Synthesis and Characterization of Novel Diorganotin(IV) Complexes Derived from N-Methyl-phenethyl Dithiocarbamate and Bis(2-ethoxyethyl) Dithiocarbamate

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Organotin(IV) dithiocarbamate complexes are extensively studied worldwide as they have proven to exhibit promising anticancer, antimicrobial and larvicidal properties. In this study, three new organotin(IV) dithiocarbamate complexes have been successfully synthesized *via in situ* reaction between the appropriate secondary amines with carbon disulphide and organotin(IV) salts, in a basic solution at temperature below 4 °C. The complexes were characterized by CHNS elemental analysis, FTIR and ¹H, ¹³C and ¹¹⁹Sn NMR. All complexes displayed the important NCS₂ peak from 200.02-201.35 ppm in ¹³C NMR, signifying the presence of the dithiocarbamate ligand. The complexes also produced the essential IR bands, ν(C-N), ν(C-S) and ν(Sn-C) in the ranges 1489 to 1479 cm⁻¹, 986.2 to 971.2 cm⁻¹ and 568.2 to 550.8 cm⁻¹, respectively. From the ¹¹⁹Sn NMR, both the ligands were suggested to coordinate to the tin atom in a bidentate manner in all three complexes.

Keywords: Organotin(IV), Dithiocarbamate, Anticancer, Nanoparticles.

INTRODUCTION

Organotin compounds have at least one covalent carbon-tin bond [1,2]. This bond plays one of the major roles in the activity of the whole compound [3]. Organotin derivatives have gotten a lot of attention in the previous decades due to its numerous biological activities ranging from antibacterial and antifungal properties [4-8] to antiproliferative and anticancer properties [9-14] as well as larvicidal properties [15]. Most organotin(IV) compounds are found to be very toxic, even at low concentrations [1]. Their ability to induce various biological activities in different organisms and in small concentrations makes them the suitable candidates to be developed into future drugs.

One of the most popular organotin compounds are organotin(IV) dithiocarbamate compounds, which exhibited various biological activities as reported by numerous previous studies. Organotin dithiocarbamate compounds are also good precursors for tin sulfide nanoparticles [16]. Dithiocarbamates are the analogs of carbamates, whereby both oxygen atoms of the carbamates are replaced by sulphur atoms. The dithiocar-

bamate's possession of two donor sulphur atoms enables it to exhibit strong metal binding properties as they readily form chelates strongly and selectively with all transition metal ions [17], as well as with most main group metal ions [3]. In this particular ligand, coordination to the tin atom can occur in three different ways, *i.e.*, monodentate, bidentate and an isobidentate [18], with bidenticity being the most common form of chelation [19]. Another interesting characteristic of the dithiocarbamate ligand is its ability to stabilize metal compounds with high oxidation number [19]. On the other hand, organotin(IV) cation has an ability to form complexes freely with ligands possessing S, N, O and P donor atoms [1]. This makes dithiocarbamate a good ligand for complexation with tin ions.

In an organotin compound, the organotin moiety exerts the cytotoxicity [20]. It is the nature and the number of alkyl groups bonded to the tin atom that give organotin compounds varying degrees of toxicity [1,21]. Meanwhile, the ligand plays an important role in transporting the molecules to the target while preventing premature interactions with biomolecules. For this purpose, sulfur-containing ligands are particularly suitable to carry out the task [20].

In this study, three new diorganotin(IV) complexes derived from *N*-methyl-phenethyl and *bis*(2-ethoxyethyl) dithiocarbamate ligands were successfully synthesized *via in situ* method of synthesis as described by Ivin and Lillie [22], with modifications. The new complexes were characterized by CHNS elemental analysis, FTIR and ^1H , ^{13}C and ^{119}Sn NMR to further clarify their structures.

EXPERIMENTAL

All chemicals and solvents were purchased and used as received without further purification from the suppliers. The chemicals and solvents were purchased from: *N*-methyl-phenethylamine (Sigma-Aldrich, USA), *bis*(2-ethoxyethyl)amine (TCI Chemicals, Japan), denatured ethanol (HmbG Chemicals, Germany), 25 % ammonia solution (Merck, Germany), carbon disulphide (Merck, Germany), 97 % dimethyltin(IV) dichloride (Sigma-Aldrich, USA) and 96 % dibutyltin(IV) dichloride (Sigma-Aldrich, USA).

The percentage of carbon, hydrogen, nitrogen and sulphur were determined using an elemental analyzer (CHNS-O), model LECO 932. FTIR spectra were recorded in the range $4000\text{--}400\text{ cm}^{-1}$ using a Perkin-Elmer GX spectrophotometer on KBr disc. The ^1H , ^{13}C and ^{119}Sn nuclear magnetic resonance spectra were recorded in deuterated chloroform using Bruker Avance 400 III HD. The melting points were determined in open capillary tubes using an automated melting point apparatus, MPA120 EZ-Melt. All the analyses were conducted in Universiti Kebangsaan Malaysia, Bangi, Malaysia.

