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Dialkyltin(IV)bis(*O*-tolyl/benzyldithiocarbonate) Complexes: Spectroscopic, Thermogravimetric, Antifungal and Crystal Analysis of $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$

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Abstract

Novel compounds of dimethyl- and dibutyltin(IV) with *O*-tolyl/benzyldithiocarbonates were successfully obtained by the reaction of Me_2SnCl_2 and $n\text{-}Bu_2SnCl_2$ with sodium salt of *O*-tolyl/benzyldithiocarbonates, [*o*-, *m*- and *p*-$CH_3C_6H_4OCS_2Na$ and $C_6H_5CH_2OCS_2Na$], in 1:2 molar ratio in dry toluene. These newly synthesized complexes have been characterized by elemental analysis, FT–IR and multinuclear NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. The thermal behaviour of the complex **8** has been studied by TGA/DTA analysis. The complex $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**) crystallizes in the monoclinic space group *C2/c*, in which tin adopts a distorted octahedron or skew trapezoidal bipyramidal geometry accompanied by two *n*-butyl chains and the two dithiocarbonate ligands coordinated in an anisobidentate fashion. Antifungal activities against fungus *Fusarium sp.* of these organotin(IV) derivatives exhibited enhanced activity compared to the free ligands.

Keywords: Organotin(IV); Xanthate; Tolyl/benzyl dithiocarbonate; Crystal structure; Antifungal

1. Introduction

Tin is known to produce a large number of organometallic derivatives of commercial use. Inorganic and organotin compounds have found industrial use as catalysts like in heterogeneous oxidation catalysts based on tin(IV) oxide[1–2] and homogeneous catalysts for industrial organic and polymeric reactions.[3–4] Apart from the well–established uses of tin catalysts in polyurethanes,[5] RTV silicones[6] and esterification reactions,[7] new developments have included their use as anti-tumor drugs,[8–9] ion carriers in electrochemical membrane,[10] in synthetic vitamin E production[11] and in the manufacture of certain novel polymeric materials.[12] A remarkable but little known fact about tin is to save energy and reduce emissions when added to fuel[13] and are effective premixed methane flame inhibitors.[14] Over the years, a variety of uses have been found for organic and inorganic tin compounds as fungicides,[15] moluscicides[16] and stabilizers in plastics.[17] The organotin complexes exhibit a wide range of biological activities[18–20] including the inhibition of a wide variety of cancer cell lines including cell lines associated with ovarian, colon, lung, prostrate, pancreatic and breast cancer.[20] Recently there have been a number of concerns raised regarding possible human health effects associated with organotins such as the use of tributyltin (TBT) in paints caused contamination in coastal waters and marine sediments.[21] On the other hand, in recent years many different types of organotin(IV) compounds have been tested for their *in vitro* activity against a large array of tumour cell lines and have been found to be as effective as traditional heavy metal anticancer drugs such as cis-platin and paraplatin.[22–23] Clear distinctions must be drawn between triorganotin compounds used as biocides and pesticides, and those mono- and dialkyltin compounds used as polymer additives, which exhibit no biocidal properties. As such, it is inappropriate to categorize all tin compounds as having equivalent toxicological and ecotoxicological profiles. In fact, organotin(IV) complexes are extensively studied due to its coordination geometries as well as structural diversity (monomer, dimer, hexamer and oligomer).[24–26] Organotin(IV) compounds are well known to form complexes with ligands having oxygen,[27] sulfur[28] and nitrogen[29] donor sites.

Alkyldithiocarbonates are well known organosulfur compounds with high donating properties[30] and have attracted considerable attention in the last decades, because of their academic interest,[31–32] industrial applications[33–34] and potential role as anti-carcinogenic agents.[35–36] However, literature survey revealed paucity of information especially about (*o-, m-* and *p*-tolyl/benzyl)dithiocarbonate ligands and their derivatives.[37–39] The structural data on aryl xanthates of nickel(II), palladium(II) and cobalt(III) complexes have been reported for the first time by Chen *et al.*[40] The properties of aryl xanthates are similar to those of 1,1-dithiolates. These ligands and their metal derivatives are somewhat more susceptible to thermal and atmospheric decomposition than the analogous alkyl derivatives.[41] Because of the importance of both tin and dithiocarbonate complexes as antitumour agents and due to their synthetic versatility and practical utility, we undertake the synthesis of new tin(IV) complexes with dithiocarbonate ligands as no attempt has been made to synthesize and characterize organotin(IV) complexes with these ligands.

2. Experimental

2. 1. Materials and Instrumentation

Stringent precautions were taken to exclude moisture during the preparation of ligands. Moisture was carefully excluded throughout the experimental manipulations by using standard Schlenk techniques. High grade chemicals were used for synthetic purposes. Solvents were dried and distilled before use. Sodium salts of dithiocarbonate were obtained using literature procedures.[37] Tin was estimated gravimetrically as SnO_2.[42] Elemental analyses (C, H, N, S) were conducted using the Elemental Analyser Vario EL–III. The IR spectra were recorded in KBr pallets in the range of 4000–400 cm^{-1} on a Perkin Elmer spectrum RX1 FT–IR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance III spectrophotometer (400 MHz) using TMS as internal reference. The ^{119}Sn NMR spectra were recorded on a Bruker Avance II (400 MHz) spectrometer using Me_4Sn as an external standard. The thermogram was analyzed by using Perkin Elmer, diamond TG/DTA instrument. The thermogram was recorded in the temperature range from 30 °C to 1000 °C under nitrogen atmosphere. The antifungal activity was tested under laboratory condition using classical poison food technique method.

