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Synthesis and characterization of some triorgano, diorgano, monoorganotin and a triorganolead heteroaromatic dithiocarbamate complexes

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The reactions of benzyl-thiophen-2-ylmethyldithiocarbamate and 4-methyl-benzyl-thiophen-2-ylmethyldithiocarbamate with six organotin compounds and one organolead compound resulted in seven dithiocarbamate complexes exhibiting different structural forms. The compounds have been characterized by multinuclear NMR and IR spectral studies. X-ray crystallographic study of the compounds were made to understand the structure and bonding in these molecules. The dithiocarbamate ligands in all the organotin and organolead complexes showed anisobidentate bonding mode, however, in case of dichlorotin bis(dithiocarbamate) symmetrically bidentate mode of bonding was observed. Representative compounds $[Ph_3Sn\{(C_6H_5)(CH_2)\}\{(C_4H_3S)(CH_2)\}NCS_2]$ **1** and $[Ph_3Pb\{(C_6H_5)(CH_2)\}\{(C_4H_3S)(CH_2)\}NCS_2]$ **7** on pyrolysis yielded corresponding sulfides, SnS and PbS showing the usefulness of these dithiocarbamate complexes as single source precursors for the preparation of metal sulfides.

1. Introduction

The chemistry of dithiocarbamates has grown with prolific speed on account of multifaceted reasons. One of the important structural consequences of dithio ligand is the preferential stabilization of specific stereochemistry in their metal complexes. Dithio ligands are considered as soft donors showing excellent coordination ability. They form stable complexes with transition as well as non-transition metal ions [1,2] and exhibit variety of coordination modes in homo and heteronuclear complexes depending on the binding modes of the ligands towards the metal centre [3–7]. Owing to their strong metal binding capacity, dithio ligands act as inhibitors of enzymes and significantly affect biological systems [8–10]. The diethyldithiocarbamate anion, $Et_2CNS_2^-$ is extensively used as antidote for copper poisoning, i.e., Wilson's disease [11] and ameliorating nephrotoxicity associated with platinum-based chemotherapy [12]. In addition to the medicinal uses, metal dithiocarboxylates are widely used in the vulcanization of rubber [13], as pesticides [14] and as synthetic precursors for the formation of SnS nanocrystals by their solvothermal decomposition [4,15]. In the series of extensive application of dithiocarbamates, a novel class of dithiocarbamate terminated dendrimer and their use as ligand for the synthesis of ruthenium complexes has been reported recently [16].

The work described in this paper covers the syntheses and molecular structures of benzyl thiophene-2-ylmethyl-dithiocarbamate complexes of tetravalent tin and lead. The reason behind the choice of this ligand is the presence of an extra sulfur donor atom which can possibly be utilized for coordination with another metal salt or organometallic fragment as shown in Scheme 1.

2. Experimental

2.1. Starting materials

All solvents were of reagent grade quality and purchased commercially. These were purified by standard methods. For the synthesis of ligands solvents were dried carefully prior to their use [17]. All organotin chlorides and triphenyllead chloride (Sigma–Aldrich) were used as received. Thiophene-2-carboxaldehyde (Sigma–Aldrich), triethylamine (Merck), benzyl amine (Merck) and its methyl derivative were distilled before use.

2.2. Instrumentation

Elemental analyses were performed using an Exeter Model E-440 CHN analyser. NMR spectra were obtained using a JEOL AL 300 FTNMR spectrometer. Infrared spectra were recorded from KBr pellets on a Varian 3100 FT-IR spectrophotometer in the region 400–4000 cm^{-1}.

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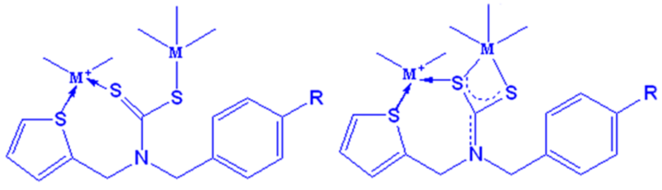


Scheme 1. Possible bonding modes of ligands involving the thiophene sulfur.

2.3. X-ray crystal structure determination

Single-crystal X-ray data of some of the complexes were collected on Xcalibur Eos (Oxford) CCD diffractometer using graphite monochromated Mo Kα radiation ($k = 0.71073$ Å). The data integration and reduction were processed with SAINT+ [18] software. The structures were solved by the direct method and then refined on F2 by the full matrix least-squares technique with the SHELXL-97 software [19] using the WinGX (version 1.70.01) program package [20]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as riding atoms using SHELX default parameters. Other crystallographic data are summarized in Table 1. Since the data collections were done at room temperature the thermal ellipsoids on the carbon atoms are large leading to large *esds* on the C–C distances.

2.4. Syntheses

2.4.1. Synthesis of ligands

2.4.1.1. (A) Bthdtc. A solution of benzyl amine (2.0 g, 18.66 mmol) in methanol (20 mL) was added to thiophene-2-carboxaldehyde (2.0 g, 17.83 mmol) dissolved in methanol (15 mL) and the reaction mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure. The resulting yellow liquid was dissolved in methanol (15 mL) and kept in an ice bath to which a solution of $NaBH_4$ (2.11 g, 55.77 mmol) in methanol (20 mL) was added drop wise with stirring. Stirring was continued for 3 h followed by evaporation of the solvent under reduced pressure. The residue was washed with water and then extracted with THF (20 mL). The solvent was removed under reduced pressure and the residue was dissolved in THF (15 mL). To this solution added a solution of CS_2 (1.41 g, 18.55) and triethyl amine (1.88 g, 18.61) in THF (20 mL) drop wise at ~5 °C. The reaction mixture was stirred for 3 h. The solvent was then evaporated and dried the viscous liquid under vacuum for 3 h/1 mm Hg. Yield- 94%. IR (KBr) (cm^{-1}) 1495 ν(C=N), 2833, 2919, 3028, 3063, 3313 ν(C–H), 951 $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ ^{1}H NMR ($CDCl_3$) (ppm): 1.40–1.45 (t, 3H, CH_3, $J_{H-H} = 7.2$ Hz), 3.27–3.34 (q, 2H, CH_2, $J_{H-H} = 7.5$ Hz), 5.45 (s, 2H, CH_2), 5.49 (s, 2H, CH_2), 6.90–7.33 (m, Ar), ^{13}C NMR ($CDCl_3$) (ppm): 8.60 (CH_3), 45.77 (CH_2), 49.66, 54.42 (Ar–CH_2), 124.97–140.04 (5C, Ph; 4C, Thioph), 213.60 (C$\cdots$S).

2.4.1.2. (B) MBthdtc. A similar procedure was followed to synthesise MBthdtc, by using 4-methyl benzyl amine in place of benzylamine. Yield- 93%. IR (KBr) (cm^{-1}) 1497 ν(C=N), 2831, 2919, 3025, 3061, 3315 ν(C–H), 950 $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$. ^{1}H NMR ($CDCl_3$) (ppm): 2.28 (s, 3H, CH_3), 1.42–1.48 (t, 3H, CH_3, $J_{H-H} = 6.99$ Hz), 3.29–3.35 (q, 2H, CH_2, $J_{H-H} = 7.2$ Hz), 5.46 (s, 2H, CH_2), 5.52 (s, 2H, CH_2), 6.88–7.20 (m, Ar), ^{13}C NMR ($CDCl_3$) (ppm): 8.53 (CH_3), 25.30 (Ph-CH_3), 44.60 (CH_2), 48.32, 52.88 (Ar–CH_2), 123.89–148.77 (Ph; Thioph), 212.90 (C$\cdots$S).

