Research Article

Jerry O. Adeyemi, Damian C. Onwudiwe*, Nirasha Nundkumar, Moganavelli Singh

Diorganotin(IV) benzylidithiocarbamate complexes: synthesis, characterization, and thermal and cytotoxicity study

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Abstract: Ammonium benzylidithiocarbamate, represented as NH4L, was prepared and used in the complexation reaction involving three organotin(IV) salts, represented as R2SnCl2 (R = CH3, C4H9, and C6H5). The structures of the synthesized complexes [([CH3]2SnL2) (1), ([C4H9]2SnL2) (2), and ([C6H5]2SnL2) (3)] were established using various spectroscopic techniques (Fourier transform infrared spectroscopy, 1H NMR, 13C NMR, and 119Sn NMR) and elemental analysis. Thermal decomposition of the complexes using thermogravimetric analysis under nitrogen showed no definite pathway in the pattern of the complexes even though they are structurally related. X-ray diffraction studies of the final residue showed a common diffraction pattern for the complexes and confirmed SnS as the product of the thermal treatment. Cytotoxicity studies of these complexes against the human tumor cell lines (HeLa and MCF-7) compared favorably with the used standard 5-fluorouracil drug, with complexes 2 and 3 showing very good activity toward the used cell lines.

Keywords: dithiocarbamate, organotin(IV), thermal decomposition, X-ray diffraction, cytotoxicity

1 Introduction

Interest in the chemistry of ligands bearing sulfur atom(s) has been on the rise due to their diverse applications in various industrial and biological fields [1]; there is also interest in the chemistry of sulfur (S) atom compared with its congener oxygen (O). Sulfur possesses different donor properties, characterized by a lower electronegative property than that of oxygen. This in turn decreases its ionic character, alters the stability of various bonds, and reduces the influence of hydrogen in compounds where they exist [1]. Notable in this group of sulfur ligands are xanthates, dithiocarbamates, and dithiophosphates [1]. Among these, dithiocarbamate compounds have gained more attention due to their versatility. These have proved to be a useful structural motif, lending themselves to the metal-directed assembly of a range of structures [2]. These compounds are capable of stabilizing the different oxidation states of various metal ions due to their small bite angle (usually found to be ≈2.8–2.9 Å) [2]. Even though the transition metal complexes of this ligand have been predominantly studied, the tin(IV) complexes of dithiocarbamate have been only rarely explored until recently when these compounds began to gain attention due to their increased applications and interesting variable structural chemistry [3,4].

Understanding the thermal behavior of the metal complexes of dithiocarbamate has become pertinent due to their widespread applications as effective heat stabilizers, fungicides, antioxidants, foam rubber, polymers, etc. [5]. The thermal studies of these complexes have shown that they either volatilize, leaving a negligible amount of residue, or form metal sulfide/oxide, depending on the selected conditions (air or inert) [6]. A notable intermediate product often obtained in the thermal decomposition of metal dithiocarbamate is metal thio cyanate [5]. Furthermore, the trends in the decomposition pattern have been reported to be influenced by the electronic effects of the ligands and the environment of the coordinated metal [7]. Tin(IV) dithiocarbamate has become an important synthetic precursor for a wide range of
organometallic complexes, especially those involved in ligand replacement. It is, thus, pertinent to understand their thermal behavior due to their commercial application in materials of high thermal conditions and as active ingredients in fungicides and pesticides [7]. Dithiocarbamate complexes of organotin(n) derivatives have attracted attention due to their diverse applications as biological agents [6], their chemistry [6], and their supramolecular chemistry [3,8]. Furthermore, they have also been used as a single-source precursor for the nanoparticle synthesis of the different tin sulfide phases (SnS, SnS2, and Sn2S3), because their thermal decomposition under nitrogen often leaves a residue of tin sulfide [9–12]. Tin sulfide has a very good semiconducting property and a good band gap energy in all its phases; therefore, it is supported to use it as a semiconductor in solar cells [6,12]. The SnS phase has attracted more attention than the other phases due to its electronic band gap (1.3 eV), which lies between that of Ga and Si [12,13]. As such, it has become more imperative to continue to study the thermal behavior of derivatives of tin(n) dithiocarbamate group such as organotin(n) dithiocarbamate complexes with the goal of understanding the possible trend in the decomposition pattern of the compound.