2. 2. Synthesis of Complexes

2. 2. 1. [(Me)$_2$Sn(S$_2$COC$_6$H$_4$CH$_3$-*o*)$_2$] (1)

To a suspension of NaS$_2$COC$_6$H$_4$CH$_3$-*o* (1.00 g, 4.85 mmol) in toluene was added a toluene solution of Me_2SnCl_2 (0.53 g, 2.42 mmol) dropwise with constant stirring. The reaction mixture became clear immediately after addition of Me_2SnCl_2. The white precipitates of sodium chloride were formed after stirring for 24 h at room temperature. The precipitated sodium chloride was filtered off using a funnel fitted with G–4 sintered disc and the solvent from filtrate was removed *in vacuo* which results a pale yellow viscous oily liquid. The oily liquid was dissolved in minimum amount of *n*-hexane and the solution was kept for 2–3 days at 4–5 °C to obtain a white crystalline solid. Yield: 1.12 g (90%); m.p. 61 °C; Anal. Calcd. for $C_{18}H_{20}O_2S_4Sn$ (%): C, 41.95; H, 3.91; S, 24.89; Sn, 23.04. Found: C, 41.92; H, 3.88; S, 24.86; Sn, 23.01. IR (KBr, cm^{-1}): 3022 br, ν(C–H), 1612 br ν(C–C), 1232 s, ν(C–O–C), 1060 s, ν(C=S), 999 s, ν(C–S), 532 w, ν(Sn–C), 454 m, 420 w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 1.12 (s, 6H, CH_3Sn), 2.22 (s, 6H, CH_3), 6.72 (d, 2H, *ortho*), 6.75 (m, 4H, *meta*), 6.96 (t, 2H, *para*) ppm. ^{13}C NMR ($CDCl_3$): 16.80 (CH_3Sn), 20.75 (CH_3), 119.73 (C–*ortho*), 120.22 (C–*para*), 122.91 (C–CH_3), 125.76–128.72 (C–*meta*), 152.84 (C–O), 167.85 (OCS_2) ppm. ^{119}Sn NMR ($CDCl_3$): –128.26 ppm.

2. 2. 2. [(Me)$_2$Sn(S$_2$COC$_6$H$_4$CH$_3$-*m*)$_2$] (2)

A similar method to that of **1** was utilized for the synthesis of [(Me)$_2$Sn(S$_2$COC$_6$H$_4$CH$_3$-*m*)$_2$] as white crystalline solid from NaS$_2$COC$_6$H$_4$CH$_3$-*m* (1.00 g, 4.85 mmol) and Me_2SnCl_2 (0.53 g, 2.42 mmol). Yield: 1.02 g (82%); m.p. 62 °C; Anal. Calcd. for $C_{18}H_{20}O_2S_4Sn$ (%): C, 41.95; H, 3.91; S, 24.89; Sn, 23.04. Found: C, 41.93; H, 3.88; S, 24.85; Sn, 23.00. IR (KBr, cm^{-1}): 3014 br, ν(C–H), 1607 br, ν(C–C), 1248 s, ν(C–O–C), 1082 s, ν(C=S), 1011 s, ν(C–S), 536 w, ν(Sn–C), 452 m, 419 w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 1.10 (s, 6H, CH_3Sn), 2.21 (s, 6H, CH_3), 6.82 (m, 4H, *ortho*), 6.92 (d, 2H, *para*), 7.00 (t, 2H, *meta*) ppm. ^{13}C NMR ($CDCl_3$): 17.24 (CH_3Sn), 21.67 (CH_3), 119.47–121.84 (C–*ortho*), 120.40 (C–*para*), 124.65 (C–*meta*), 126.80 (C–CH_3), 150.82 (C–O), 168.24 (OCS_2) ppm.

2. 2. 3. [(Me)$_2$Sn(S$_2$COC$_6$H$_4$CH$_3$-*p*)$_2$] (3)

Compound [(Me)$_2$Sn(S$_2$COC$_6$H$_4$CH$_3$-*p*)$_2$] **(3)** was obtained as a white crystalline solid using NaS$_2$COC$_6$H$_4$CH$_3$-*p* (1.00 g, 4.85 mmol) and Me_2SnCl_2 (0.53 g, 2.42 mmol), according to the procedure described for the synthesis of **1.** Yield: 1.07 g (86%); m.p. 77 °C; Anal. Calcd. for

$C_{18}H_{20}O_2S_4Sn$ (%): C, 41.95; H, 3.91; S, 24.89; Sn, 23.04. Found: C, 41.90; H, 3.87; S, 24.83; Sn, 22.98. IR (KBr, cm^{-1}): 3031 br, ν(C–H), 1615 br, ν(C–C), 1233 s, ν(C–O–C), 1087 s, ν(C=S), 1016 s, ν(C–S), 513 w, ν(Sn–C), 472 m, 428 w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 1.12 (s, 6H, CH_3Sn), 2.23 (s, 6H, CH_3), 6.78 (d, 4H, *ortho*), 7.05 (d, 4H, *meta*) ppm. ^{13}C NMR ($CDCl_3$): 17.01 (CH_3Sn), 21.09 (CH_3), 120.15 (C–*ortho*), 129.85 (C–*meta*), 130.45 (C–CH_3), 151.96 (C–O), 169.41 (OCS_2) ppm. ^{119}Sn NMR ($CDCl_3$): –128.92 ppm.