2.4.1.3. (1) Synthesis of $[(C_6H_5)_3Sn\{(C_6H_5)(CH_2)\}\{(C_4H_3S)(CH_2)\}NCS_2]$, ***1****.* A solution of triethylammonium salt of ligand (Bthdtc) (0.400 g, 1.05 mmol) in methanol (20 mL) was added to triphenyltin chloride (0.405 g, 1.05 mmol) in methanol (20 mL) with continuous stirring at room temperature. The solution was stirred for 4 h. The solvent was evaporated from the reaction mixture. The solid yellow residue was then extracted with benzene (25 mL) which was filtered and kept undisturbed at room temperature for crystallization. After few days single crystal blocks appeared at the bottom of round bottomed flask. Yield: 91% (0.593 g) M.p.: 100–101 °C, Anal. Calc. For C31H23NS3Sn: C, 59.25; H, 4.33; N, 2.23. Found: C, 59.20; H, 4.33; N, 2.21. IR (KBr) (cm^{-1}): 1471 ν(C=N), 2923, 3056 ν(C–H), 974, 991 $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$. ^{1}H NMR ($CDCl_3$) (ppm): 5.12 (s, 2H, CH2), 5.15 (s, 2H, CH2), 6.95–7.75 (m, 20H, Ph; 3H, Thioph), $J_{Sn-H} = 38.57$ Hz). ^{13}C NMR ($CDCl_3$) (ppm): 51.59, 56.97 (CH2), 126.27–142.02 (Ph, Thioph, $^1J(^{119}Sn-^{13}C) = 568$ Hz), 198.67 (C$\cdots$S), ^{119}Sn NMR ($CDCl_3$) (ppm): −173.5.

2.4.1.4. (2) Synthesis of $[(C_6H_5)_3Sn\{(C_6H_4)(CH_3)(CH_2)\}\{(C_4H_3S)(CH_2)\}NCS_2]$, ***2****.* A method similar to that described for the synthesis of **1** was adopted for the preparation of **2**, however MBthdtc ligand was used instead of Bthdtc. A solution of MBthdtc (0.600 g, 1.52 mmol) in methanol (20 mL) was added to triphenyltin chloride (0.587 g, 1.52 mmol) in methanol (20 mL) with continuous stirring at room temperature. After stirring for 4 h the solvent was evaporated from the reaction mixture and the residue was extracted with benzene (25 mL) and the solution was kept under ambient conditions for crystallization. After few days cuboids of single crystals appeared at the bottom of round bottomed flask. Yield: 92% (0.920 g) M.p.: 99–101 °C. Anal. Calc. for C32H25NS3Sn: C, 59.82; H, 4.55; N, 2.18. Found: C, 59.68; H, 4.49; N, 2.16. IR (KBr) (cm^{-1}) 1462 ν(C=N), 2875, 2924, 3058 ν(C–H), 970, 986 $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$. ^{1}H NMR ($CDCl_3$) (ppm): 2.36 (s, 3H, CH3), 5.07 (s, 2H, CH2), 5.14 (s, 2H, CH2), 6.96–7.75 (m, 20H, Ph; 3H, Thioph), $J_{Sn-H} = 43.71$ Hz). ^{13}C NMR ($CDCl_3$) (ppm): 21.16

Table 1
Crystallographic data and structure refinements.

Compound	**1**	**2**	**3**	**4**	**6**	**7**
Space group	$P-1$	$P-1$	$C2$	$P-1$	$P2_1/c$	$P-1$
a (Å)	8.6336(16)	9.1424(14)	18.7796(11)	10.235(7)	14.6930(6)	8.7328(15)
b (Å)	9.8645(18)	10.0017(16)	7.0397(2)	11.402(8)	20.2874(6)	9.8710(17)
c (Å)	17.462(3)	17.197(3)	16.0829(8)	14.169(10)	11.2538(5)	17.411(3)
α (°)	77.75(3)	102.927(2)	90	79.37(1)	90	77.621(3)
β (°)	84.552 (3)	91.756 (3)	124.907(8)	78.24(1)	111.363(5)	84.628(3)
γ (°)	73.195 (3)	109.639(2)	90	78.14(1)	90	72.561(3)
V(Å^3)	1390.3(4)	1433.8(4)	1743.7(2)	1566.7(19)	3124.1(2)	1397.9(4)
μ mm^{-1}	1.165	1.131	1.116	1.237	1.410	6.278
F(000)	636	652	898	724	1496	693
Crystal size (mm)	0.20 × 0.14 × 0.09	0.16 × 0.14 × 0.10	0.18 × 0.16 × 0.14	0.13 × 0.11 × 0.08	0.14 × 0.10 × 0.8	0.15 × 0.12 × 0.10
θ Range	2.29–28.39	2.26–28.35	2.65–28.08	2.19–28.67	2.01–28.79	2.21–28.39
GOF	1.048	1.081	0.965	1.067	1.003	1.051
R1	0.0363	0.0404	0.0358	0.0662	0.0481	0.0422

(CH3), 51.36, 56.73 (CH2), 126.23–142.08 (Ph; Thioph) $^{1}J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ = 571 Hz), 198.38 ($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$), ^{119}Sn NMR (CDCl$_3$) (ppm): −174.9.

2.4.1.5. (3) Synthesis of $[(CH_3CH_2CH_2)_2Sn\{(C_6H_5)(CH_2)\}_2\{(C_4H_3S)(CH_2)\}_2(NCS_2)_2]$, ***3***. A method similar to that described for the synthesis of **1** was adopted, however, dipropyltin dichloride (0.5 equivalents) was used instead of triphenyltin chloride. Needle shaped colourless single crystals were isolated. Yield: 89% (0.570 g) M.p.: 82–83 °C. Anal. Calc. for C32H30N2S6Sn: C, 50.45; H, 5.03; N, 3.68. Found: C, 50.48; H, 5.01; N, 3.66. IR (KBr) (cm^{-1}) 1462 ν(C=N), 2856, 2926, 3022, 3060 ν(C–H), 962, 934 ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$). ^{1}H NMR (CDCl$_3$) (ppm): 1.12 (t, 3H, CH$_3$, J_{H-H} = 6.9 Hz) 2.05(m, 2H, CH$_2$), 2.25(t, 2H, CH$_2$, J_{H-H} = 7.2 Hz) 5.12 (s, 2H, CH2), 5.18 (s, 2H, CH2), 6.96–7.38 (m, 10H, Ph; 6H, Thioph). ^{13}C NMR (CDCl$_3$) (ppm): 18.09 (CH$_3$), 20.28, 38.49 $^{1}J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ = 226.4 Hz, (CH$_2$), 50.32, 55.44 (CH2), 126.24–137.22 (Ph; Thioph), 197.36 ($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$), ^{119}Sn NMR (CDCl$_3$) (ppm): −336.9.

