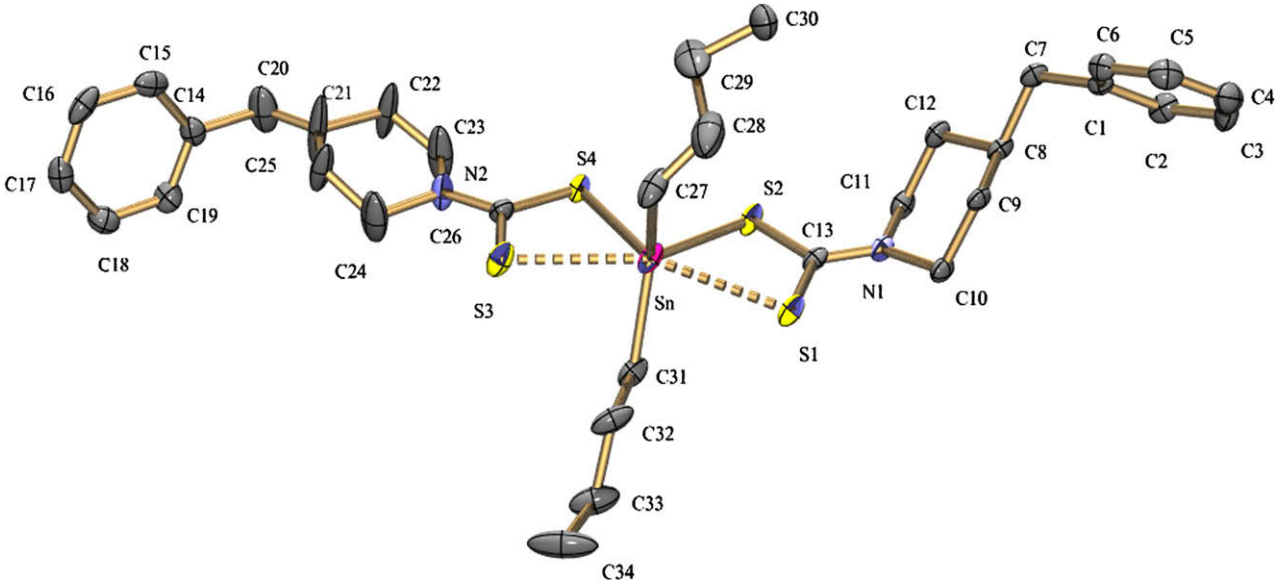


Fig. 5. ORTEP drawing of compound **6** with atomic numbering scheme.

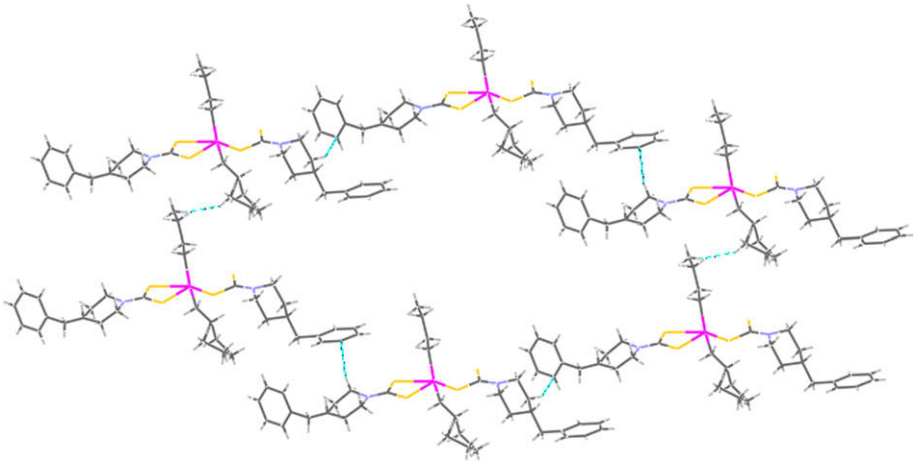


Fig. 6. Supramolecular cyclic structure of compound **9** mediated by secondary π···H and H···H interactions.