2. 2. 4. [$(Me)_2Sn(S_2COCH_2C_6H_4)_2$] (4)

The complex [$(Me)_2Sn(S_2COCH_2C_6H_4)_2$] **(4)** was synthesized as white solid from $NaS_2COCH_2C_6H_5$ (1.00 g, 4.85 mmol) and Me_2SnCl_2 (0.53 g, 2.42 mmol), according to the protocol as described for complex **1**. Yield: 1.15 g (92%); m.p. 59 °C; Anal. Calcd. for $C_{18}H_{20}O_2S_4Sn$ (%): C, 41.95; H, 3.91; S, 24.89; Sn, 23.04. Found: C, 41.93; H, 3.90; S, 24.87; Sn, 23.02. IR (KBr, cm^{-1}): 3032 br, ν(C–H), 1608 br, ν(C–C), 1242 s, ν(C–O–C), 1078 s, ν(C=S), 1005 s, ν(C–S), 509 w, ν(Sn–C), 473 m, 427 w, ν(Sn–S); ^{1}H NMR ($CDCl_3$): 0.98 (s, 6H, CH_3Sn), 4.54 (s, 4H, CH_2), 7.01–7.12 (m, 10H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$): 16.96 (CH_3Sn), 61.50 (CH_2), 125.89 (C–*ortho*), 126.75 (C–*para*), 131.02 (C–*meta*), 141.04 (C–CH_2), 185.20 (OCS_2) ppm.

2. 2. 5. [$(n\text{-Bu})_2Sn(S_2COC_6H_4CH_3\text{-}o)_2$] (5)

The synthesis of [$(n\text{-Bu})_2Sn(S_2COC_6H_4CH_3\text{-}o)_2$] **(5)** was carried out as described for the complex **1** from $NaS_2COC_6H_4CH_3$-*o* (1.00 g, 4.85 mmol) and *n*-Bu_2SnCl_2 (0.74 g, 2.42 mmol). Yield: 1.34 g (93%); m.p. 64 °C; Anal. Calcd. for $C_{24}H_{32}O_2S_4Sn$ (%): C, 48.09; H, 5.38; S, 21.40; Sn, 19.80. Found: C, 48.03; H, 5.32; S, 21.36; Sn, 19.76. IR (KBr, cm^{-1}): 3030 br, ν(C–H), 1614 br, ν(C–C), 1238 s, ν(C–O–C), 1056 s, ν(C=S), 997 s, ν(C–S), 511 w, ν(Sn–C), 450 m, 412, w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 0.93 (t, 6H, Me), 1.35–1.69 {m, 12H, $Sn(CH_2)_3$}, 2.21 (s, 6H, CH_3), 6.70 (d, 2H, *ortho*), 6.82 (m, 4H, *meta*), 7.05 (t, 2H, *para*) ppm. ^{13}C NMR ($CDCl_3$): 14.02, 17.48, 27.40, 28.21 ($CH_3CH_2CH_2CH_2Sn$), 20.18 (CH_3), 119.30 (C–*ortho*), 121.20 (C–*para*), 122.50 (C–CH_3), 125.62–126.81 (C–*meta*), 152.01 (C–O), 167.82 (OCS_2) ppm.

2. 2. 6. [$(n\text{-Bu})_2Sn(S_2COC_6H_4CH_3\text{-}m)_2$] (6)

A similar method to that of **1** was utilized from $NaS_2COC_6H_4CH_3$-*m* (1.00 g, 4.85 mmol) and *n*-Bu_2SnCl_2 (0.74 g, 2.42 mmol) for the synthesis of [$(n\text{-Bu})_2Sn(S_2COC_6H_4CH_3\text{-}m)_2$] **(6)** as white crystalline solid. Yield: 1.16 g (80%); m.p. 62 °C; Anal. Calcd. for $C_{24}H_{32}O_2S_4Sn$ (%): C, 48.09; H, 5.38; S, 21.40; Sn, 19.80. Found: C, 48.02; H, 5.32; S, 21.35; Sn, 19.75. IR (KBr, cm^{-1}): 3029 br, ν(C–H), 1599 br, ν(C–C), 1236 s, ν(C–O–C), 1084 s, ν(C=S), 1012 s, ν(C–S), 535 w, ν(Sn–C), 477 m, 425 w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 0.92 (t, 6H, Me), 1.36–1.65 {m, 12H, $Sn(CH_2)_3$}, 2.23 (s, 6H, CH_3), 6.81 (m, 4H, *ortho*), 6.91 (d, 2H, *para*), 7.09 (t, 2H, *meta*) ppm. ^{13}C NMR ($CDCl_3$): 14.01, 17.12, 27.38, 28.12 ($CH_3CH_2CH_2CH_2Sn$), 20.62 (CH_3), 119.91–122.35 (C–*ortho*), 120.85 (C–*para*), 126.35 (C–*meta*), 130.82 (C–CH_3), 152.84 (C–O), 168.25 (OCS_2) ppm. ^{119}Sn NMR ($CDCl_3$): –154.82 ppm.