2.4.1.6. (4) Synthesis of $[(CH_3)_2Sn\{(C_6H_5)(CH_2)\}_2\{(C_4H_3S)(CH_2)\}_2(NCS_2)_2]$, ***4***. A method similar to that described for the synthesis of **1** was adopted; however, dimethyltin dichloride (0.5 equivalents) was used instead of triphenyltin chloride. Colourless single crystals were obtained. Yield: 90% (0.583 g) M.p.: 138–140 °C. Anal. Calc. for C28H22N2S6Sn: C, 47.66; H, 4.29; N, 3.97. Found: C, 47.62; H, 4.29; N, 3.95. IR (KBr) (cm^{-1}) 1462 ν(C=N), 2855, 3021, 3067 ν(C–H), 975, 989 ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$). ^{1}H NMR (CDCl$_3$) (ppm): 1.68 (s, 3H, Sn–CH3, J_{Sn-H} = 45 Hz), 5.10 (s, 2H, CH2), 5.15 (s, 2H, CH2), 6.97–7.39 (m, 10H, Ph; 6H, Thioph). ^{13}C NMR (CDCl$_3$) (ppm): 16.02 (Sn–CH3), 50.31, 55.51 (CH2), 126.24–137.04 (Ph; Thioph), 202.34 ($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$), ^{119}Sn NMR (CDCl$_3$) (ppm): −332.4.

2.4.1.7. (5) Synthesis of $[(CH_3CH_2CH_2CH_2)Sn\{(C_6H_5)(CH_2)\}_3\{(C_4H_3S)(CH_2)\}_3(NCS_2)_3]$, ***5***. A method similar to that described for the synthesis of **1** was adopted, however, *n*-butyltin trichloride (0.33 equivalents) was used instead of triphenyltin chloride. Needle shaped crystals were obtained. Yield: 85% (0.383 g) M.p.: 140–141 °C. Anal. Calc. for C43H33N3S9Sn: C, 51.08; H, 4.49; N, 4.16. Found: C, 51.0; H, 4.49; N, 4.18. IR (KBr) (cm^{-1}) 1474 ν(C=N), 2724, 2782; 2858, 2925 3032, 3071 ν(C–H), 975, 923 ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$). ^{1}H NMR (CDCl$_3$) (ppm): 0.94 (t, 3H, CH$_3$, J_{H-H} = 7.2 Hz), 1.44–1.53 (m, 2H, CH$_2$), 1.77–1.87 (m, 2H, CH$_2$), 2.11–2.17 (t, 2H, CH$_2$, J = 7.4 Hz), 4.99 (s, 2H, CH2), 5.02 (s, 2H, CH2), 6.98–7.37 (m, (15H, Ph; 9H, Thioph). ^{13}C NMR (CDCl$_3$) (ppm): 13.84 (CH3), 25.29 (CH2), 28.50 (CH2, $^{1}J(^{119}\mathrm{Sn}-^{13}\mathrm{C})$ = 777.13 Hz), 47.58 (CH2), 51.76, 57.32 (CH2), 126.77–135.55 (Ph; Thioph), 201.48 ($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$), ^{119}Sn NMR (CDCl$_3$) (ppm): −574.6.

2.4.1.8. (6) Synthesis of $[Cl_2Sn\{(C_6H_5)(CH_2)\}_2\{(C_4H_3S)(CH_2)\}_2(NCS_2)_2]$, ***6***. A method similar to that described for the synthesis of **1** was adopted, however, tin tetrachloride (0.25 equivalents) was used instead of triphneyltin chloride. Yellow single crystal rods were isolated. The resulting product was the same even after taking the metal salt and ligand in 1:2 stoichiometric ratio. Yield: 90% (0.220 g) M.p.: 118–120 °C. Anal. Calc. for C26H16N2Cl2S6Sn: C, 41.83; H, 3.24; N, 3.75. Found: C, 41.89; H, 3.22; N, 3.74. IR (KBr) (cm^{-1}) 1493 ν(C=N), 2855, 2927, 3028, 3098 ν(C–H), 970 ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$). ^{1}H NMR (CDCl$_3$) (ppm): 4.93 (s, 2H, CH2), 4.96 (s, 2H, CH2), 7.01–7.44 (m, (10H, Ph; 6H, Thioph)). ^{13}C NMR (CDCl$_3$) (ppm): 52.68, 58.45 (CH2), 127.12–134.38 (Ph; Thioph), 198.729 ($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$).

2.4.1.9. (7) Synthesis of $[(C_6H_5)_3Pb\{(C_6H_5)(CH_2)\}\{(C_4H_3S)(CH_2)\}(NCS_2)]$, ***7***. A method similar to that described for the synthesis of **1** was adopted, however, triphenyllead chloride (1.0 equivalent) was used instead of triphneyltin chloride. Light yellow single crystals were obtained. Yield: 86% (0.811 g) M.p.: 128–129 °C. Anal. Calc. for C31H23NS3Pb: C, 51.93; H, 3.80; N, 1.95. Found: C, 51.90; H, 3.82; N, 1.99. IR (KBr) (cm^{-1}) 1462 ν(C=N), 2857, 2924, 3058 ν(C–H), 970, 995 ν(C⋯S). ^{1}H NMR (CDCl$_3$) (ppm): 5.17 (s, 2H, CH2), 5.21 (s, 2H, CH2), 6.94–8.03 (m, 20H, Ph; 3H, Thioph). ^{13}C NMR (CDCl$_3$) (ppm): 51.79, 57.01 (CH2), 125.99–158.32 (Ph; Thioph), 201.19 ($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$)

