



Spectral Characterization and X-Ray Crystallographic Studies of Some Triphenyltin(IV) Dithiocarbamates Compounds

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Three novel triphenyltin(IV) compounds with *N*-(2-methoxyethyl)-*N*-methylthiocarbamate (**1**), *N*-benzyl-*N*-phenethylthiocarbamate (**2**) and *N*-methyl-*N*-hexylthiocarbamate (**3**) ligands have been successfully synthesized *via in situ* insertion method. The newly synthesized compounds gave fairly sharp melting points indicating their purity and were successfully isolated as crystalline solids. All the compounds have been characterized by CHNS elemental analysis, FT-IR, ¹H, ¹³C and ¹¹⁹Sn NMR spectroscopies. A single C-S vibration band around 1000 cm⁻¹ was observed in all compounds, suggesting bidentate bonding of dithiocarbamate ligand to tin metal through both sulfur donor atoms. The crystal structures of all the compounds were determined by X-ray crystallography. All the compounds were crystallized in triclinic system having P1 space group. The single crystal X-ray diffraction data illustrated all three dithiocarbamate ligands are bidentate but in asymmetric fashion due to Δ(Sn-S) bond length and the geometry at the tin center is described as distorted trigonal-bipyramidal.

Keywords: Triphenyltin(IV), Dithiocarbamates, X-ray crystallography.

INTRODUCTION

Dithiocarbamate (DTC), a four-electron donating ligand that is capable of either π -electron donation or withdrawal, has played a role in the study of a wide variety of compounds. This monoanionic ligand has been used in the synthesis of lower and higher oxidation state transition metal compounds [1]. The ability of the ligand to adopt dithiocarbamate and thioureide tautomers gives it unique properties to stabilize both low- and high-valent metal ions (Fig.1). The dithiocarbamate form (A) is considered as a soft ligand that is capable in binding to low-valent metal atoms such as tin, while extra negative charge localized on sulfur in the thioureide tautomer (D) is best described as a hard ligand and best suited to high-valent metal binding [2].

The coordination geometry of tin atom in the complexes may be tetrahedral, trigonal-bipyramidal, square-pyramidal, octahedral or pentagonal bipyramidal, depending on the number of organic groups, the coordination mode of CS₂ moiety and

the number of ligands attached to tin atom [3]. It is worth mentioning that organotin derivatives have a wide range of applications, from agriculture and biology, to catalysis and organic synthesis [4]. Organotin compounds are mostly known for their biocidal effects and have been widely used as wood preservatives, acaricides, disinfectants, bactericides, fungicides, molluscicides, PVC stabilizers, and marine antifouling products [5]. Since, serendipitous discovery of the antiproliferative activity of cisplatin; which was the first metal-containing anticancer drug, much effort have been shifted to the design of new metal-based drugs for oncology therapies [6]. Tin complexes are proposed to have therapeutic potential as alternatives to cisplatin and similar anticancer agents [5] since platinum and tin atoms possess common chemical properties [7]. The antitumor activity of several tin based compounds have also been investigated and reported, which sparked an interest in tin compounds [5]. A large number of organotin(IV) compounds have been tested *in vitro* and *in vivo*, firstly against murine leukemia cell lines, followed by different panels of human cancer cell lines [8].