2. 2. 7. [$(n\text{-Bu})_2Sn(S_2COC_6H_4CH_3\text{-}p)_2$] (7)

Compound [$(n\text{-Bu})_2Sn(S_2COC_6H_4CH_3\text{-}p)_2$] **(7)** was obtained from $NaS_2COC_6H_4CH_3$-*p* (1.00 g, 4.85 mmol) and *n*-Bu_2SnCl_2 (0.74 g, 2.42 mmol) as white crystalline solid according to the procedure described for the synthesis of **1.** Yield: 1.27 g (88%); m.p. 78 °C; Anal. Calcd. for $C_{24}H_{32}O_2S_4Sn$ (%): C, 48.09; H, 5.38; S, 21.40; Sn, 19.80. Found: C, 48.03; H, 5.33; S, 21.35; Sn, 19.75. IR (KBr, cm^{-1}): 3031 br, ν(C–H), 1615 br, ν(C–C), 1232 s, ν(C–O–C), 1090 s, ν(C=S), 1020 s, ν(C–S), 512 w, ν(Sn–C), 476 m, 429 w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 0.91 (t, 6H, Me), 1.33–1.68 {m, 12H, $Sn(CH_2)_3$}, 2.23 (s, 6H, CH_3), 6.75 (d, 4H, *ortho*), 7.04 (d, 4H, *meta*) ppm. ^{13}C NMR ($CDCl_3$): 13.86, 17.26, 26.92, 27.83 ($CH_3CH_2CH_2CH_2Sn$), 21.06 (CH_3), 120.80 (C–*ortho*), 123.62 (C–*meta*), 128.30 (C–CH_3), 151.92 (C–O), 169.50 (OCS_2) ppm.

2. 2. 8. [$(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2$] (8)

The complex [$(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2$] **(8)** was synthesized from $NaS_2COCH_2C_6H_5$ (1.00 g, 4.85 mmol) and *n*-Bu_2SnCl_2 (0.74 g, 2.42 mmol) as white crystalline solid according to the protocol as described for complex **1**. Yield: 1.42 g (98%); m.p. 60 °C; Anal. Calcd. for $C_{24}H_{32}O_2S_4Sn$ (%): C, 48.09; H, 5.38; S, 21.40; Sn, 19.80. Found: C, 48.06; H, 5.35; S, 21.37; Sn, 19.78. IR (KBr, cm^{-1}): 3034 br, ν(C–H), 1608 br, ν(C–C), 1240 s, ν(C–O–C), 1080 s, ν(C=S), 1007 s, ν(C–S), 513 w, ν(Sn–C), 475 m, 427 w, ν(Sn–S). ^{1}H NMR ($CDCl_3$): 0.93 (t, 6H, Me), 1.34–1.65 {m, 12H, $Sn(CH_2)_3$}, 4.62 (s, 4H, CH_2), 7.27–7.34 (m, 10H, C_6H_5). ^{13}C NMR ($CDCl_3$): 13.91, 17.52, 26.94, 27.80 ($CH_3CH_2CH_2CH_2Sn$), 62.08 (CH_2), 127.05 (C–*ortho*), 128.65 (C–*para*), 131.28 (C–*meta*), 141.20 (C–CH_2), 187.65 (OCS_2) ppm. ^{119}Sn NMR ($CDCl_3$): –154.99 ppm.

2. 3. Antifungal Activity

Potato dextrose medium (PDA) was prepared in a flask and sterilized. Now 100 μL of each sample was added to the PDA medium and poured into each sterilized petri plate. Mycelial discs taken from the standard culture (*Fusarium oxysporum*) of fungi were grown on PDA medium for 7 days. These cultures were used for aseptic inoculation in the sterilized Petri dish. Standard cultures, inoculated at 28 ± 1 °C, were used as the control. The efficiency of each sample was determined by measuring the radial fungal growth. The radial growth of the colony was measured in two directions at right angles to each other and the average of two replicates was recorded in each case. Data were expressed as percent inhibition over the control from the size of the colonies. The percent inhibition was calculated using the formula % Inhibition = $((C–T)/C) \times 100$, where C is the diameter of the fungus colony in the control plate after 96 hrs incubation and T is the diameter of the fungus colony in the tested plate after the same incubation period.

2. 4. X–ray Crystallography

A white block-shaped single crystal of **8**, measuring 0.30 × 0.20 × 0.10 mm, was picked up for X–ray intensity data collection. X–ray intensity data were collected by using an X'calibur Oxford Diffraction system with graphite monochromatic Mo K_α radiation (λ = 0.71073 Å), and reduced with CrysAlis RED.[43] A total number of 5152 reflections were collected of which 2664 reflections were unique. Data were corrected for Lorentz, polarization and absorption factors. The structure was solved by direct methods using SHELXS97 and refined by SHELXL97.[44] The geometry of the molecule is determined by PLATON[45] and PARST[46] software. All H atoms were geometrically fixed and allowed to ride on their parent C atoms, with C–H distances of 0.925–0.970 Å and with U_{iso}(H) = 1.5U_{eq}(methyl C) and 1.2U_{eq}(C) for other hydrogen atoms. The crystallographic data are summarized in Table 1.

Table 1. Summary of the crystal structure, data collection and structure refinement parameters for the complex [$(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2$] (**8**).