3. Results and discussion

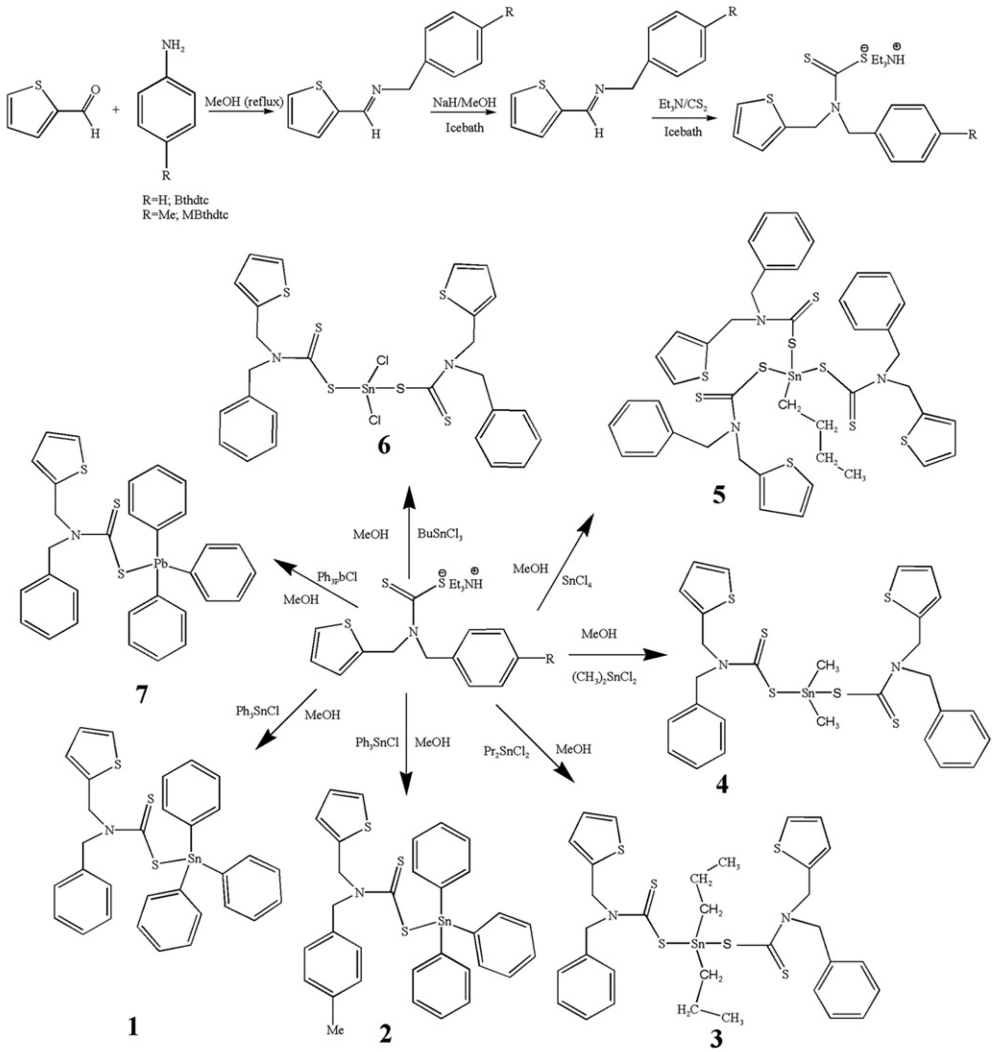
*3.1. Preparation and spectroscopic characterization of complexes **1**–**7***

Six new tin/organotin **1**–**6** and one organolead dithiocarbamate **7** compounds have been isolated as shown in Scheme 2. The synthetic reactions involved treatment of the appropriate organotin(IV) chlorides (Ph$_3$SnCl, Pr$_2$SnCl$_2$, Me$_2$SnCl$_2$, BuSnCl$_3$ and SnCl$_4$) with stoichiometric amounts of triethylammonium salt of ligands in methanol. The tin(IV) complex Cl$_2$Sn(Bthdtc)$_2$ was obtained in an attempt to prepare the homoleptic tin(IV) complex, Sn(Bthdtc)$_4$. Notably, the latter could not be synthesised by treating SnCl4 with the ligand salt in 1:4 M ratio even in refluxing methanol, possibly due to the high steric bulk of the ligands. A search in the literature revealed that a few tin *tetrakis*-dithiocabramates are known and have been prepared conveniently under ambient conditions [21]. An organolead dithiocarbamate compound **7** was also isolated by an analogous reaction using triphenyllead chloride. All the compounds were characterized by elemental analysis, FT-IR, and multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) spectroscopy and single crystal X-ray diffraction analysis.

IR spectroscopy has been used as a diagnostic tool to study the bonding mode of dithiocarbamate ligands. The ligand is known to bind with a metal atom monodentately as well as bidentately. The former case displays a characteristic strong absorption band below 1485 cm^{-1} due to ν($\mathrm{C}\overset{\cdots}{-}\mathrm{N}$) vibrations. In the case of a bidentate mode of binding the ($\mathrm{C}\overset{\cdots}{-}\mathrm{N}$) stretching appears above 1485 cm^{-1} and a single band due to ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$) around 1000 cm^{-1} [22–24]. According to Bonati and Ugo [25] the $\mathrm{C}\overset{\cdots}{-}\mathrm{S}$ stretching vibrational mode appearing in the range of 950–1050 cm^{-1} with bonding type of CS$_2$ moiety proposed that the single symmetrical peak in this region is indicative of bidentate coordination where as splitting in peak indicate the monodentate or anisobidentate bonding.

The infrared spectra of all the seven dithiocarbamate compounds showed very intense absorption assignable to ν($\mathrm{C}\overset{\cdots}{-}\mathrm{N}$) vibration in the region 1450–1500 cm^{-1}. The dithiocarbamate ligands bind to the metal monodentately using only one sulphur atom showing a pair of bands due to ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$) below 1000 cm^{-1} in all the six organometallic compounds. Interestingly, only dichlorotin dithiocarbamate compound exhibited spectral features corresponding to a bidentate mode of binding having a single symmetrical peak at 970 cm^{-1} for ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$) and a vibration at 1493 cm^{-1} for ν($\mathrm{C}\overset{\cdots}{-}\mathrm{N}$). Notably, the triethylammonium salts of the ligands showed a strong $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching band at 1495–1496 cm^{-1} and a single peak at 950–951 cm^{-1} due to ν($\mathrm{C}\overset{\cdots}{-}\mathrm{S}$) vibration which is consistent with the dianionic canonical form.

The ^{1}H NMR spectrum of all the seven compounds exhibited two peaks in the range of 4.93–5.21 and 6.95–8.03 ppm for –CH2 groups and phenyl, thiophene rings respectively. In a given series of compounds the chemical shift values in the ^{119}Sn NMR spectra have been observed to move upfield as the coordination number of tin increases from four to seven [26]. In tetrahedral compounds the ^{119}Sn signal is usually observed between +200 and −60 ppm while the same for pentacoordinate and hexacoordinate tin appears in the ranges −90 to −190 ppm and −210 to −400 ppm respectively [27]. ^{119}Sn signal in the NMR spectrum of the compounds **1** and **2** clearly indicated the existence of five



Scheme 2. Preparation of the ligands and complexes.

coordinated tin in both the cases. (*cf.* −46.5 ppm for Ph3SnCl) [28]. The signal observed in the cases of **3** and **4** are suggestive of the presence of six coordinate tin while the signal at −574.6 ppm evinced for a seven coordinated tin in compound **5**. $^1J(^{119}Sn-^{13}C)$ values have been used to calculate C–Sn–C angles in solution [29]. The C–Sn–C angles in **1** and **2** were found to be 127° which suggests a trigonal bipyramidal geometry around Sn(IV). On the other hand, the C–Sn–C angle is 97° in complex **3** indicating *cis*-orientation of the two organyl groups in a hexacoordinate environment.

From the NMR spectral features one would conclude the bidentate bonding of the dithiocarbamate ligands in all these complexes, which is not in consistence with the IR spectral features. Though the possibility of structural differences in solution and solid state can not be ruled out, the IR spectral pattern may also indicate an anisobidentate bonding of the dithiocarbamate ligands. To get further insight we have recorded ^{119}Sn NMR data of a representative compound at a higher temperatures also. A downfield shift was observed in the spectrum of 3 when recorded at 45 °C ($\delta = -333$ ppm) suggesting that with increase in temperature there is some change in coordination environment. Which is possibly because of the anisobidentate bonding of the ligands; the weak Sn–S bonds become weaker with increase in temperature.

3.2. *Crystal and molecular structures*

Single crystals suitable for X-ray diffraction analysis of all the compounds, except one (**5**), could be grown. The details of crystallographic data and structure refinement are given in Table 1.