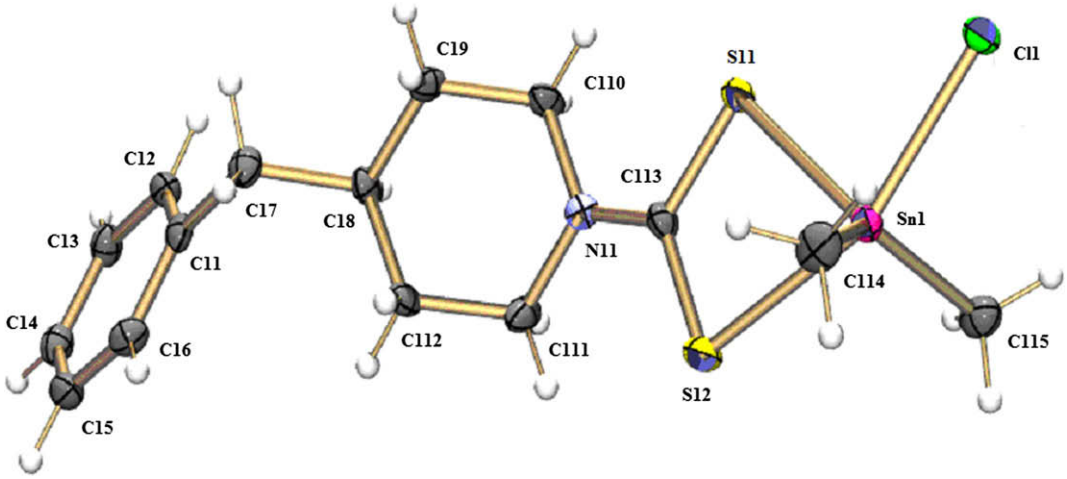


Fig. 7. ORTEP drawing for one of two independent molecules of compound **9** with atomic numbering scheme.

Table 6
Selected bond lengths (Å) and bond angles (°) for compound (**9**).

	x = 1	*x* = 2		*x* = 1	*x* = 2
Snx–Clx	2.5024(10)	2.4976(10)	Snx–Sx1	2.4908(9)	2.6961(11)
Snx–Sx2	2.6765(11)	2.4866(9)	Snx–Cx14	2.122(3)	2.123(3)
Snx–Cx15	2.123(4)	2.131(4)	Sx1–Cx13	1.745(5)	1.706(3)
Sx2–Cx13	1.711(3)	1.763(5)			
Clx–Snx–Sx1	86.57(3)	155.38(3)	Clx–Snx–Sx2	155.58(3)	86.49(3)
Clx–Snx–Cx14	96.86(16)	97.38(13)	Clx–Snx–Cx15	96.32(16)	96.38(13)
Sx1–Snx–Sx2	69.18(4)	69.08(4)	Sx1–Snx–Cx14	112.38(10)	95.20(13)
Sx1–Snx–Cx15	114.86(11)	92.02(13)	Sx2–Snx–Cx14	95.12(16)	113.47(10)
Sx2–Snx–Cx15	91.51(13)	116.36(11)	Cx14–Snx–Cx15	131.48(15)	128.86(15)
Snx–Sx1–Cx13	89.76(11)	84.63(17)	Snx–Sx2–Cx13	84.50(17)	90.16(11)
Sx1–Cx13–Sx2	116.4(3)	116.1(2)			

By comparing the Sn–S bond lengths, the shorter Sn–S bond distance decreases in the following order: **6** > **4** > **2** > **9** and the longer Sn···S bond value decreases in the sequence: **2** > **6** > **4** > **9**. The smallest Sn–S bond distances for compound **9** in the series is presumably due to two reasons: firstly the less steric hindering methyl groups and secondly electron-withdrawing effect of the chloride group that increases electron accepting capability of the Sn atom. For Sn–$S_{shorter}$, the high value for compound **4** might be due to the back-donation capability of the phenyl groups, thus stabilizing Sn atom d-orbitals and reducing their interactions with S-orbitals of the ligand. For complex **6** the highest value can be explained on the basis of electron-donating effect of the butyl groups which increase the electron density on Sn atom as a consequence repulsion between Sn and S atoms increase. In the case of Sn–S_{longer}, the order for complexes **2**, **4** and **6** can be explained on the basis of steric reasons. The high value for complex **2** is due to high steric hindrance of the cyclohexyl groups as compared to the phenyl and butyl groups.

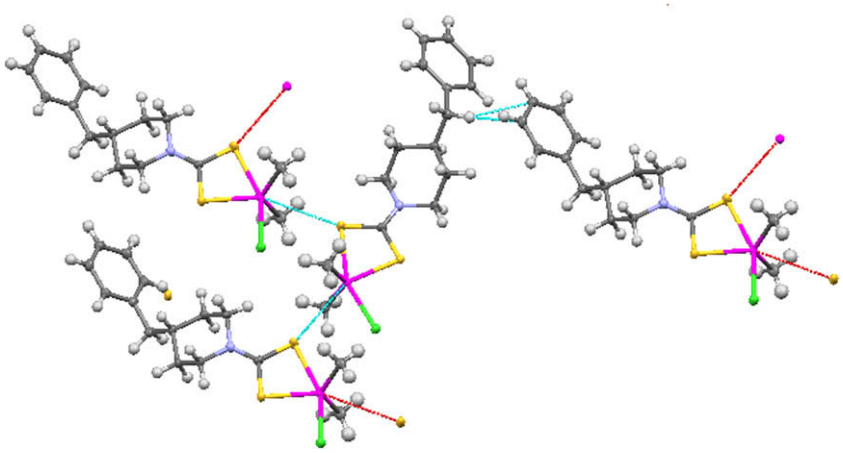


Fig. 8. Supramolecular zig–zag chain in the structure of compound **9** mediated by secondary Sn···S and benzyl-C···H interactions.