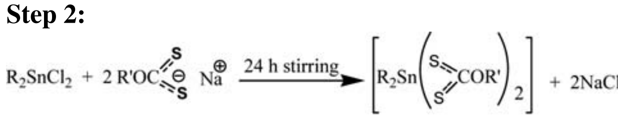
Chemical formula:	**$C_{24}H_{32}O_2S_4Sn$**
Crystal size	0.30 × 0.20 × 0.10 mm^3
Formula weight	599.43
Crystal description	white block
T	293(2) K
Crystal system	Monoclinic
Space group	$C\,2/c$
Unit cell dimensions	a = 30.943(2) Å, b = 5.9261(4) Å
	c = 17.1020(13) Å, β = 120.201(5)°
Z	4
V	2710.4(3) Å^3
D_x	1.469 g/cm^3
Absorption coefficient, μ	1.269 mm^{-1}
F(0 0 0)	1224
No. of reflections collected	5152
No. of unique reflections	2664
θ range for data collection	3.6 to 26.00°
Range of indices	h= –36 to 38, k= –7 to 4, l= –21 to 16
Goodness–of–fit	1.018
R indices [$I > 2\sigma(I)$]:	$R1$ = 0.0342, $wR2$ = 0.0682
R indices (all data):	$R1$ = 0.0489, $wR2$ = 0.0754
$(\Delta\rho)$max	0.525 eÅ^{-3}
$(\Delta\rho)$min	–0.575 eÅ^{-3}

3. Results and Discussion

The sodium salts of *O*-tolyl/benzyl dithiocarbonates were prepared according to the published method[37] (Step 1). Reactions of dimethyl/di(*n*-butyl)tin(IV) dichloride with sodium salts of *O*-tolyl/benzyl dithiocarbonates in 1 : 2 molar ratio in toluene yielded dimethyl/di(*n*-butyl) tin(IV)bis{*o*-, *m*- or *p*-tolyl/benzyl dithiocarbonate} complexes of the type, $R_2Sn(S_2COR')_2$ in quantitative yield as white crystalline solids (Step 2).

Step 1:

Step 2:



(R = Me (1-4) and *n*-Bu (5-8);
R' = *o*-, *m*-, *p*-$CH_3C_6H_4$– and –$CH_2C_6H_5$)

All these complexes are soluble in organic solvents like toluene, benzene, chloroform, methylene chloride. These complexes appear to be a bit moisture sensitive; however, can be kept unchanged in dry and nitrogen atmosphere. The elemental analyses, particularly C, H, S and Sn were found consistent with the molecular formula of these compounds. These compounds were further characterized by thermogravimetric analysis (TGA) and various spectral studies *viz.* IR, ^{1}H, ^{13}C and ^{119}Sn NMR. The crystal and molecular structure of **8** was determined by single crystal X–ray technique.

3. 1. IR Spectra

Tentative assignments have been made on the basis of comparison with the earlier reports.[31–32,37–41] The absorptions of interest in the spectra of the complexes are ν(CSS), ν(Sn–C), and ν(Sn–S). The presence of weak to medium intensity bands of ν(Sn–S) in the range 477–412 cm^{-1} indicates the coordination of the dithio ligand with the tin as expected. The vacant 5d orbital of tin atoms tends toward high coordination with ligands containing lone pairs of electrons. Bands of weak intensity due to ν(Sn–C) lay in the region 536–509 cm^{-1}. Comparison of IR stretching frequencies of the ligands provide quite seminal information for determining the structures particularly when there are interactions between the sulfur atoms of the dithio groups and the tin atom. Strong absorptions in the region 1090–1056 cm^{-1} and 1020–997 cm^{-1} which are characteristics of dithiocarbonate ligands were displaced to lower frequency in all the complexes (**1–8**) and were assigned to the stretching vibrations of ν(C=S) and ν(C–S) respectively. The IR spectra also show the characteristic sharp band for (C–O–C) and broad band for (C=C) (tolyl and benzyl ring stretching) in the range 1248–1232 and 1615–1599 cm^{-1}, respectively.

3. 2. ^{1}H NMR Spectra

The ^{1}H NMR spectra ($CDCl_3$) for organotin(IV) bis(*o*-, *m*- or *p*-tolyl/benzyl) dithiocarbonate complexes were similar to those of the corresponding salts of dithiocarbonates, probably, due to the large separation between tin and the hydrogen atoms. Negligible shift toward lower frequency (0.98–1.12 ppm) for the methyl protons on tin were observed in complexes **1–4** compared with the corresponding Me_2SnCl_2. The multiplet in the region 0.91–1.69 ppm is due to protons of butyl group attached with tin. The ^{1}H NMR signal for the methyl protons of the tolyldithio moiety in the complexes **1–3** and **5–7** appeared as singlet at 2.21–2.23 ppm whereas the methylene protons of the benzyldithio moiety resonated at 4.54–4.62 ppm as singlet. The phenyl protons appeared in the expected region of 6.70–7.34 ppm, undergoing a negligible upfield shift of ca. 0.03–0.20 ppm as compared with their position in the free ligand, presumably, as a consequence of coordination. There were two resonances for the ring protons of *para* complexes whereas four resonances were observed for *ortho* and *meta* derivatives.