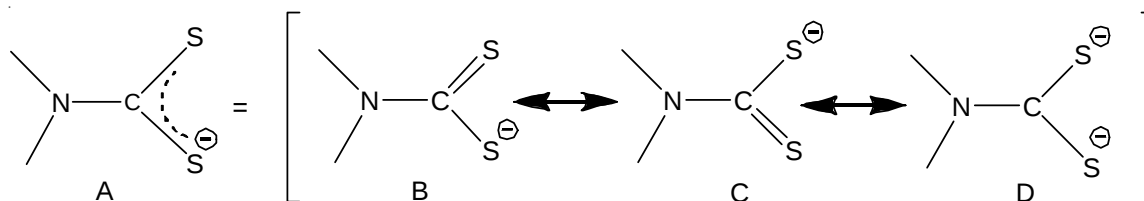


Fig. 1. Resonance forms of the dithiocarbamic -NCSS- moiety

In general, the cytotoxic activity of organotin(IV) compounds is influenced by the organotin moiety, ligand and coordination number of tin atoms [3]. Their toxicity decreases in the order $R_3SnX > R_2SnX_2 > RSnX_3$ [9]. The literatures have shown that the triphenyltin(IV) derivatives possess higher cytotoxic effects as compared to diorganotin(IV) derivatives at various concentrations when tested on different types of cancer cells [10]. Thus, the design and synthesis of new organotin(IV) dithiocarbamate compounds are encouraged by changing ligands and organotin substrates. In order to continue the expansion of structural chemistry of organotin(IV) dithiocarbamate compounds, we have synthesized three new triphenyltin(IV) compounds with *N*-(2-methoxyethyl)-*N*-methyl dithiocarbamate (**1**), *N*-benzyl-*N*-phenethyl dithiocarbamate (**2**) and *N*-methyl-*N*-hexyl dithiocarbamate (**3**) ligands. Herein, we report the synthesis, spectral characterization and X-ray crystallographic study of these three triphenyltin(V) dithiocarbamate compounds.

EXPERIMENTAL

All the chemicals and solvents were purchased from Sigma-Aldrich and Merck and used without purification. The melting points were determined using an automated melting point apparatus (MPA 120 EZ-Melt). The percent compositions of the elements (CHNS) for the compounds were determined using a Leco CHNS-932 elemental analyzer. The infrared spectra were recorded as potassium bromide discs using a Perkin Elmer Spectrum GX in the range of 4000 to 370 cm^{-1} . The ^1H , ^{13}C and ^{119}Sn nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker AVANCE 400 III HD instrument with deuterated chloroform (CDCl_3) as solvent and tetramethylsilane as an internal standard. Chemical shift values are given in parts per million (ppm) quoted with respect to the residual protons/carbon of the solvent signals for CDCl_3 at 7.24

and 77.0 ppm for ^1H and ^{13}C , respectively, while ^{119}Sn NMR data are given. Crystal structure determination was carried out on a Bruker Smart Apex II. All data collection was carried out at 139–169 K.

Synthesis of triphenyltin(IV) dithiocarbamate compounds (Fig. 2): *N*-(2-methoxyethyl)-*N*-methylamine (1.1 mL, 10 mmol), *N*-benzyl-*N*-phenethylamine (2.1 mL, 10 mmol) and *N*-methyl-*N*-hexylamine (1.52 mL, 10 mmol) dissolved in ethanol (30 mL) was stirred for 30 min. After that, carbon disulphide (CS_2) (0.6 mL, 10 mmol) in cold ethanol was slowly added and the resulting mixture was stirred for the next 2 h. Ammonia solution (25 %, 1–2 mL) was added to generate a basic condition. Then, triphenyltin(IV) chloride (3.85 g, 10 mmol) dissolved in ethanol was added dropwise into the solution and stirred for 2 h. All the reactions were carried out at under 4 $^\circ\text{C}$. The precipitate formed was dried and collected.

Recrystallization and X-ray crystallography: Recrystallization was achieved by dissolving the compound in a chloroform and ethanol mixture with ratio (1:2 v/v) for compound **1** and (1:1 v/v) for compounds **2** and **3**. This solution was allowed to slowly evaporate at room temperature yielding colourless crystals. Data collection: CrysAlis PRO10, cell refinement: CrysAlis PRO11, Data reduction: CrysAlis PRO [11]. Program(s) used to solve structure: SHELXL97 [12]. Program(s) used to refine structure: SHELXL2014 [13]. Molecular graphics: ORTEP-3 for Windows [14] and DIAMOND [15]. The range of theta for data collections together with other crystallographic information are given in Table-1.