3.2.1. *(a) Molecular structure of **1***

Molecular structure and numbering scheme of **1** is given in Fig. 1. As can be seen from the structure (Fig. 1) the dithiocarbamate ligand (Bthdtc) binds to the metal primarily in a monodentate fashion. Several organotin compounds containing one or more dithiocarbamates are known which reveal that these ligands are rarely symmetrically bound to the tin [30–35]. In the present case Sn1–S3 is a normal covalent bond with a bond distance of 2.48 Å, while the Sn1–S2 distance is very long (3.04 Å). The latter is however, significantly shorter than the sum of the van der Walls' radii of the two atoms (3.97 Å) indicating the possibility of a weak bonding interaction between the two. The Sn–C bonds vary between 2.11 and 2.16 Å which are well within the usually observed C–Sn distances in organotin compounds.

The structure of **1** is comparable to that of [Ph3Sn(S2CNEt2)] where the longer Sn···S distance is 3.11 Å [36]. Hall and Tiekink have shown how the electron donating/withdrawing effect of the ligands bound to tin markedly affect both the anisobidentate nature of the

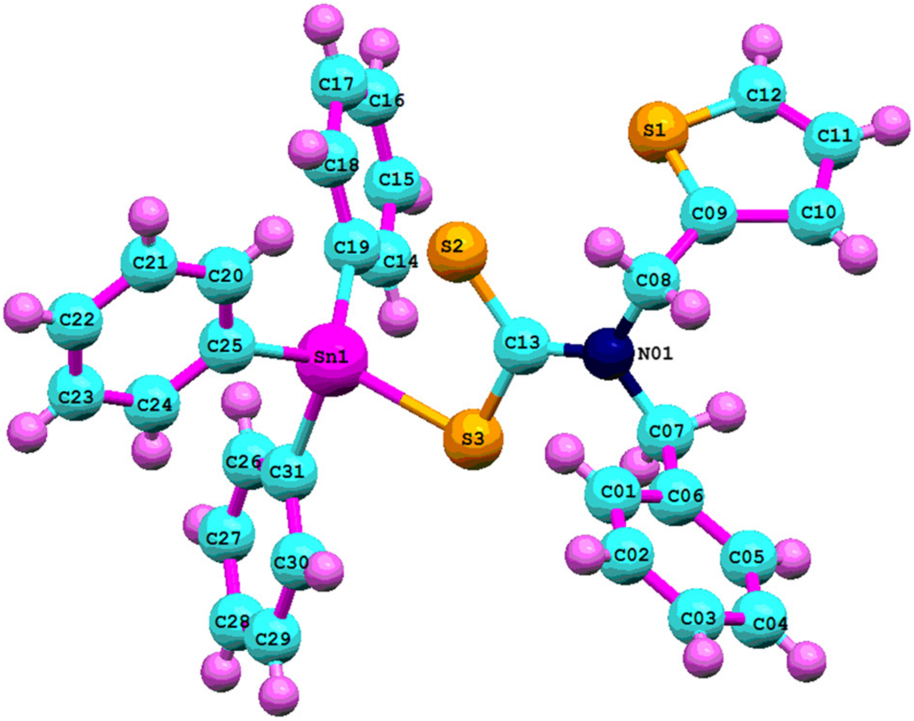


Fig. 1. Molecular structure of **1**. Selected bond lengths (Å) and bond angles (°): S1–C09 = 1.676(13), S1–C12 = 1.708(10), Sn1–S3 = 2.4753(8), N01–C08 = 1.472(4), Sn1–C19 = 2.122(3), C19–Sn1–C25 = 115.84(11), C19–Sn1–C31 = 107.10(11), C25–Sn1–C31 = 105.22(11), C19–Sn1–S3 = 115.04(8), C25–Sn1–S3 = 117.14(8), C31–Sn1–S3 = 92.52(8), N01–C13–S3 = 117.8(2), S2–C13–S3 = 119.21(16).

Sn–S chelation (ΔSn–S) and the solid state structure for compounds of the type $R_2Sn(S_2CNR'_2)_2$ (R = alkyl, aryl, vinyl, chloride; R′ = alkyl) [37]. The coordination geometry around tin in **1** is deviated from that of a regular tetrahedron towards a trigonal bipyramid may be due to the weak Sn1–S2 interaction. The atoms/groups bonded to tin expand the angles towards the 120° expected for equatorial substituents [C19–Sn1–C25 = 116.32, S3–Sn1–C25 = 116.64°] where as the substituents placed at axial site subtend a much wider angle (S2–Sn–C31 = 156.75°). On the other hand the atoms at axial and equatorial sites subtend angles smaller than the ideal

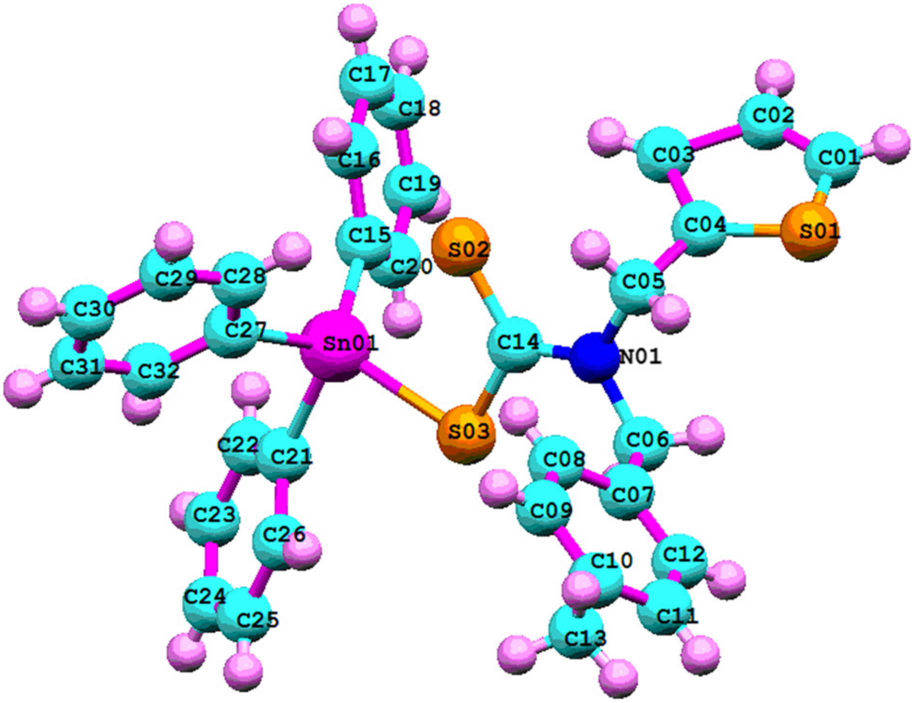


Fig. 2. Molecular structure of **2**. Selected bond lengths (Å) and bond angles (°):S2–C1 = 1.682(3), S1–C1 = 1.759(3), Sn1–C15 = 2.133(3), Sn1–S1 = 2.4885(9), N1–C1 = 1.334(4), C15–Sn1–C27 = 120.08(12), C15–Sn1–C21 = 106.48(12), C27–Sn1–C21 = 101.22(12), C15–Sn1–S1 = 115.35(9), N1–C1–S1 = 118.5(2), S2–C1–S1 = 118.99(19).