3. 3. ^{13}C NMR Spectra

Evidence for the formation of the complexes is clearly exhibited in the ^{13}C NMR spectra by occurrence of a sharp peak for CS_2 carbon with the downfield shift in the range 167.82–187.65 ppm compared to that of the free ligands. The other carbon nuclei did not show any appreciable deviation in the chemical shift value compared to the parent dithio moiety. The chemical shift for methyl ($–CH_3$) and methylene ($–CH_2$) carbon occurred in the range 20.18–21.67 and 61.50–62.08 ppm, respectively. The carbon nuclei of phenyl ring ($–C_6H_5$ and $–C_6H_4$) have displayed their resonance in the region 119.30–152.84 ppm. These complexes show the chemical shifts for CH_3 and CH_2 carbons of methyl and butyl moities in their expected regions.

3. 4. ^{119}Sn NMR Spectra

The ^{119}Sn NMR spectra of few representative complexes **1, 3, 6** and **8** scanned in chloroform showed singlet in the region –128.26 to –128.92 and –154.82 to –154.99 ppm for dimethyltin and dibutyltin derivatives, respectively. These values may be interpreted in terms of a tetra coordinated Sn atom in chloroform solution. These results are consistent with earlier reports on δ ^{119}Sn as suggested by Dakternieks *et al.*[47] These ^{119}Sn resonances appear at significantly lower frequencies than those of their precursors Me_2SnCl_2 (+137 ppm) and *n*–Bu_2SnCl_2 (+123 ppm), which is indicative of the removal of the electronegative group from the precursors.

3. 5. Thermogravimetric Analysis

The thermal properties of the complex **8** were studied by TGA in the temperature range 30–1000 °C under nitrogen atmosphere. The content of a particular component in a complex changes with its composition and structure. These can be determined based on mass losses of these components in the thermogravimetric plots of the complexes. The thermogravimetric analysis of the complex, $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**) displayed a thermolysis step that covers a temperature range from 150 to 900 °C. The thermogram (Figure 1) exhibited the decline curve characteristic for dithiocarbonate complexes. The diagnostic weight loss occurs in the steeply descending segment of the TGA curve. This weight loss *i.e.* 30.07% at 296.8 °C is due to the formation of $[(n\text{-Bu})_2Sn(S_2COH)_2]$, (the calculated weight loss is 30.11%) as an intermediate product, which agrees with thermogravimetric data for dithiocarbonates. Another important weight loss 49.46% (obs.) occur at 416.8 °C temperature corresponding to the formation of $[Sn(S_2COH)_2]$ (weight loss calculated 50.02%), The decomposition continue to about 711.8 °C at which most of the organic part of the compound has been lost. This sharp decomposition period brings about 67.6% (obs.) 68.0% (calc.) weight loss in the tin complex and led to the complete formation of metal sulfide *i.e.* SnS_2.

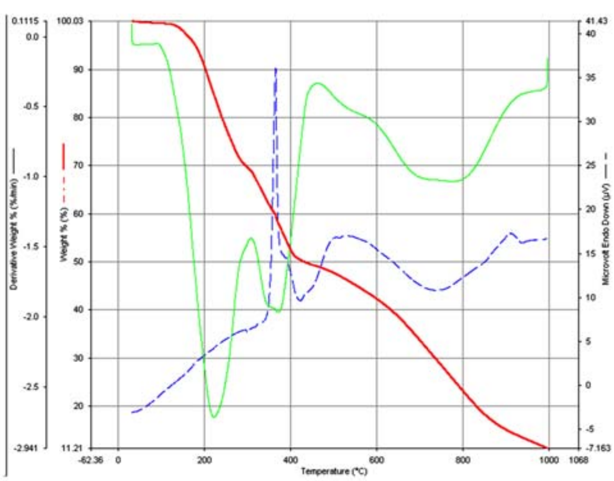


Figure 1. TGA curve for the complex $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**).

3. 6. Antifungal Activity

The inhibitory activities of the dithiocarbonate ligands and its organotin(IV) complexes were examined against the fungus *Fusarium oxysporium* and are summarized in Table 2. The values obtained suggest that the dithiocarbonate derivatives of tin are more fungitoxic than the parent dithio ligand. Furthermore, the data also indicate that with the increase in concentration of the complexes the inhibitory effect on the mycelial growth of the fungus also increases, which can be explained on the basis of Overtone's concept and Tweedy's Chelation theory.[48] All the complexes showed promising result in inhibiting the mycelial growth of the fungus at a concentration of 250 ppm. The different inhibitory effect of the complexes can be correlated by their different structures.

Table 2. *In vitro* evaluation of ligand and complexes against the fungus *Fusarium oxysporum* f. Sp. *Capsici*.

Complex. No.	Conc. (ppm)	Colony diameter(mm)	%Inhibition $I = [(C–T)/C] \times 100$
Ligand	50	4.3	4
	100	3.8	16
	150	3.4	24
	200	3.0	33
	250	2.6	42
1.	50	2	55
	100	1.7	62
	150	1.5	67
	200	1.0	78
	250	0.7	84
4.	50	1.9	58
	100	1.7	62
	150	1.4	69
	200	1.2	73
	250	0.6	87
8.	50	2.2	51
	100	2.0	56
	150	1.7	62
	200	1.3	71
	250	0.5	89

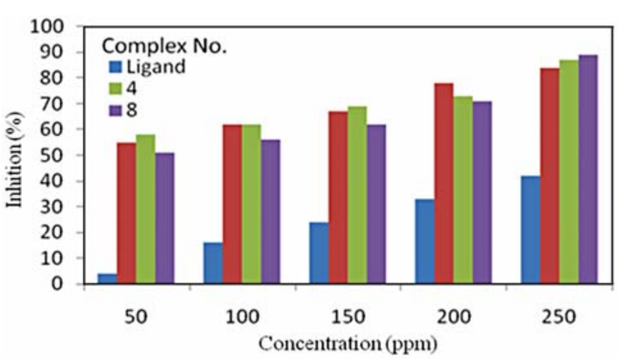


Figure 2. Graph showing comparative result of antifungal activity

The comparison of antifungal activity of the ligand and some of the complexes is described diagrammatically in Figure 2.