RESULTS AND DISCUSSION

Synthesis of triphenyltin(IV) dithiocarbamate compounds: Compounds **1–3** were synthesized from the corresponding secondary amines, CS_2 and triphenyltin(IV) chloride in ethanol.

TABLE-1
CRYSTALLOGRAPHIC PARAMETERS FOR THE TRIPHENYLTIN(IV) COMPOUNDS 1-3

Crystal data	Compound 1	Compound 2	Compound 3
Gross formula	$\text{C}_{23}\text{H}_{25}\text{NOS}_2\text{Sn}$	$\text{C}_{34}\text{H}_{31}\text{NS}_2\text{Sn}$	$\text{C}_{26}\text{H}_{31}\text{NS}_2\text{Sn}$
M	514.3	636.47	540.38
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$\text{P}\bar{1}$	$\text{P}\bar{1}$	$\text{P}\bar{1}$
Crystal shape	Slab	Slab	Block
Colour	Colorless	Colorless	Colorless
a, b, c ($\text{\AA}$)	7.6258(3), 10.2178(3), 14.8621(6)	9.5856(2), 11.6140(2), 13.6795(3)	9.8590(6), 10.4256(5), 14.3960(8)
α , β , γ ($^\circ$)	91.976(3), 90.655(3), 107.875(3)	78.043(2), 77.868(2), 82.358(2)	110.557(5), 94.057(5), 110.730(5)
V ($\text{\AA}^3$)	1101.19(7)	1450.20(5)	1263.24(13)
Z	2	2	2
T (K)	148	139	169
Crystal size (mm)	$0.5 \times 0.3 \times 0.3$	$0.50 \times 0.30 \times 0.20$	$0.3 \times 0.2 \times 0.05$
Reflections with $I > 2\sigma(I)$	6089	8428	4580
R_{int}	0.046	0.038	0.043

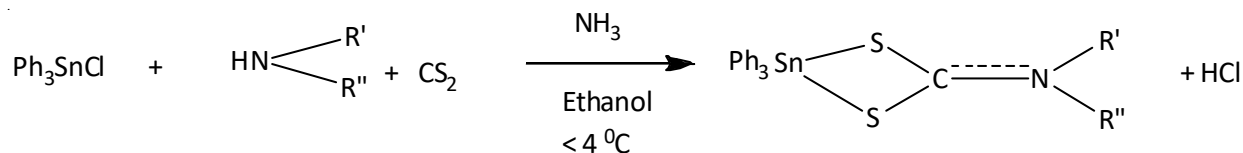


Fig. 2. General equation for the preparation of triphenyltin(IV) compounds with their respective dithiocarbamate ligands

TABLE-2
PHYSICAL AND ELEMENTAL ANALYSIS OF COMPOUNDS 1-3

Compound	Yield (%)	m.p. (K)	Elemental analysis (%): Found (calcd.)			
			C	H	N	S
1	78	366.3-366.8	54.3 (53.71)	5.3 (4.9)	2.7 (2.72)	12.5 (12.47)
2	85	419.0-421.0	64.5 (64.20)	5.3 (4.9)	2.3 (2.20)	9.9 (10.10)
3	52	364.6-365.4	56.5 (57.80)	6.2 (5.8)	2.5 (2.60)	11.7 (11.90)

All three compounds are white in colour and their crystals are colourless. These compounds are stable in air and highly soluble in chloroform. The elemental analyses obtained are in good agreement with the proposed molecular formulae as presented in Table-2.