Synthesis of dimethyltin(IV) *N*-methyl-phenethyl dithiocarbamate (complex 1) and dibutyltin(IV) *N*-methyl-phenethyl dithiocarbamate (complex 2): Initially, *N*-methyl-phenethylamine (0.01 mol, 1.5 mL) was stirred with denatured ethanol (10 mL) and 25 % ammonia solution (3 mL) in an ice bath for 15 min to maintain the temperature at $< 4^\circ\text{C}$. A cold ethanolic solution of CS_2 (0.01 mol, 0.6 mL) was then added into the solution drop-wise and the solution was left to stir for 3 to 6 h for ligand formation. A faint yellowish solution was observed immediately upon addition of CS_2 to the amine mixture. Next, organotin salt (0.005 mol-1.1 g dimethyltin, 1.5 g dibutyltin) was dissolved completely in cold ethanol and the solution was added to the dithiocarbamate ligand mixture drop-wise. The mixture was stirred for another 2 h until thick

white precipitate was obtained. The white precipitate was then filtered and washed adequately with cold ethanol and dried in a desiccator overnight. Both complexes were synthesized according to the stoichiometric ratios of 2:2:1 for amine: CS_2 :organotin salt. The synthesis of complexes **1** and **2** is illustrated in **Scheme-I**.

Synthesis of dibutyltin(IV) *bis*(2-ethoxyethyl) dithiocarbamate (complex 3): In an ice bath, 25 % ammonia solution (8 mL) was stirred with denatured ethanol (10 mL) for a few minutes to attain temperature of $< 4^\circ\text{C}$. To the stirring mixture, *bis*(2-ethoxyethyl)amine (0.01 mol, 1.8 mL) was added drop-wise. After 30 min, a cold ethanolic solution of CS_2 (0.01 mol, 0.6 mL) was slowly drop-wise added and the solution was left to stir at $< 4^\circ\text{C}$ for 3 h. A faint yellowish solution was observed immediately upon addition of CS_2 to the amine mixture. Next, organotin salt (0.005 mol, 1.5 g) was dissolved completely in cold ethanol and dropwise added to the ligand. The mixture was left to stir for another 3 h until minimal white precipitate was observed. After removing the magnetic stirrer, the beaker was covered with parafilm and left in the fridge without disturbance for 3 days. Crystalline solids were obtained in the mixture after 3 days and then dried in a desiccator overnight. The complex was synthesized according to the stoichiometric ratios of 2:2:1 for amine: CS_2 :organotin salt. The synthesis of complex **3** is illustrated in **Scheme-II**.

RESULTS AND DISCUSSION

Synthesis: The dithiocarbamate ligands were successfully synthesized *via in situ* method in equimolar amounts between the secondary amines (*N*-methyl-phenethyl amine and *bis*(2-ethoxyethyl) amine and CS_2 in a basic condition at $< 4^\circ\text{C}$. The complexes were successfully prepared from the reaction between respective organotin(IV) salts dissolved in cold ethanol with the freshly prepared ligands in a stoichiometric ratio. Complexation occurs when the chloride ions in the organotin(IV) salts were displaced by the respective ligands [3].

Complexes **1** and **2** were produced with fairly high yield ($> 50\%$), which indicates that the *in situ* method is a suitable method of synthesis [7]. Both complexes are stable at room temperature and are in white powder form. Complex **3**, which is in crystalline solid form, is fairly stable at room temperature *albeit* having a relatively low melting point compared to the

Scheme-I: Reaction mechanism of complex **1** ($\text{R} = \text{CH}_3$) and complex **2** ($\text{R} = \text{C}_4\text{H}_9$)

Scheme-II: Reaction mechanism of complex **3** ($\text{R} = \text{C}_4\text{H}_9$)

other two complexes. However, complex **3** is stored at low temperature to maintain its structure and stability. All the complexes exhibited narrow melting point ranges ($< 3\text{ }^{\circ}\text{C}$), showing that they are pure [7]. All the complexes are soluble in chloroform and dichloromethane. Figs. 1-3 illustrate the proposed structures of complexes **1**, **2** and **3**, respectively.

Fig. 1. Structure of dimethyltin(IV) *N*-methyl-phenethyl dithiocarbamate (**1**)

Fig. 2. Structure of dibutyltin(IV) *N*-methyl-phenethyl dithiocarbamate (**2**)

Fig. 3. Structure of dibutyltin(IV) *bis*(2-ethoxyethyl) dithiocarbamate (**3**)

CHNS elemental analysis has been done on all three complexes to determine the percentage of carbon, hydrogen, nitrogen and sulphur in the complex molecules. It was found that the observed percentages of C, H, N and S in all three complexes are within acceptable range compared to their theoretical values. Table-1 summarizes the physical and elemental analysis of all three complexes.