Molecules containing sulfur atoms have been widely studied as chemoprotectants in Pt-based chemotherapy due to their promising modulating activity in cisplatin nephrotoxicity, which has shown improved therapeutic indices under acidic conditions. This may have significant implications in the treatment of cancer due to the acidic conditions often observed in a solid tumor, which is caused by the fermentation of glucose-secreting acid in the tumor tissue [8]. Both organotin and dithiocarbamate moieties have been reported to play a significant role in the cytotoxic activities of various cancerous cell lines. This may be attributed to the increased lipophilicity due to the complexion or the transportation role played by the ligand, which facilitates the movement of the metal to the site of action, where the cytotoxic effect can be induced [6].

This study reports the thermal and cytotoxicity studies of new dithiocarbamate complexes derived from benzyl-dithiocarbamate and selected diorganotin(n) salts.

2 Materials and methods

The chemicals used in this work were all purchased from Sigma-Aldrich Chemical, Co, and used as recommended. The percentages of C, H, N, and S in the obtained complexes were determined using an elemental, Vario EL Cube. The infrared (IR) spectra, in the range 400–4,000 cm⁻¹, were obtained with an Alpha Bruker FTIR spectrophotometer. The NMR spectra (¹H and ¹³C) of the complexes (in CDCl₃) were obtained at room temperature with a Bruker Avance III NMR spectrometer (600 MHz). Similarly, the ¹¹⁹Sn NMR spectra were obtained with Bruker Ascend Avance III (500 MHz) HD using broadband observe (BBO) as a probe and (CH₃)₂Sn reference as an external standard. SDT Q600 Thermal Analyzer (under N₂ flow) was used for the thermal study [thermogravimetric analysis (TGA) and derivative thermogravimetry] between 50 and 700°C at a heating rate of 10°C min⁻¹. The crystalline phases of the obtained residues from the TGA measurement were identified using a Röntgen PW3040/60 X Pert Pro X-ray diffractometer, equipped with a nickel filtered Cu Ka radiation (k = 1.5418 Å) at room temperature and a scanning rate of 0.0018° min⁻¹.

2.1 Preparation of ammonium

N-benzylidithiocarbamate (NH₄L)

The ligand was synthesized according to a guided procedure with slight modifications [14]. A mixture of benzylaniline (5.50 mL, 0.05 mol) and ammonium hydroxide (15 mL, 0.05 mol) was stirred in an ice bath for 30 min, followed by the dropwise addition of cold carbon disulfide (3 mL, 0.05 mol). The resulting mixture was stirred for 3 h at an approximate temperature of 4°C. Using a suction pump, a pale yellow solid precipitate was extracted, which was thoroughly rinsed with a mixture of absolute ethanol and ether. This precipitate was stored at low temperature.

2.2 Preparation of diorganotin(n) complexes

(R₂SnL₂ [R = CH₃, C₆H₅, C₆H₅])

The respective diorganotin(n) chloride salts (0.025 mol) were dissolved in 10 mL ethanol, and the resulting mixture was added to an already stirred solution of ethanolic ammonium N-benzylidithiocarbamate (0.01 mol). This mixture was stirred for 2 h, and the white precipitates obtained were filtered and rinsed with cold ethanol to remove the unreacted substances in the solution.