Infrared spectroscopy: Solid state infrared spectra of the compounds have been recorded in the range 4000-375 cm^{-1} and the most important bands are presented in Table-3. From the data, the absorption in the range 1498-1477 cm^{-1} was assigned to thioureide $\nu(\text{C-N})$ vibration which can also be found in other chelated dithiocarbamates [10,16]. This thioureide band arises from the stretching vibration of C-N bond with a partial double bond and polar character, $\text{C}=\text{N}^+$ and is normally present at 1500-1450 cm^{-1} [17]. The stretching vibration peaks of C-N in the studied complexes lie between the range of C-N single bonds (1360-1250 cm^{-1}) and C=N double bond (1690-1640 cm^{-1}) which is an indication of partial double bond character in the C-N bond [18]. The thioureide bands in compounds **1-3** appeared near the higher frequency, showing a stronger carbon-nitrogen double bond character and hence, exhibiting a greater contribution to structure D (Fig. 1).

TABLE-3

IMPORTANT IR ABSORPTION BANDS OF THE COMPOUNDS

Compound	IR spectra (cm^{-1})			
	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{Sn-C})$	$\nu(\text{Sn-S})$
1	1477	997	527	451
2	1476	1021	502	448
3	1498	983	530	445

The $\nu(\text{C-S})$ vibration that appears in the range 1050-950 cm^{-1} can be used to determine the chelation nature of the dithiocarbamate ligand, which is monodentate or bidentate [17,19].

The set of $-\text{CS}_2$ fragments are unique since they provide information of the coordination mode of the complexes [4]. The bands due to $-\text{CSS}$ are usually coupled to other vibrations and are very sensitive to the environment around this group, but they are also useful to distinguish between mono- and bidentate coordination [20]. The presence of a single band in the $\nu(\text{C-S})$ region is an indication of bidentate character whereas the presence of two bands with separation value $> 20 \text{ cm}^{-1}$ suggests that ligand bonding is monodentate [18]. In present study, the appearance of single bands for C-S in compounds **1-3** suggested the bidentate bonding of dithiocarbamate ligands to Sn center.

Another important peak observed in the infrared spectrum is the signal for $\nu(\text{Sn-C})$ that usually occurs in the range of 600-500 cm^{-1} [4]. The peaks within the range 527-502 cm^{-1} signify the presence of Sn-C stretching bands for compounds with phenyl moiety. The next region is at the lower frequencies (450-250 cm^{-1}) which is attributed to the vibration of Sn-S bond [4], suggesting the complexation of organotin moiety with the dithiocarbamate ligands which appeared at 451-445 cm^{-1} .

NMR spectroscopy: ^1H NMR spectra of all the compounds were recorded in CDCl_3 solution and tetramethylsilane is used as an internal standard at room temperature. The chemical shifts (ppm) of the various observed protons are presented in Table-4. The aromatic protons of phenyl groups directly attached to Sn atom in compounds **1, 2** and **3** were observed at 7.414-7.821, 7.439-7.861 and 7.278-7.767 ppm, respectively. In addition, ^1H NMR spectrum of compound **1** showed two triplets at 4.051 and 3.719 ppm which were assigned to the methylene protons bound to nitrogen and oxygen. Two singlets at 3.514 and 3.376 have been attributed to the terminal methyl protons. In compound **2**, a multiplet was observed at 7.163-7.393 ppm corresponding to the presence of aromatic protons of benzyl groups. The methylene protons of benzyl group appeared as a singlet at 5.031

TABLE-4
 ^1H NMR AND ^{119}Sn NMR DATA

Compound	^1H NMR (ppm)		^{119}Sn NMR (ppm)
	H (Arom.)	H (Aliph.)	
1	7.414-7.821 (15H)	N-CH ₂ = 3.719 (2H); O-CH ₂ = 4.051 (2H); N-CH ₃ = 3.376 (3H); O-CH ₃ = 3.514 (3H)	-183.84
2	7.439-7.861 (15H) 7.163-7.393 (10H)	NCH ₂ -Ben= 5.031 (2H); NCH ₂ CH ₂ -Ar= 3.964 (2H); NCH ₂ CH ₂ -Ar= 3.044 (2H)	-180.18
3	7.408- 7.767 (15H)	N-CH ₃ = 3.419 (3H); N-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ = 3.3838 (2H); N-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ = 2.208 (2H); N-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ = 1.753 (2H); N-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ = 1.592 (2H); N-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ = 1.337 (2H); N-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ = 0.921 (3H)	-187.56

while the triplets at 3.964 and 3.044 ppm are assigned to the methylene protons of the phenethyl group. In 0.921-3.838 ppm region of ^1H NMR spectrum of compound **3**, a few signals were observed, which can be attributed to the terminal methyl and methylene protons of the aliphatic hexyl chain.