3. 7. Crystal Structure of [$(n$-Bu$)_2$Sn$(S_2COCH_2C_6H_5)$2] (8)

The molecular structure of the complex **8** features that Sn is coordinated by two dithiocarbonato ligands and two α-C atoms of the *n*-butyl groups (Figure 3). Selected interatomic parameters are given in Table 3. The C–S bond lengths of the two dithiocarbonate ligands can be separated into shorter C–S bond lengths (1.651 Å) and longer C–S bond lengths (1.718 Å). The former are significantly longer than the sum of the double bond covalent bond radii, while latter are roughly intermediate between their single and double bond covalent radii. The Sn–S

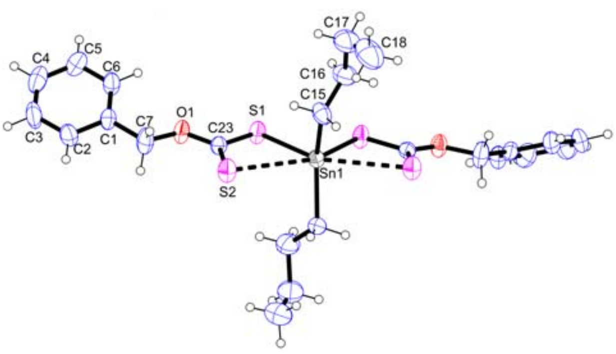


Figure 3. *ORTEP* view of the complex [$(n$-Bu$)_2$Sn$(S_2COCH_2C_6H_5)_2$] (**8**) with displacement ellipsoids drawn at 40% probability level.

Table 3. Selected bond lengths (Å) and bond angles (°) for the complex [$(n$-Bu$)_2$Sn$(S_2COCH_2C_6H_5)_2$] (**8**)[a].

Bond Lengths			
Sn1–C15	2.130(6)	Sn1–C15^i	2.130(6)
Sn1–S1	2.507(5)	Sn1–S1^i	2.507(5)
Sn1–S2	3.091(11)	Sn1–S2^i	3.091(11)
S1–C23	1.718(5)	S1^i –C23^i	1.718(5)
S2–C23	1.651(3)	S2^i–C23^i	1.651(3)
O1–C23	1.328(5)	O1–C7	1.442(6)
Bond Angles			
C15^i–Sn1–C15	134.66(17)	C15–Sn1–S1^i	109.03(12)
C15^i–Sn1–S1	109.03(12)	C15–Sn1–S1	104.32(12)
C15^i–Sn1–S1^i	104.32(12)	S1–Sn1–S2	63.24(3)
S1^i–Sn1–S2^i	63.24(3)	S1^i–Sn–S2	146.92(3)
S1–Sn1–S2^i	146.92(3)	S2–Sn1–S2^i	149.79(3)
S1–Sn1– S1^i	83.87(3)	C15–Sn1–S2^i	84.47(12)
C15–Sn1–S2	84.00(12)	C23–S1–Sn1	95.25(11)
C23^i –S1^i–Sn1	95.25(11)	C23–S2–Sn1	77.24(12)
C23^i –S2^i–Sn1	77.24(12)	S1–C23–S2	124.13(19)
S1^i–C23–S2^i	124.13(19)		

[a]Symmetry transformations used to generate equivalent atoms: (i) $–x, y, 1½ – z$.

bond lengths in the complex **8** for the two dithio groups are 2.507 Å and 3.091 Å which reveal that the two dithiocarbonate ligands are chelating but form asymmetric Sn–S distances. The shorter Sn–S distances (2.507 Å) in $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ are almost similar to Sn–S distances in $Sn(S_2COEt)_4$ (2.488 Å)[49] and (oxine)$_2$Sn$(S_2COEt)_2$(2.484 Å).[50] In the complex **8** Sn–S distances are long compared to the sum of the covalent radii for Sn and S (2.42 Å) but well within the sum of the van der Waals radii for these atoms (4 Å). So the tin atom exists in a skew trapezoidal bipyramidal geometry akin to that described for analogous tin compounds (Ph(Me)Sn$(S_2COMe)_2$, $Ph_2Sn(S_2COMe)_2$,[51] $Ph_2Sn(S_2COEt)_2$,[52] $Me_2Sn(S_2COCy)_2$,[53] and $[\{(3,5\text{–}CH_3)_2C_6H_3O)_2PS_2\}_2Sn(nBu)_2]$.[54] Crystallographic investigations of related xanthate[55] and dithiophosphate[56] complexes of nickel have shown bidentate mode of bonding where distances of (Ni–S1 and Ni–S2) are almost equivalent leading to octahedral geometry compared to the present tin complex having distortion in octahedral geometry owing to anisobidentate linkage of dithiomoiety. The sum of the four angles S1–Sn1–S1^i, S1–Sn1–S2, S2–Sn1–S2^i and S1^i–Sn1–S2^i is 360.14°, which is almost planar and supporting the plane formed by tin and the four sulfur atoms. The dibutyltin(IV) complex **8** has the C15–Sn1–S1 and C15^i–Sn1–S1 bond angles fairly close to tetrahedral angle ranging from 104.32(12)° and 109.03(12)°. However, the bond angles including S1–Sn1–S1^i [83.87(3)°] and C15–Sn1–C15^i [134.66(17)°] revealed a marked deviation from an ideal tetrahedral value. The wider angle, C15–Sn1–C15^i, is ascribed to the influence of the proximate S2 and S2^i atoms [Sn···S2 = 3.091(11) Å and Sn···S2^i = 3.091(11) Å]. Thus the complex $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**) can be identified as a distorted octahedral or skew trapezoidal bipyramidal complex (Figure 4) in solid state as reported for analogous complexes.[44, 48–50]