2.2.1 [(CH₃)₂SnL₂]

Yield, 2.21 g (71.29%); M. pt., 125–126°C; FTIR, ν (cm⁻¹): 1,503 (C≡N), 1,241 (C=–N), 981 (C≡S), 2,908 (–CH), 3,147 (–CH), 3,333 (N–H), 507 (Sn–C), 451 (Sn–S); ¹H NMR
2.2.2 [(C₄H₉)₂Sn(L₂)]

Yield, 2.68 g (74.65%); M. pt., 133–134°C; FTIR, ν (cm⁻¹): 1,487 (C≡N), 1,237 (C=N), 1,008 (C=S), 2,954 (−CH), 3,117 (−CH₃), 3,300 (N–H), 512 (Sn–C), 440 (Sn–S); ¹H NMR (DMSO) δ (ppm) = 7.47–7.24 (m, 10H, C₆H₅–CH₂–NH), 4.85 (s, 2H, C₆H₅–CH₂–NH), 3.56 (s, 4H, C₂H₅–CH₂–NH), 2.35 (t, 4H, Sn–CH₂CH₂CH₂CH₃), 1.76 (m, 4H, Sn–CH₂CH₂CH₂CH₃), 1.48 (m, 4H, Sn–CH₂CH₂CH₂CH₃), 0.88 (t, 6H, Sn–CH₂CH₂CH₂CH₃); ¹³C NMR (DMSO) δ (ppm) = 210.0 (−NCS₂), 135.6, 129.0, 128.4, 127.1 (C₆H₅–CH₂–NH), 52.8 (C₂H₅–CH₂–NH), 31.2 (Sn–CH₂CH₂CH₂CH₃), 27.8 (Sn–CH₂CH₂CH₂CH₃), 23.3 (Sn–CH₂CH₂CH₂CH₃), 13.9 (Sn–CH₂CH₂CH₂CH₃); ¹⁵⁵Sn NMR (CDCl₃); δ ppm = −351.0; C₂H₅N₅S₅Sn (598.06); C, 48.34; H, 5.75; N, 4.68; S, 21.67; found; C, 47.94; H, 5.24; N, 4.26; S, 22.07.

2.3 Cytotoxicity evaluation using MTT assay

A similar method used in this study has already been reported by our group [15]. The human cervical carcinoma (HeLa) cells were obtained from the ATCC, Manassas, USA. These cells were cultured in a 25 cm² tissue flask with Dulbecco’s Modified eagle’s medium (DMEM), already containing 10% fetal bovine serum, 100 U ml⁻¹ penicillin, and 100 μg ml⁻¹ streptomycin. The MTT assay (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) was performed in a 96-well plate containing 2.5 x 10^⁵ cells/well in 100 μL DMEM. The cells were used to investigate the viability of the HeLa cells. These cells were incubated at 37°C overnight, followed by the addition of the respective complexes at various concentrations of 20, 40, 80, and 100 μg ml⁻¹. Then, the cells were incubated at 37°C for 48 h, followed by the MTT assay. The untreated cells were used as positive control 1 and the untreated cells with DMSO were used as positive control 2, while 5-fluorouracil (5-FU) was used as a standard. The fresh medium containing 10% MTT reagent was used to replace the medium in the assay, followed by incubation at 37°C for 4 h. After these were removed, insoluble formazan crystals were dissolved in 100 μL DMSO, then the absorbance was studied at 570 nm with DMSO as a blank. These assays were carried out in triplicates.

Ethical approval: The research conducted is not related to either human or animal use.

3 Results and discussion

3.1 Synthesis

Dithiocarbamate ligands obtained from primary amines are generally less stable compared with those obtained from secondary amines. This is due to the presence of the acidic hydrogen on the nitrogen [16,17]. Hence, their synthesis may sometimes require an inert atmosphere [17]. However, in this study, the reaction proceeded in air, as reported in Su et al. [18]. The complexes were synthesized as shown in Scheme 1. Good yields of about 70–78% were obtained, and the data from the elemental analytical corresponded with the stoichiometry of the complexes. The complexes were white, stable at room temperature, and soluble in dichloromethane, chloroform, and dimethyl sulfoxide but sparingly soluble in alcohol.