Table-5 shows the ^{13}C NMR data for compounds **1-3**. The chemical shifts of CS_2 peak from NCS_2 group is identified as the most significant shift to identify the dithiocarbamate moieties. This peak normally resonates in the range of 185-220 ppm [21]. In our case, the chemical shifts for CS_2 carbon can be observed at 196.97, 197.81 and 196.04 for compounds **1**, **2** and **3**, respectively. The signals that appeared at 126-142 ppm can be assigned to the aromatic carbons of phenyl groups bound to the tin atom and benzyl carbons from compound **2**. Other signals related to aliphatic carbons were also observed in the expected regions (Table-5).

^{119}Sn NMR chemical shift can be used to give tentative information of the environment around tin atoms [10]. The values of $\delta(^{119}\text{Sn})$ define the regions with different coordination numbers of the central tin atoms. Values in the ranges of +200 to -60 ppm, -90 to -190 ppm, and -210 to -400 ppm of $\delta(^{119}\text{Sn})$ are attributed to four-coordinate compounds, five-coordinate compounds and six-coordinate compounds, respectively [22]. ^{119}Sn chemical shifts in the range -180 to -188 ppm were observed for all three compounds as presented in Table-4. Thus, it is expected that compounds **1-3** exist as five-coordinate compounds with bidentate function of dithiocarbamate ligands, which are further confirmed by the single crystal X-ray structures.

X-ray crystallography: The molecular structures of compounds **1-3** are shown in Fig. 3-5. Selected bond angles and bond lengths are presented in Table-6. The crystal structures showed that tin atoms are bonded to dithiocarbamate ligands in all three compounds. The dithiocarbamate ligands in all compounds coordinate to $\text{Sn}(\text{IV})$ in an asymmetrical manner [$\text{Sn}-\text{S}1 = 2.4711(7)$, $\text{Sn}-\text{S}2 = 3.0180(7)$ Å] compound **1**, [$\text{Sn}-\text{S}1 = 2.4886(4)$, $\text{Sn}-\text{S}2 = 2.9120(3)$ Å] compound **2** and [$\text{Sn}-\text{S}1 = 2.4672(11)$, $\text{Sn}-\text{S}2 = 3.1112(12)$ Å] compound **3** with $\Delta(\text{Sn}-\text{S})$, making the difference between the $\text{Sn}-\text{S}_{\text{long}}$ and $\text{Sn}-\text{S}_{\text{short}}$ bond lengths 0.55, 0.42 and 0.64 Å, respectively. The two metal-sulfur bonds in each compound are quite different but nevertheless within the expected range for a bonding interaction as they are smaller than the sum of Van der Waals radii of Sn and S (4.0 Å), reflecting a strong covalent character [4].

This data suggests an anisobidentate coordination mode of dithiocarbamate ligands [2]. This asymmetry is reflected in the relatively large disparity in the associated C-S bond lengths with the bond involving tightly bound $\text{S}1$ atom being significantly longer than the bond involving S_2 atom (Table-6). The C-S bond length values are intermediate between the values