Table 7
Antifungal activity[a] of organotin(IV) derivatives **1**–**10**.

Sample	Tested fungi									
	A. nigar		*A. flavus*		*H. solani*		*A. solani*		*Fusarium* sp.	
	Linear growth	% inhibition	Linear growth	% inhibition	Linear growth	% inhibition	Linear growth	% inhibition	Linear growth	% inhibition
Control	85		86		87		90		70	
L[d]	48.0	43.5	63.0	26.7	76.0	12.6	74.0	17.8	56	20
(1)	50.0	41.2	65.0	24.4	80.0	8.0	84.0	6.7	70	0
(2)	78.0	8.2	73.0	15.1	80.0	8.0	76.0	15.6	70	0
(3)	80.0	5.9	78.0	9.3	81.0	6.9	76.0	15.6	70	0
(4)	68.0	20.0	66.0	23.3	70.0	19.5	68.0	24.4	60	14.2
(5)	72.0	15.3	73.0	15.1	61.0	29.9	66.0	26.7	56	20
(6)	66.0	22.4	80.0	7.0	73.0	16.1	70.0	22.2	63	10
(7)	72.0	15.3	74.0	14.0	78.0	10.3	68.0	24.4	63	10
(8)	80.0	5.9	78.0	9.3	68.0	21.8	64.0	28.9	61	12.8
(9)	66.0	22.4	69.0	19.8	73.0	16.1	66.0	26.7	60	14.2
(10)	76.0	10.6	76.0	11.6	80.0	8.0	73.0	18.9	70	0
Clotrimazole	60	29.4	52	39.5	51	41.4	48	46.7	44	37.1

[a] Concentration: 200 μg/mL of DMSO.

A comparison of the τ values for the five-coordinate complexes **2**, **4** and **9** reveals the smallest value for complex **9** because of secondary Sn···S intermolecular interactions. The presence of such kinds of interaction in compound **9** only, is due to the presence of small methyl groups on one end, that allow the molecules to approach one another closely. Secondly the presence of electronegative chloride group makes the Sn atom electron deficient and thus facilitates its interaction with S atom of the adjacent molecule.

3.5. Biocidal activities

3.5.1. Antifungal activity

The agar tube dilution protocol method was employed to test the antifungal activities of the synthesized compounds against the five different strains of fungi *Aspergillus nigar, A. flavus, Helminthosporium solani, Alternia solani, Fusarium* sp. and the results are shown in Table 7. The activity of compounds is highly strain dependent. Triorganotin(IV) derivatives are more active than are the chlorodi- and diorganotin(IV) complexes against the *A. nigar* and *A. flavus*. However, for the other three species, the order is reversed which is an indication of different mode of interaction of these compounds with the strains studied. The different mechanism of these compounds may be due to their ability to form secondary intermolecular interactions (as can be seen in crystal packing diagram) with bioreceptors in the cells of the microorganisms, which in turn block the synthesis of protein by inhibiting the movement of ribosome along with RNA. This situation would inhibit synthesis of DNA in the cell nucleus [10]. The higher activity of complex **1** may be due to highest lipophilic character of tributyltin(IV) derivatives [24]. The ligand and tributyltin(IV) complex are more active than is the standard drug against *A. nigar* and these compounds have potential to be used as fungicides in future.

3.5.2. Antibacterial activity

The compounds **1–10** were tested by agar well diffusion method against five different types of bacteria, namely, *Escherichia coli, Salmonella typhi, Pseudomonas aeroginosa, Staphylococcus auerus* and *Streptococcus, Streptomycin* was used as the reference drug and the results are presented in Table 8. Almost all the compounds were more toxic than was their parent ligand but slightly less so than the standard drug. Among the triorganotin(IV) derivatives, the bactericidal activity of **1** and **4** are fairly good; however, neither of these complexes (**1–4**) demonstrated any activity against *Staphlococcus aureus*. The chlorodiorganotin(IV) complexes were found to be more active than their counterparts without chloride substituents. The most probable reason is the ease of hydrolysis of the former [25]. The enhanced bactericidal activity of the ligand on complexation with organotin moiety may be explained by chelation theory [26], according to which chelation reduces the polarity of the central Sn atom because of the partial sharing of its positive charge with donor groups and possible π-electrons delocalization within the whole chelating ring. As a result, the lipophilic nature

Table 8
Antibacterial activity data[a,b] of organotin(IV) derivatives **1**–**10**.