Fourier-transform infrared spectroscopy (FTIR) spectral studies: The FTIR spectra were recorded in the range of $4000\text{--}400\text{ cm}^{-1}$. All complexes produced a strong thioureide $\nu(\text{C}=\text{N})$ band in the range $1489\text{--}1479\text{ cm}^{-1}$ comparable to previous literature [23], which could be due to the increase of

the carbon-nitrogen double bond character as the band is observed at a lower frequency in a free ligand [24]. This phenomenon occurs when electrons are delocalized towards the tin atom upon complexation [3].

The coordination nature of the ligand to the tin centre can be suggested from the number of bands observed in $1050\text{--}950\text{ cm}^{-1}$ region [23], which stands for the $\nu(\text{C}\text{--}\text{S})$ band. Single sharp bands occurring in this region signifies bidenticity whereas splitting of the same band within a difference of 20 cm^{-1} in the same region signifies monodenticity or anisobidenticity [24]. A sharp single peak in the range of $986\text{ to }971\text{ cm}^{-1}$ was observed in all three complexes, suggesting the bidentate behaviour of the ligand upon the tin center [25].

The $\nu(\text{Sn}\text{--}\text{C})$ band of all three complexes occurred in the range $568.2\text{ to }550.8\text{ cm}^{-1}$, in agreement with reported data for organotin(IV) dithiocarbamate compounds [7]. Table-2 summarizes the important FTIR absorption bands of all three complexes.

TABLE-2
IMPORTANT FTIR ABSORPTION
BANDS (cm^{-1}) OF COMPLEXES **1-3**

Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{C}\text{--}\text{S})$	$\nu(\text{Sn}\text{--}\text{C})$
1	1488.8	975.4	550.8
2	1487.8	971.2	553.4
3	1479.3	986.2	568.2

Nuclear magnetic resonance studies: The ^1H NMR chemical shifts of all three complexes were recorded in CDCl_3 solution with tetramethylsilane as internal standard. The sharp singlet found at 1.59 ppm is attributed to the proton of the methyl group attached to the tin atom in complex **1**. For complexes **2** and **3**, the presence of the butyl group attached to the central tin atom produced broad signals for the methylene protons in the ranges $1.42\text{--}2.10\text{ ppm}$ (complex **2**) and $1.40\text{--}2.08\text{ ppm}$ (complex **3**), together with a triplet in the ranges $0.94\text{--}0.98\text{ ppm}$ (complex **2**) and $0.92\text{--}0.96\text{ ppm}$ (complex **3**) produced by the methyl protons. The shielding effect is caused by the attachment of the butyl group to the electropositive tin atom *via* carbon nuclei [26]. This effect is experienced all through the butyl carbon chain. The multiplet signals observed at $7.26\text{--}7.36\text{ ppm}$ (complex **1**) and $7.24\text{--}7.34\text{ ppm}$ (complex **2**) are ascribed to the protons in the phenyl groups of the ligand in both complexes. Since complexes **1** and **2** are made up of the same ligand, the protons in the ligand appear at the same chemical shifts [27]. In complex **3**, a triplet can be seen at $1.18\text{--}1.22\text{ ppm}$, comprising of 12 protons from the double ethoxy group on each side of the symmetrical complex. Other important ^1H chemical shifts of the complexes can be seen in Table-3.

TABLE-1
PHYSICAL AND ELEMENTAL ANALYSIS OF COMPLEXES **1-3**

Complex	m.f.	Yield (%)	Physical form	m.w. (g/mol)	m.p. ($^{\circ}\text{C}$)	Elemental analysis (%): Observed (Expected)			
						C	H	N	S
1	$\text{C}_{22}\text{H}_{30}\text{N}_2\text{S}_4\text{Sn}$	62	White powder	569.46	107.3-109.2	45.82 (46.40)	5.47 (5.31)	4.89 (4.92)	21.74 (22.52)
2	$\text{C}_{28}\text{H}_{42}\text{N}_2\text{S}_4\text{Sn}$	58	White powder	653.62	103.9-106.9	49.74 (51.45)	6.78 (6.48)	4.75 (4.29)	19.69 (19.62)
3	$\text{C}_{26}\text{H}_{54}\text{N}_2\text{O}_4\text{S}_4\text{Sn}$	35	Crystalline solids	705.69	32.3-34.8	45.99 (44.25)	7.24 (7.71)	3.22 (3.97)	18.91 (18.18)