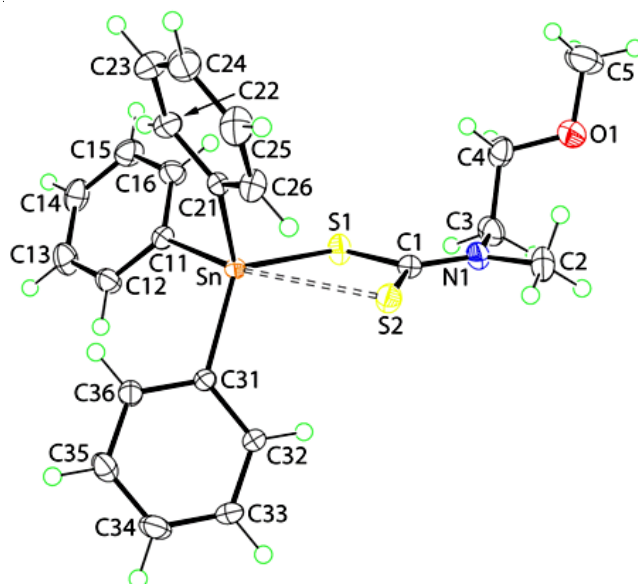


TABLE-6
 GEOMETRIC DATA (Å, °) FOR COMPOUNDS 1-3

Bond length (Å)					
Compound 1		Compound 2		Compound 3	
Sn-S1	2.4711(7)	Sn-S1	2.4886 (4)	Sn-S1	2.4672(11)
Sn...S2	3.0180(8)	Sn-S2	2.9120 (3)	Sn...S2	3.1112(12)
S1-C1	1.755(3)	S1-C1	1.7532 (13)	S1-C1	1.761(4)
S2-C1	1.686(3)	S2-C1	1.6902 (13)	S2-C1	1.688(4)
Sn-C31	2.133(2)	Sn-C17	2.1696 (13)	Sn-C31	2.156(4)
Sn-C21	2.136(3)	Sn-C23	2.1309 (13)	Sn-C21	2.123(4)
Sn-C11	2.162(3)	Sn-C29	2.1469 (13)	Sn-C11	2.159(4)
N1-C1	1.333(4)	N1-C1	1.3305(18)	N1-C1	1.330 (5)
Bond angles (°)					
Compound 1		Compound 2		Compound 3	
C31-Sn-C11	105.78(10)	S1-Sn-S2	65.919 (10)	C21-Sn-C31	112.73(14)
C21-Sn-C11	104.11(10)	S2-Sn-C17	158.55 (4)	C21-Sn-C11	114.88(15)
C31-Sn-S1	119.09(7)	C29-Sn-C17	101.34(5)	C31-Sn-C11	104.73(15)
C21-Sn-S1	115.84(7)	C17-Sn-S1	92.98(4)	C21-Sn-S1	109.94(11)
C11-Sn-S1	91.17(8)	C23-Sn-S1	108.24(4)	C31-Sn-S1	90.00(11)
C1-S1-Sn	96.57(10)	C29-Sn-S1	124.31(4)	C11-Sn-S1	121.53(10)

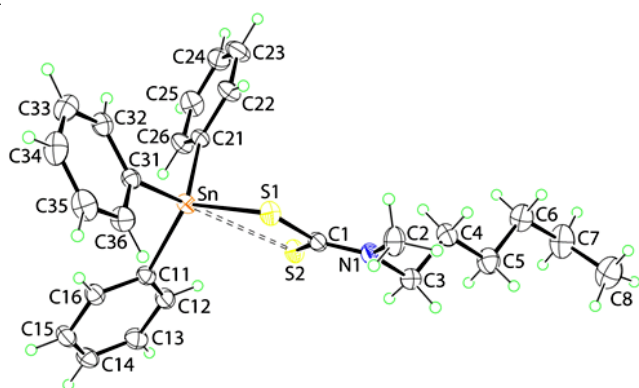


Fig. 5. Molecular structure of (3), showing the atom labelling scheme and displacement ellipsoid at 35% probability level