Bacterium	Clinical implication	Zone of inhibition (mm)											Reference drug
		L	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	
E. coli	infection of wounds, urinary tract and dysentery	22	25	12	11	23	14	13	19	17	18	0	34
S. typhi	typhoid fever, localized infection	16	23	12	17	19	19	17	23	20	21	13	31
P. aeroginosa	infection of wounds, eyes, septicemia	17	16	0	13	0	10	0	14	16	14	0	24
Staphylococcus aureus	food poisoning, scaled skin syndrome, endocarditis	12	0	0	0	0	15	19	15	11	11	10	38
Streptococcus	Strep throat	0	18	11	0	21	11	13	17	17	17	11	38

[a] *In vitro*, agar well diffusion method, conc. 1 mg/mL of DMSO.
[b] Reference drug, *Streptomycin*.

of the central Sn atom increases, which favors the permeation of the complexes through the lipid layer of the cell membrane.

4. Conclusions

The presence of intermolecular interactions in packing diagrams can be exploited to conclude that these compounds exert their toxic actions on microorganisms by making similar contacts with the cells constituents. The influence of the metal is clearly visible in the antibacterial activity. This study provides a further step in designing novel antifungal metal-based drugs.

Supplementary data

CCDC 717026, 717715, 717024, and 717025 contain the supplementary crystallographic data for **2, 4**, **6** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

[1] F.W. Sunderman, Ann. Clin. Lab. Sci. 9 (1979) 1.
[2] D.L. Bodenner, P.C. Dedon, P.C. Keng, R.F. Borch, Cancer Res. 46 (1986) 2745.
[3] P.J. Nieuwenhuizen, J. Reedijk, M. van Duin, W.J. McGill, Rubber Chem. Technol. 70 (1997) 368.
[4] M. Cicotti, Handbook of Residue Analytical Methods for Agrochemicals, vol. 2, Wiley, Chichester, 2003.
[5] D. Fan, M. Afzaal, M.A. Malik, C.Q. Nguyen, P. O'Brien, P.J. Thomas, Coord. Chem. Rev. 251 (2007) 1878.
[6] P.K. Gogoi, D.P. Phukan, D.K. Das, Asian J. Chem. 11 (1999) 1291.
[7] H.P.S. Chauhan, N.M. Shaik, J. Inorg. Biochem. 99 (2005) 538.
[8] G. Eng, X. Song, Q. Duong, D. Strickman, J. Glass, L. May, Appl. Organomet. Chem. 17 (2003) 218.
[9] H.D. Yin, S.C. Xue, Appl. Organomet. Chem. 20 (2006) 283.
[10] R. Mash, Ann. Appl. Biol. 41 (1954) 652.
[11] Z. Rehman, A. Shah, N. Muhammad, S. Ali, R. Qureshi, I.S. Butler, J. Organomet. Chem. 694 (2009) 1998.
[12] W.F.L. Armarego, C. Chai, Purification of Laboratory Chemicals, 5th ed., Butterworth, Oxford, 2003.
[13] A. Mohammad, C. Varshney, S.A.A. Nami, Spectrochim. Acta, Part A 73 (2009) 20. reference therein.
[14] L. Ronconi, C. Maccato, D. Barreca, R. Saini, M. Zancato, D. Fregona, Polyhedron 24 (2005) 521.
[15] O. Jung, Y.S. Sohn, J.A. Ibers, Inorg. Chem. 25 (1986) 2273.
[16] T.P. Lockhart, W.F. Manders, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 6611.
[17] S. Shahzadi, S. Ali, K. Wurst, M.N. Haq, Heteroat. Chem. 18 (2007) 664. reference therein.
[18] M. Nádvorník, J. Holeček, K. Handlíř, J. Organomet. Chem. 275 (1984) 43.
[19] R. William, I. Verbruggen, M. Gielen, M. Biesemans, B. Mahieu, T.S.B. Baul, E.R.T. Tiekink, Organometallics 17 (1998) 5758.
[20] T.S.B. Baul, S. Dhar, S.M. Pyke, E.R.T. Tiekink, E. Rivarola, R. Butcher, F.E. Smith, J. Organomet. Chem. 633 (2001) 7.
[21] A. Tarassoli, T. Sedaghat, B. Neumüller, M. Ghassemzadeh, Inorg. Chim. Acta 318 (2001) 15.
[22] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[23] G.M. Sheldrick, W.S. Sheldrick, J. Chem. Soc. A (1970) 490.
[24] G.J.M. Van der Kerk, J.G.A. Luijten, J. Appl. Chem. 6 (1956) 56.
[25] E.R.T. Tiekink, Appl. Organomet. Chem. 22 (2008) 533.
[26] R.S. Srivastava, Inorg. Chim. Acta 56 (1981) 65.