TABLE-3
¹H, ¹³C AND ¹¹⁹Sn NMR CHEMICAL SHIFTS δ (ppm) OF COMPLEXES 1-3

NMR	Chemical shift, δ (ppm)		
	Complex 1	Complex 2	Complex 3
¹ H	1.59 (s, 6H, Sn-CH ₃); 3.05-3.09 (t, 4H, N-CH ₂); 3.34 (s, 6H, N-CH ₃); 4.04-4.08 (t, 4H, C ₆ H ₅ -CH ₂); 7.26-7.36 (m, 10H, C ₆ H ₅)	0.94-0.98 (t, 6H, Sn-C ₃ H ₆ -CH ₃); 1.42-1.51 (m, 4H, Sn-C ₂ H ₄ -CH ₂); 1.92-1.97 (m, 4H, Sn-CH ₂ -CH ₂); 2.07-2.10 (m, 4H, Sn-CH ₂); 3.05-3.08 (t, 4H, Aromatic-CH ₂); 3.32 (s, 6H, N-CH ₃); 4.05-4.09 (t, 4H, N-CH ₂); 7.24-7.34 (m, 10H, C ₆ H ₅)	0.92-0.96 (t, 6H, Sn-C ₃ H ₆ -CH ₃); 1.18-1.22 (t, 12H, O-CH ₂ -CH ₃); 1.40-1.49 (m, 4H, Sn-C ₂ H ₄ -CH ₂); 1.87-1.95 (m, 4H, Sn-CH ₂ -CH ₂); 2.04-2.08 (m, 4H, Sn-CH ₂); 3.48-3.53 (m, 8H, O-CH ₂); 3.74-3.77 (t, 8H, N-CH ₂); 4.12-4.15 (t, 8H, N-CH ₂ -CH ₂)
¹³ C	15.55 (Sn-CH ₃); 33.06 (C ₆ H ₅ -CH ₂); 43.36 (N-CH ₃); 58.80 (N-CH ₂); 126.74 - 138.02 (C ₆ H ₅); 200.02 (N-CS ₂)	13.90 (Sn-C ₃ H ₆ -CH ₃); 26.50 (Sn-CH ₂); 28.59 (Sn-CH ₂ -CH ₂); 33.05 (Sn-C ₂ H ₄ -CH ₂); 34.43 (C ₆ H ₅ -CH ₂); 43.42 (N-CH ₃); 58.74 (N-CH ₂); 126.69 - 138.12 (C ₆ H ₅); 200.79 (N-CS ₂)	13.82 (Sn-C ₃ H ₆ -CH ₃); 15.10 (O-CH ₂ -CH ₃); 26.38 (Sn-CH ₂); 28.53 (Sn-CH ₂ -CH ₂); 34.24 (Sn-C ₂ H ₄ -CH ₂); 55.82 (N-CH ₂); 66.64 (O-CH ₂); 67.68 (N-CH ₂ -CH ₂); 201.35 (N-CS ₂)
¹¹⁹ Sn	-335.30	-338.85	-335.75

In ¹³C NMR, the presence of NCS₂ peak indicates the presence of dithiocarbamate moiety [10], which is normally found in the range of 185-220 ppm [28]. In a free dithiocarbamate ligand, NCS₂ peak can be found at 205 ppm and above [3]. Upon complexation, NCS₂ carbon is more shielded, thus the ¹³C signal is moved to a higher field compared to free ligand [29]. In case of these three complexes, a single low field resonance appeared in all complexes at 200.02-201.35 ppm, confirming the presence of the dithiocarbamate ligands. Other important ¹³C chemical shifts of the complexes are given in Table-3.

Essentially, coordination number of the central tin atom in complexes can be identified by using ¹¹⁹Sn NMR spectroscopy [30]. Values in the ranges of +200 to -50 ppm, -90 to -190 ppm and -210 to -400 ppm on the ¹¹⁹Sn spectra are attributed to four-coordinate compounds, five-coordinate compounds and six-coordinate compounds, respectively [30]. As observed, all three complexes showed a peak at -335.30 ppm (complex 1), -338.85 ppm (complex 2) and -335.75 ppm (complex 3), which are all in the range of -210 to -400 ppm. This suggests that both dithiocarbamate ligands chelate to the central tin atom in a bidentate fashion in all three complexes, in agreement with the results from the FTIR.

Conclusion

Three organotin(IV) dithiocarbamate complexes were successfully synthesized *via in situ* method at < 4 °C. The CHNS elemental analysis, FTIR studies and ¹H, ¹³C and ¹¹⁹Sn NMR studies showed data consistent with the proposed structures of the complexes. All the characterized complexes produced the important IR bands and NMR peaks for organotin(IV) dithiocarbamate complexes, in accordance with literature.

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