atom can be characterized by the value of τ ; an indicator of a five-coordinate coordination geometry with τ values of 0.0 and 1.0 being ideal square-pyramidal and trigonal-bipyramidal geometries, respectively [24]. The geometry found is not ideal, with τ values of 0.61 (compound 1), 0.57 (compound 2) and 0.52 (compound 3). For compound 1, the value indicated a distorted trigonal-bipyramidal arrangement around Sn atom with C11 from a phenyl group and S₂ from dithiocarbamate ligand in the axial positions while C21 and C31 from two phenyl groups and S1 in the planar positions. The sum of equatorial angles, [C31-Sn-C21= 115.55(10)°, C31-Sn-S1= 119.09 (7)° and C21-Sn-S1= 115.84 (7)°], is 350.48° instead of the ideal 360°. Being a part chelate, the angle S2-Sn-S1 is only 64.37°, thus S₂ does not occupy the exact corresponding *trans* apical position of C11, with the angle between the apical groups being 155.54° [18].

The same pattern can be observed in the distorted trigonal-bipyramidal arrangement of compounds 2 and 3 around Sn atom with [C17 and S2] compound 2 and [C31 and S2] compound 3 in the axial positions while [C23, C29 and S1] compound 2 and [C11, C31 and S1] compound 3 in the planar positions. The equatorial angles, [C29-Sn-S1 = 124.31 (4)°, C29-Sn-C23 = 118.33 (5)° and C23-Sn-S1= 108.24 (4)°] compound 2 and [C11-Sn-C21= 114.88 (15)°, C21-Sn-S1= 109.94 (11)° and C11-Sn-S1= 121.53 (10)°] compound 3 total up to 350.88°

for compound 2 and 345.35° for compound 3. Meanwhile, the S2-Sn-S1 is only 65.92° (compound 2) and 63.26° (compound 3) instead of the ideal 90°. Distortions from the ideal can be related to dissimilar Sn-donor atom bond lengths and the acute chelate angle [25].

Conclusion

In this study, three new triphenyltin(IV) compounds featuring *N*-(2-methoxyethyl)-*N*-methylthiocarbamate (1), *N*-benzyl-*N*-phenylthiocarbamate (2) and *N*-methyl-*N*-hexylthiocarbamate (3) ligands have been successfully synthesized and characterized. Spectroscopic studies suggest a bidentate coordination mode of all three dithiocarbamate ligands, which are supported by X-ray crystallographic data. The bidentate ligands are found to be asymmetrical in manner, which is also commonly known as an isobidentate. The geometry around tin metal center is best described as distorted trigonal-bipyramidal in all the crystal structures of compounds 1-3.