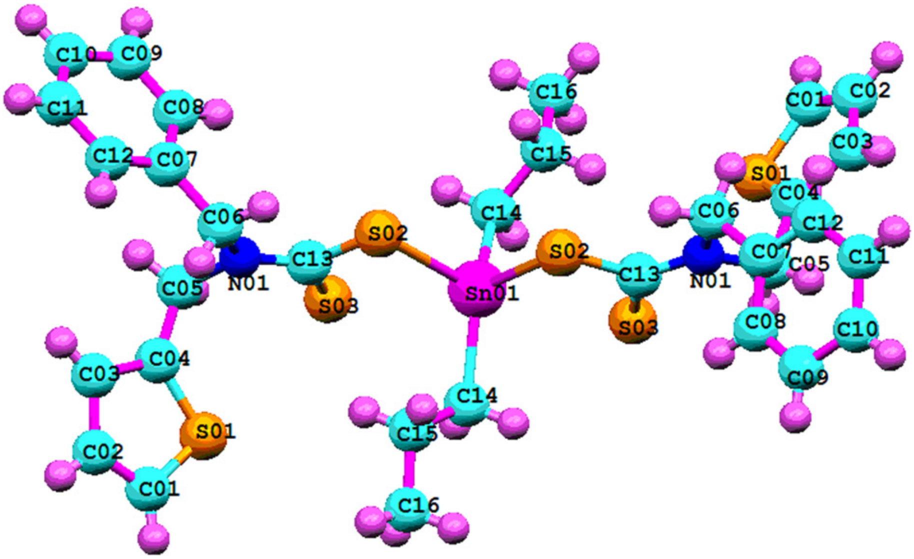


Fig. 3. Molecular structure of **3**. Selected bond lengths (Å) and bond angles (°):S03–C13 = 1.693(5), S02–C13 = 1.738(6), Sn01–C14 = 2.145(6), Sn01–S02 = 2.5391(13), Sn01–S02 = 2.5391(13), N01–C13 = 1.346(7), C14–Sn01–C14 = 138.8(4), C14–Sn01–S02 = 106.18(19), S02–Sn01–S02 = 84.06(6), N01–C13–S03 = 121.3(4), S03–C13–S02 = 119.3(4).

tetrahedral angle (C25–Sn1–S2 = 87.87°, C19–Sn1–C31 = 107.13°, S3–Sn1–C31 = 91.51°). ^{119}Sn NMR spectrum of the compound clearly indicated that the Sn atom present in this compound is five coordinated.

3.2.2. (b) Molecular structure of **2**

The molecular structure of **2** (Fig. 2) is identical to that of **1**. The anion of **a** binds to tin basically in a monodentate fashion and the two Sn–S distances are highly unequal Sn1–S2 is longer (2.96 Å) than Sn1–S3 (2.49 Å). However, the coordination environment about tin in this complex is also distorted from the ideal tetrahedral geometry and can be described as a distorted trigonal bipyramid considering the S2 atom within the coordination sphere.

3.2.3. (c) Molecular structure of **3**

Dipropyltin *bis*-dithiocarbamate **3** crystallizes in monoclinic system with space group *C*2. Molecular structure and numbering scheme is given in Fig. 3. The coordination sphere around the tin atom in the compound can be described as a highly distorted tetrahedron. However, the alternative descriptions could be that of a bicapped tetrahedron or a skew trapezoidal bipyramid. The latter merits some comments. The four sulfur atoms constitute a trapezoid and the two propyl groups occupy the axial positions to complete the six coordination of the tin atom. This model is based on the presumption that the dithio ligand chelates the tin center in an asymmetric way. The anisobidentate mode of coordination in this compound is accompanied by unequal Sn–S bond distances. The two strong Sn01–S02 bonds (2.54 Å) are *cis* to each other with a very acute angle S02–Sn01–S02 (84.06°). The weaker Sn01–S03 (2.96 Å) bonds with S03–Sn01–S03 angle of 146.94° deviate only by ∼33° from being linear. The Sn01–S03 (2.96 Å) distance is quite longer than the sum of covalent radii of Sn and S atoms (2.42 Å) but significantly less than the sum of van der waals radii of these atoms (3.97 Å). The Sn01–S02 bond length is much

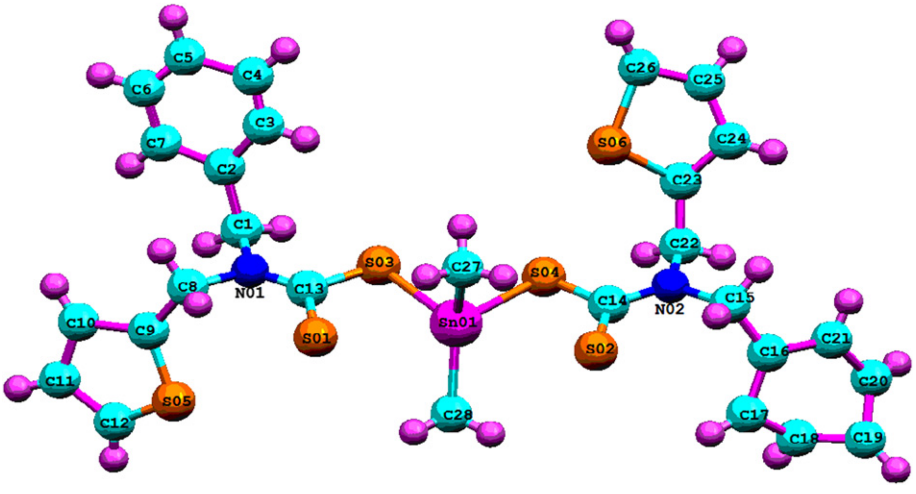


Fig. 4. Molecular structure of **4**. Selected bond lengths (Å) and bond angles (°):S1–C3 = 1.755(15), S2–C3 = 1.666(18), S3–C15 = 1.6454(7), S4–C18 = 1.704(17), C18–S5 = 1.680(16), C28–S6 = 1.8279(11), Sn1–C1 = 2.13(2), Sn1–S1 = 2.520(5), Sn1–S4 = 2.532(5), N1–C4 = 1.44(2), C2–Sn1–C1 = 139.6(10), C2–Sn1–S1 = 107.7(7), C1–Sn1–S1 = 104.5(6), C1–Sn1–S4 = 101.6(7), S1–Sn1–S4 = 83.27(14), C15–S3–C12 = 104.44(4), N1–C3–S1 = 116.6(12), S2–C3–S1 = 119.6(10).