3.2 IR spectral study

The IR spectra of the three complexes showed the characteristic dithiocarbamate bands, as presented in Figure 1a. A strong band assigned to the C–N vibration of the thioureide bond was found in the region between 1,503 and 1,478 cm⁻¹ for all the complexes, due to the delocalization of electron toward the tin center in the
complexes \[19\]. A single band in the region 1,008–996 cm\(^{-1}\) was attributed to the vibrational mode of C–S, which is suggestive of a bidentate mode of coordination \[20\]. A stretching vibration due to the aromatic ring (=C–H) was found in the region of 3,147–3,030 cm\(^{-1}\), while the stretching vibration due to the CH\(_2\) bond appeared in the region 2,954–2,912 cm\(^{-1}\) \[21\]. The N–H stretching vibration was found in the region 3,300–3,378 cm\(^{-1}\) \[22\]. In the far-IR region, the characteristic peaks associated with organotin dithiocarbamate complexes were found in the regions 512–508 cm\(^{-1}\) and 451–440 cm\(^{-1}\), ascribed to the stretching vibrations of Sn–C and Sn–S, respectively \[23\].

### 3.3 NMR (\(^1\)H, \(^{13}\)C, and \(^{119}\)Sn) spectral study

In the \(^1\)H NMR spectra of the complexes, the expected chemical shifts were found at their appropriate regions. A representative spectrum of the complex ([\((\text{CH}_3)_2\text{SnL}_2]\)) is presented in Figure 1b. The signals due to the aromatic protons of the ligand moiety were found as multiplets around the region 7.47–7.24 ppm for the complexes. The signals attributed to the methylene protons of the organotin moiety appeared in the region 3.93–3.56 ppm due to the electronegative N atom, while the signals in the region 4.85–4.62 ppm attributed to the proton on the N atom were found in all the spectra of the complexes. The proton signals in the organotin moiety appeared in the high field region as a singlet at 1.53 ppm for the dimethyltin(\(iv\)) derivative and as a complex multiplet in the region 8.06–7.78 ppm for the dibutyldimethyldithiocarbamate complexes.

The \(^{13}\)C NMR spectra showed a weak signal of the thioureide carbon (−NCS\(_2\)) for all the complexes in the region between 202 and 200 ppm \[19\], while carbon signals of the phenyl moiety resonated between 135 and 125 ppm. The signal in the region 59.8–57.0 ppm, found in the spectra of the complexes, has been attributed to the methylene carbon close to the electronegative N atom. Carbons of the alkyl substituents in the complexes resonated at 13.94 ppm \[25\] in the spectra of the dimethyl complex; the diphenyl complex was found in the region 135 to 127 ppm; and the dibutyl complex was found between 31.2 and 13.9 ppm \[22\]. The \(^{119}\)Sn chemical shift values (\(\delta\)) for this group of complexes ranged from −335 to −350 ppm, which indicates a hexacoordinated geometry around the Sn metal.

### 3.4 Thermal study

The thermogravimetric plots of the complexes are presented in Figure 2(a–c). The change in the composition of each complex based on mass losses with respective temperature changes is summarized in Table 1. These complexes decomposed in a two-step pathway, except for 3, which has a single step. In complexes 1 and 2, the first decomposition step occurred from approximately...
90 to 168°C and 122 to 171°C, respectively. These cause the respective mass losses of about 17.30% (1) and 10.43% (2) of the starting masses. These mass losses have been attributed to the two \(-\text{C}_6\text{H}_5\) group in complex 1 emanating from the ligand moiety and the mass of one \(-\text{C}_4\text{H}_9\) group in complex 2 emanating from the organotin(IV) moiety. The masses found (1: 82.70% and 2: 89.57%) at this stage were in close agreement with the calculated values (1: 83.74% and 2: 90.55%). The remaining mass underwent more decomposition in the second and final steps for both complexes in the