Supplementary information: CCDC reference numbers (1821128, 1505733 and 1833664) contain the supplementary crystallographic data for the compounds 1-3. These data can be obtained via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. R.S. Herrick, C.J. Ziegler, S. Sripathongnak, N. Barone, R. Costa, W. Cupelo and A. Gambella, *J. Organomet. Chem.*, **694**, 3929 (2009); <https://doi.org/10.1016/j.jorganchem.2009.08.008>.
2. G. Hogarth, *Mini Rev. Med. Chem.*, **12**, 1202 (2012); <https://doi.org/10.2174/138955712802762095>.
3. L. Tian, X. Zheng, X. Zheng, Y. Sun, D. Yan and L. Tu, *Appl. Organomet. Chem.*, **25**, 785 (2011); <https://doi.org/10.1002/aoc.1834>.
4. I.P. Ferreira, G.M. de Lima, E.B. Paniago, W.T. Rocha, J.A. Takahashi, C.B. Pinheiro and J.D. Ardisson, *Eur. J. Med. Chem.*, **58**, 493 (2012); <https://doi.org/10.1016/j.ejmech.2012.10.021>.
5. A. Varela-Ramirez, M. Costanzo, Y.P. Carrasco, K.H. Pannell and R.J. Aguilera, *Cell Biol. Toxicol.*, **27**, 159 (2011); <https://doi.org/10.1007/s10565-010-9178-y>.
6. A.-L. Lainé and C. Passirani, *Curr. Opin. Pharmacol.*, **12**, 420 (2012); <https://doi.org/10.1016/j.coph.2012.04.006>.
7. M. Gielen, *Appl. Organomet. Chem.*, **16**, 481 (2002); <https://doi.org/10.1002/aoc.331>.
8. M.K. Amir, S. Khan, Zia-ur-Rehman, A. Shah and I.S. Butler, *Inorg. Chim. Acta*, **423**, 14 (2014); <https://doi.org/10.1016/j.ica.2014.07.053>.
9. I.P. Ferreira, G.M. de Lima, E.B. Paniago, W.R. Rocha, J.A. Takahashi, C.B. Pinheiro and J.D. Ardisson, *Polyhedron*, **79**, 161 (2014); <https://doi.org/10.1016/j.poly.2014.05.001>.
10. N. Khan, Y. Farina, L.K. Mun, N.F. Rajab and N. Awang, *J. Mol. Struct.*, **1076**, 403 (2014); <https://doi.org/10.1016/j.molstruc.2014.08.015>.
11. Agilent.CrysAlis PRO. Agilent Technologies Inc., Santa Clara, CA, USA (2015).
12. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008); <https://doi.org/10.1107/S0108767307043930>.
13. G.M. Sheldrick, *Acta Crystallogr. C*, **71**, 3 (2015); <https://doi.org/10.1107/S2053229614024218>.
14. L.J. Farrugia, *J. Appl. Cryst.*, **45**, 849 (2012); <https://doi.org/10.1107/S0021889812029111>.
15. K. Brandenburg, DIAMOND Crystal Impact GbR, Bonn, Germany (2006).
16. Y. Farina, A.H. Othman, I. Baba, S.W. Ng and H.-K. Fun, *Main Group Met. Chem.*, **25**, 67 (2002); <https://doi.org/10.1515/MGMC.2002.25.1-2.67>.
17. F. Bonati and R. Ugo, *J. Organomet. Chem.*, **10**, 257 (1967); [https://doi.org/10.1016/S0022-328X\(00\)93085-7](https://doi.org/10.1016/S0022-328X(00)93085-7).
18. Z.U. Rehman, A. Shah, N. Muhammad, S. Ali, R. Qureshi, A. Meetsma and I.S. Butler, *Eur. J. Med. Chem.*, **44**, 3986 (2009); <https://doi.org/10.1016/j.ejmech.2009.04.031>.
19. O.S. Jung, J. Hwa Jeong and Y.S. Sohn, *Polyhedron*, **8**, 1413 (1989); [https://doi.org/10.1016/S0277-5387\(00\)86254-3](https://doi.org/10.1016/S0277-5387(00)86254-3).
20. L. Giovagnini, L. Ronconi, D. Aldinucci, D. Lorenzon, S. Sitran and D. Fregona, *J. Med. Chem.*, **48**, 1588 (2005); <https://doi.org/10.1021/jm049191x>.
21. H.L.M. Van-Gaal, J.W. Diesveld, F.W. Pijpers and J.G.M. Van der Linden, *Inorg. Chem.*, **18**, 3251 (1979); <https://doi.org/10.1021/ic50201a062>.
22. J. Holeček, M. Nádvorník, K. Handlíř and A. Lyèka, *J. Organomet. Chem.*, **315**, 299 (1986); [https://doi.org/10.1016/0022-328X\(86\)80450-8](https://doi.org/10.1016/0022-328X(86)80450-8).
23. P.F. Lindley and P. Carr, *J. Cryst. Mol. Struct.*, **4**, 173 (1974); <https://doi.org/10.1007/BF01197912>.
24. A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn and G.C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1349 (1984); <https://doi.org/10.1039/DT9840001349>.
25. R. Mohamad, N. Awang, N.F. Kamaludin, M.M. Jotani and E.R.T. Tiekink, *Acta Crystallogr. Sect. E Struct. Rep. Online*, **72**, 1480 (2016); <https://doi.org/10.1107/S2056989017001098>.