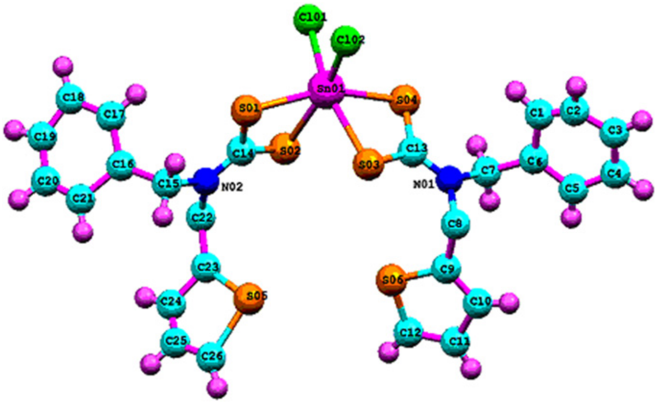


Fig. 5. Molecular structure of **6**. Selected bond lengths (Å) and bond angles (°):S1–C14 = 1.734(8), S2–C14 = 1.714(8), S3–C13 = 1.729(8), S4–C13 = 1.731(9), Sn1–Cl1 = 2.390(3), C9–S5 = 1.705(13), C23–S6 = 1.677(18), Sn1–Cl2 = 2.371(3), Sn1–S1 = 2.514(2), Sn1–S2 = 2.569(2), Sn1–S3 = 2.587(2), Sn1–S4 = 2.511(2), N1–C13 = 1.321(10), Cl2–Sn1–Cl1 = 92.17(11), Cl2–Sn1–S4 = 102.52(10), Cl1–Sn1–S4 = 91.58(9), Cl2–Sn1–S1 = 92.79(9), Cl1–Sn1 = S1 = 102.09(9), S4–Sn1–S1 = 159.10(7), Cl2–Sn1–S2 = 163.42(10), Cl1–Sn1–S2 = 93.61(9), S4–Sn1–S2 = 92.85(8), S1–Sn1–S2 = 70.81(7).

shorter (2.54 Å) and is definitely a covalent bond but it will not be inappropriate to infer that a bonding interaction exists between Sn01 and S03 atoms. The C–Sn–C angle (138.79°) is far from ideal angles of both tetrahedron and octahedron. In skew trapezoidal bipyramidal molecules the C–Sn–C angles in *cis*-diorganotin complexes are in the range of 102–110° while the same range between 180° and 145° in the case of *trans*- isomers. Since the C1–Sn–C2 angle in **3** is 138.79°. It may be considered to resemble the transition state of the *cis-trans* pathway which starts forming at about a C–Sn–C angle 134°.

3.2.4. (d) Molecular structure of **4**

The molecular structure of **4** is very much similar to that of **3**. It crystallizes in triclinic system with space group *P*-1. Molecular structure and numbering scheme is shown in Fig. 4. In this compound also the dithiocarbamate ligands bind to tin in anisobidentate fashion. The asymmetry in bonding of the ligand is also reflected in carbon–sulphur bond distances for both the ligand moieties which are not equal (1.67 and 1.73 Å). The thiocarbonyl sulfur atoms of the ligands weakly interact to the metal leading to a distorted structure. The compound adopts a skew trapezoidal bipyramidal structure with the Sn atom at the centre and four S atoms at the corners of the trapezoid. The two methyl groups occupy the axial sites subtending an angle of 135.26° resembling the *cis–trans* pathway which starts forming at about a C–Sn–C angle of 134°.

As observed in **3** there are two strong Sn–S bonds with shorter bond lengths (2.53 and 2.52 Å) and two weak Sn–S bonds with longer bond lengths (2.99 and 2.94 Å). The two strong Sn–S bonds are *cis* to each other subtending an acute angle of 83.26°. The weaker Sn–S bonds with S2–Sn01–S1 angle of 147.75° lie 32° less from being co-linear to each other. The two Sn–S bond lengths, (S1–Sn01 = 2.52 Å and S2–Sn01 = 2.53 Å) are longer than the sum of the covalent radii of the tin and sulfur (2.42 Å) but significantly below the sum of the van der Waals radii of these atoms (4.0 Å).

3.2.5. (e) Molecular structure of **6**

In SnCl2(Bthdtc)2 due to the bulkiness of the ligand only two Cl atoms are substituted by the ligands and two Cl atoms remain intact to the metal atom. As can be seen from the crystallographic data, it crystallizes in monoclinic system with space group $P2_1/c$. Molecular structure and numbering scheme is shown in Fig. 5. This is the only compound of this series in which the dithiocarbamate ligands behave as a bidentate species and chelate the tin atom by means of both the sulfur atoms giving a *cis*-octahedral geometry around the tin atom. Distortion from the regular octahedral structure is possibly due to the small ligand bites of the dithiocarbamate ligands which can not span the ideal *cis* angle of 90°. Sn–S distances are not exactly equal, and the S–C bond distances also vary accordingly. However, the difference in Sn–S distance in a Sn–dithiocarbamate unit is not very significant (Sn–S01 = 2.51; Sn–S02 = 2.57 Å). The longer S–C bond (1.74 Å) is associated with shorter Sn–S bond and the shorter C–S bond (1.71 Å) is associated with the longer Sn–S bond. The S–C bond lengths are noticeable in the dithiocarbamate groups being intermediate between the values expected for single and double bonds. $C\overset{\cdots}{-}N$ bond distances are also in their usual bonding range of 1.31–1.32 Å and are shorter than those observed in the structures of **1**–**4** (ranging between 1.32 and 1.35 Å) in consistence with the bidentate mode of ligand bonding. The two Sn–Cl bonds are almost equal (2.38 and 2.39 Å) and are comparable to the sum of the covalent radii of the two atoms (2.38 Å). Weak interactions such as hydrogen bonding along c axis in crystal lattice (of 6) have been clearly shown in Fig. 6.

3.2.6. (f) Molecular structure of **7**

Compound **7** crystallizes in triclinic system with space group *P*-1. In this complex the dithiocarbamate ligand binds to the lead

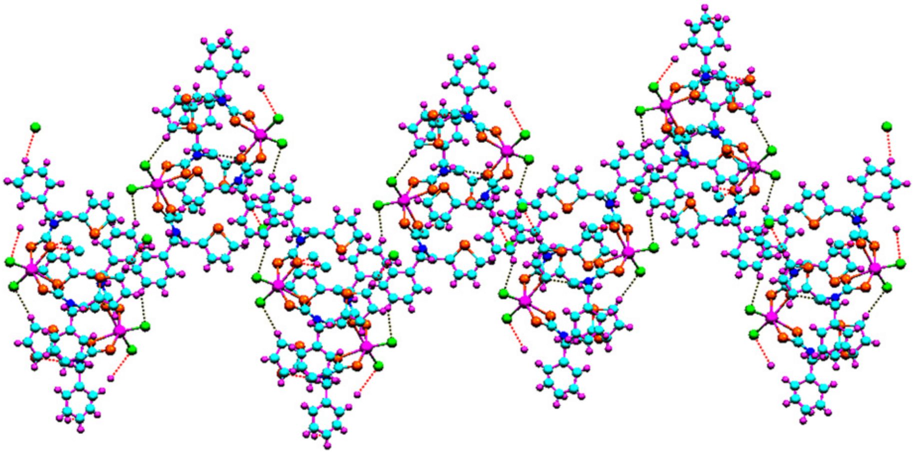


Fig. 6. Arrangement of molecules along c axis in lattice showing weak interactions.