Figure 1: The (a) FTIR, (b) $^1$H NMR, (c) $^{13}$C NMR, and (d) $^{119}$Sn NMR (ppm) spectra of $[\text{CH}_3\text{SnL}_2]_2$ (1).
temperature range of 172–263 and 184–293°C, respectively. The masses of the obtained residues were 14.42% and 24.12% of the starting masses for complexes 1 and 2, respectively, and this concurred with the theoretical estimated value of SnS (16.87% (1) and 25.0% (2)). The thermogravimetric graph of complex 3 showed the decomposition to proceed in a single step pathway in the temperature range of 57–296°C. The remaining mass was found to be 21.30% of the starting mass; this concurred with the calculated weight of SnS (23.43%).
Therefore, the only rational trend observed in the thermal decomposition of these complexes is as follows: for the alkyltin(IV) derivatives, two decomposition steps were found, while a single decomposition step was found for the aryltin(IV) derivative. Furthermore, there appears to be some intrinsic features in the ligand and its binding mode to the metal center, which in turn governs the decomposition mechanism. Hence, the structural feature of the complexes appears to have very little effect on the mechanism of decomposition. As previously reported by Hill et al. [7], the thermal decomposition pattern of tin dithiocarbamate complexes is unpredictable and complicated even for a series of structurally similar complexes. It is often difficult to rationalize a trend [7]. However, in the thermal decomposition study of these complexes, a stable SnS residue was found at the end of their decomposition. A representative X-ray diffraction pattern obtained from the residue of complex 1 is presented in Figure 3, and this clearly confirms that the SnS Herzenbergite (JCPDS no. 39-0354) phase was obtained after the decomposition.

### 3.5 Cytotoxicity study

The HeLa cell lines were obtained from human cervical cancer cells [26], while the MCF-7 are cell lines were obtained from human breast cancer cells [27]. These cell lines are often used for research purposes. Table 2 shows the activity of the complexes at different concentrations and the estimated minimum inhibitory concentration (IC\textsubscript{50}) values against the cell lines. The plots of the percentage viability against the concentration are also depicted in Figures 4a and b. These results show a concentration-dependent profile with some good activities toward the used cell lines. These are better than the standard drug, with an IC\textsubscript{50} value of 40 and 58 µM for the Hela and MCF-7, respectively. For HeLa cell lines, complex 1 had a good cytotoxic activity, which is comparable to that of the standard 5-FU drug, and complex 2 had outstanding IC\textsubscript{50} values, which were 2,100 times better than that of the standard drug. However, complex 3 displayed a high IC\textsubscript{50} value, which may be due to its selectivity toward the HeLa cell lines, contrary to the expected trend within the group of organotin(IV) complexes. Thus, the diphenyl derivative (3) had poor activity against the HeLa cell lines.

### Table 2: In vitro cytotoxicity of the complexes on the HeLa and MCF-7 cells (IC\textsubscript{50})

| HeLa cell line | 25 µg mL\(^{-1}\) | 50 µg mL\(^{-1}\) | 100 µg mL\(^{-1}\) | 150 µg mL\(^{-1}\) | IC\textsubscript{50} (µM) |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Control 1\(^a\) | 100.00 ± 0.79 | 100.00 ± 0.79 | 100.00 ± 0.79 | 100.00 ± 0.79 | — |
| Control 2\(^b\) | 104.09 ± 2.43 | 104.09 ± 2.43 | 104.09 ± 2.43 | 104.09 ± 2.43 | — |
| 5-FU | 36.57 ± 4.15 | 27.47 ± 6.14 | 23.54 ± 2.90 | 17.72 ± 4.34 | 40 |
| 1 | 17.17 ± 6.73 | 11.34 ± 13.80 | 8.49 ± 4.98 | 7.41 ± 1.81 | 40 |
| 2 | 9.05 ± 13.98 | 4.75 ± 9.64 | 6.87 ± 14.81 | 5.14 ± 10.68 | 0.019 |
| 3 | 10.81 ± 6.35 | 17.67 ± 5.09 | 30.97 ± 9.18 | 37.51 ± 4.85 | 330 |