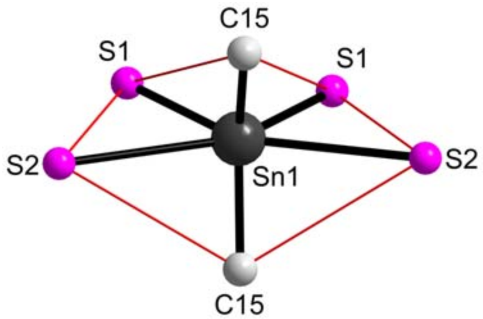


Figure 4. Skew trapezoidal bipyramidal view of the complex $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**).

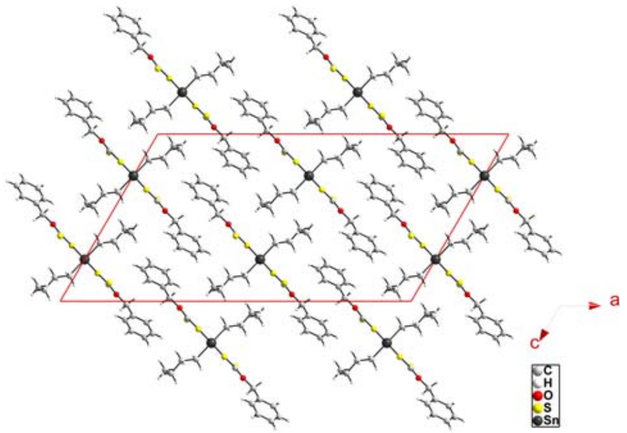


Figure 5. The packing arrangement of the complex $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**) viewed along the b-axis.

Packing of the molecules in the unit cell down the *b*-axis is shown in Figure 5. The molecules within the unit cell are arranged in a manner to form layers. The crystal structure is stabilized by intramolecular C–H···O interactions (Table 4).

4. Conclusion

Eight new organotin complexes of *O*-tolyl/benzyl dithiocarbonic acids containing Sn–C bond were isolated in quantitative yield and characterized by spectroscopic methods and single crystal X–ray analysis. TGA shows decomposition upto 711.8 °C and led to the formation of SnS_2. Single crystal analysis of the complex $[(n\text{-Bu})_2Sn(S_2COCH_2C_6H_5)_2]$ (**8**) shows a skew–trapezoid bipyramidal geometry around the tin atom due to the anisobidentate linkage of the two dithio ligands. The complexes have shown potential antifungal activity against fungus *Fusarium sp*. compared to the free ligands, which may be correlated to the coordination of tin with dithiocarbonate ligands.

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Table 4. The geometry of intramolecular interactions.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	θ [D–H···A (°)]
C6–H6···O1	0.930	2.463	2.776	99.76(2)

mentation Facility, Punjab University, Chandigarh, and National Chemical Laboratory, Pune, for providing spectral facilities.

6. Supplementary Data

CCDC 963074 contains the supplementary crystallographic data for complex **8**. The 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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Povzetek

Nove spojine dimetil- in dibutilkositra(IV) z *O*-tolil/benzilditiokarbonati so bile uspešno pripravljene z reakcijo Me_2SnCl_2 in *n*-Bu_2SnCl_2 z natrijevo soljo *O*-tolil/benzilditiokarbonata, [*o*-, *m*- in *p*-$CH_3C_6H_4OCS_2Na$ in $C_6H_5CH_2OCS_2Na$], v molskem razmerju 1:2 v suhem toluenu. Spojine so bile okarakterizirane z elementno analizo, FT–IR in NMR (^1H, ^{13}C and ^{119}Sn) spektroskopijo. Termične lastnosti spojine **8** so bile določene z TGA/DTA analizo. Spojina [(*n*-Bu)$_2$Sn($S_2COCH_2C_6H_5$)$_2$] (**8**) kristalizira v monoklinski prostorski skupini *C2/c* s popačeno oktaedrično oziroma deformirano trapezoidno bipiramidalno razporeditvijo dveh *n*-butilnih skupin in dveh anizobidentatnih ditiokarbonato ligandov okoli kositrovega atoma. Fungicidne aktivnosti organokositrovih(IV) derivatov proti *Fusarium sp*. izkazujejo povečano aktivnost glede na proste ligande.