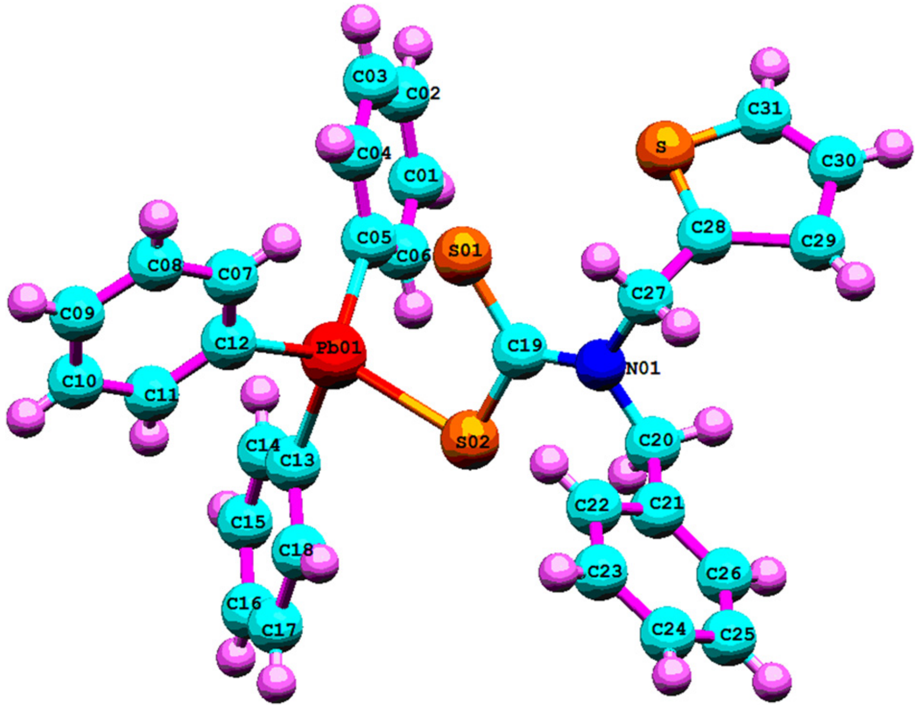


Fig. 7. Molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): S01—C19 = 1.683(6), S02—C19 = 1.754(6), Pb01—C05 = 2.193(5), Pb01—S02 = 2.5682(15), N01—C027 = 1.466(7), C05—Pb01—C13 = 118.6(2), C05—Pb01—C12 = 107.1(2), C13—Pb01—C12 = 108.7(2), C05—Pb01—S02 = 113.02(15), C19—S02—Pb01 = 98.19(19), S01—C19—S02 = 121.2(3).

atom in monodentate fashion. The structure (Fig. 7) of this compound is very much similar to that of **1**. Like organotin dithio complexes organolead dithio complex also possesses tetrahedral geometry. The distortion in tetrahedral geometry is evinced by the angles about the Pb atom. The C—S bond lengths are comparable to the corresponding bond lengths in **1** and **2**. Intermolecular weak interactions are significantly present in this compound which can be seen in Fig. 8.

4. Thermogravimetric analysis

We have carried out TGA analysis of **1**, **6** and **7** at atmospheric pressure under N2 flow. The TGA of **1** and **7** showed formation of SnS and PbS at about 350 °C with weight loss of compounds ~76% and ~67% while in compound **6**, different weight losses at 150 °C, 260 °C and 400 °C have been observed (Fig. 9) and it is not possible to make a guess about the end product from the percentage weight loss.

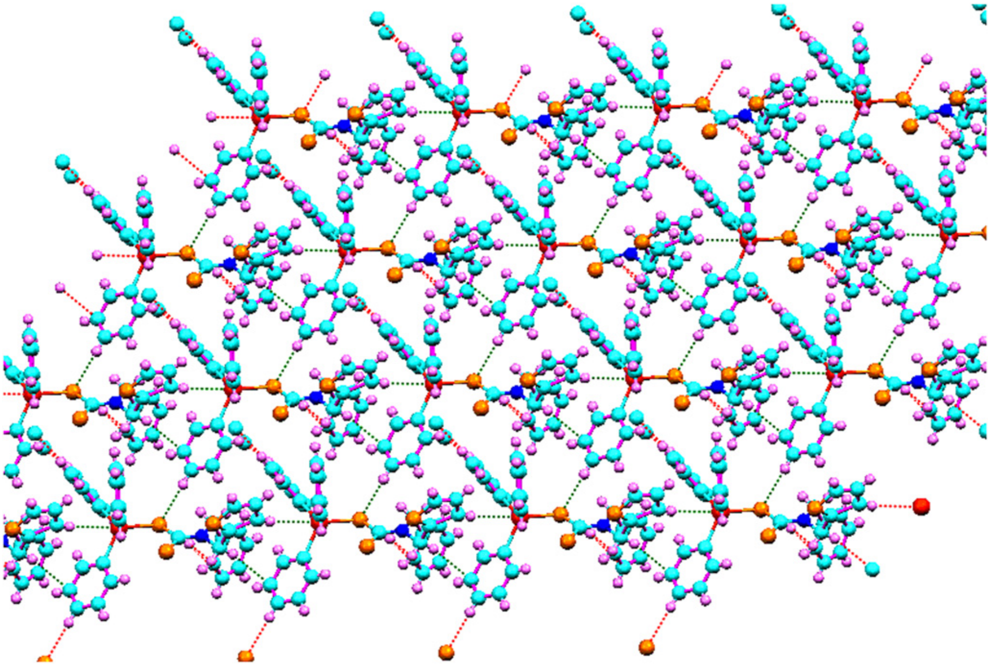


Fig. 8. Arrangement of molecules (of **7**) along an axis in a lattice showing intermolecular interactions.

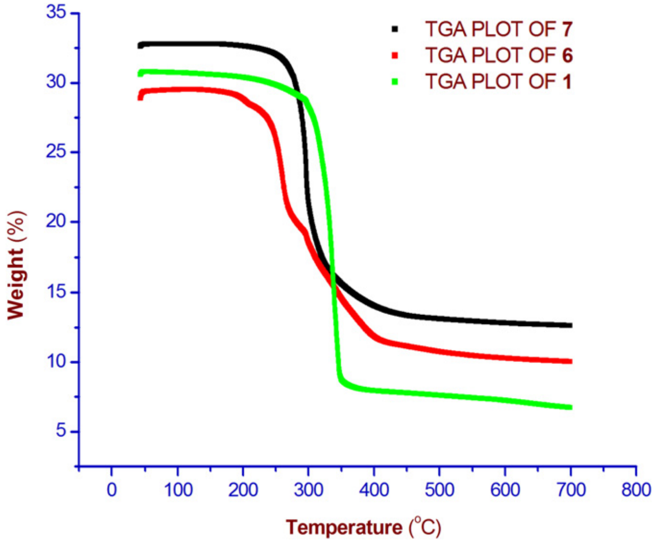


Fig. 9. TGA plot of **1**, **6** and **7** (Compound **1** and **7** showing formation of SnS and PbS).

5. Conclusion

In conclusion, the bonding of the dithiocarbamate ligands was found to vary from anisobidentate to bidentate according to the nature of the co-ligands present on the metal. In none of the cases the sulfur atom of the thiophene ring is involved in bonding with the metal. Very recent studies from our laboratory have showed that the thiophene sulfur carries a partial positive charge in the case of thiophene-2-thiocarboxylates and a dative bond from this sulfur is not quite favourable [38]. The triphenyltin and triphenyllead dithiocarbamates can be used as single source precursors for the preparation of the corresponding metal sulfides.

Appendix A. Supplementary material

CCDC Nos. 797141, 797139, 797142, 797140, 797143 and 834820 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **6** and **7** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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