| MCF-7 cell line | 25 µg mL\(^{-1}\) | 50 µg mL\(^{-1}\) | 100 µg mL\(^{-1}\) | 150 µg mL\(^{-1}\) | IC\textsubscript{50} (µM) |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Control 1\(^a\) | 100.00 ± 0.71 | 100.00 ± 0.71 | 100.00 ± 0.71 | 100.00 ± 0.71 | — |
| Control 2\(^b\) | 99.87 ± 1.05 | 99.87 ± 1.05 | 99.87 ± 1.05 | 99.87 ± 1.05 | — |
| 5-FU | 82.40 ± 0.87 | 58.37 ± 2.80 | 48.88 ± 1.26 | 42.99 ± 1.28 | 56.2 |
| 1 | 67.74 ± 6.78 | 64.68 ± 6.23 | 65.40 ± 0.93 | 66.90 ± 4.03 | 185 |
| 2 | 64.02 ± 11.29 | 53.52 ± 2.12 | 51.01 ± 8.75 | 44.80 ± 9.21 | 57.3 |
| 3 | 50.82 ± 7.42 | 34.12 ± 7.99 | 33.81 ± 6.80 | 27.03 ± 13.99 | 20 |

\(^a\) Control 1: cell only. \(^b\) Control 2: cell + DMSO.
Furthermore, for the MCF-7, the observed IC\textsubscript{50} value obtained for complex 3 showed that it possesses better activity than the standard drug used, while complex 2 exhibited almost equal activity compared with the standard drug. Complex 1 showed weak activity. These trends concur with the previous reports for most organotin(IV) complexes, in which longer alkyl chains or aryl groups induced better cytotoxicity than their shorter chain counterparts [28]. However, this trend has also been observed to be a hindrance due to the selectivity toward the used cell lines, as observed in the HeLa cell lines reported in this study [29].

Generally, both organotin and dithiocarbamate moieties have been reported to play useful roles in the cytotoxicity of various cancer cell lines. This has been suggested to be due to complexation, which leads to increased lipophilicity and consequently facilitates the movement of the metal to the site of action, where the cytotoxic effect can be induced [28]. The electronic effect induced by the ligand in addition to the lipophilicity of the complexes has also been reported to play crucial roles in the cytoselectivity exhibited by these complexes [28]. In their right mix, these properties often give outstanding cytotoxic activities [30]. Therefore, the obtained results from this study show that on further screening in vivo and other clinical trials, these complexes may become useful compounds in the development of a new drug against cancer cells.

4 Conclusion

We have successfully synthesized and characterized three new organotin(IV) complexes using a benzyldithiocarbamate ligand. This ligand appears to bond in a bidentate fashion to the tin metal of the organotin(IV) moiety, as suggested by the presence of a single peak of...
the carbon sulfide (C=S) bond in the IR spectra. Furthermore, the $^{119}$Sn NMR also suggested a hexacoordinated geometry around the Sn atom, which indicated that two ligands moiety bonded to the tin atom. The noticeable trend observed in the thermal study showed that the two alkyltin(IV) derivatives followed two decomposition patterns, but the aryltin(IV) derivative followed a single decomposition pattern. Furthermore, all the complexes gave a final residue of SnS with a hezenberigrite structure. Thus, the as-synthesized complexes can be a good single precursor source for the SnS nanoparticle synthesis. The study on the cytotoxicity of these complexes showed a concentration-dependent profile with some good activities toward the HeLa and MCF-7 cell lines, which compared favorably with the standard drug. However, further studies with different cell lines and on the mechanism of action are needed for these complexes to be considered leading anticancer agents.

Conflicts of interest: The authors declare no conflict of interest.

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