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Synthesis and Characterisation of New Organotin (IV)(2-Methoxyethyl)-methyldithiocarbamate Complexes.

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ABSTRACT

Three new organotin(IV) dithiocarbamate complexes (complexes **1**-**3**) employing (2-methoxyethyl)-methylamine as their secondary amine were successfully synthesised *in situ*. Elemental analysis of the complexes gave the general formula of $R_nSn[S_2CN(C_2H_4OCH_3)(CH_3)]n-_2$where R=$C_4H_9$(Bu)and C_6H_5(Ph)for *n*= 2; R= C_6H_{11} (Cy) for *n*= 3. The complexes were analysed using FTIR and ^{1}H, ^{13}C, and ^{119}Sn NMR. The important absorption peaks and chemical shift of NCS_2 carbon were found in all the three complexes.^{119}Sn NMR suggested that tin atom in the complexes are coordinated by five and six coordination numbers.

Keywords: organotin, complex, elemental.

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INTRODUCTION

Dithiocarbamates have received a considerable attention as their biological effects have been researched as having antialkylation and anti-HIV properties as well as antitumour activity against leukaemic cells [9].These compounds are highly versatile ligands towards the main group metals, and their strong metal binding properties are directly related to the possession of two donor sulphur atoms [14]. One of the important structural consequences of the dithio ligands is the preferential stabilisation of specific stereochemistry in their metal complexes. Owing to their strong metal binding capacity, dithio ligands act as inhibitors of enzymes and significantly affect biological systems [11].

Dithiocarbamates are a member of the 1,1-dithiolate family that has been proven to promisingly possess interesting conductive properties when reacted with transition metals to give rise to a variety of metal clusters[17]. There has been a lot of research interest on metal dithiocarbamates due to their structural chemistry [19] and biocidal applications [16]. Dithiocarbamates with organotin(IV) are among the metal dithiocarbamates that have been studied extensively. They have a wide range of potential applications and use of their organotin derivatives in biology, catalysis, agriculture, or organic synthesis [5].This paper reports the synthesis and characterisation of three new organotin(IV) (2-methoxyethyl)methyl dithiocarbamates complexes.

MATERIALS AND METHODS

Materials

The secondary amine, (2-methoxyethyl)-methylamine and organotin(IV) chloride were purchased from Sigma Aldrich; carbon disulphide and chloroform were purchased from Merck; and ethanol was purchased from Marcon. All the chemicals were used without purification.

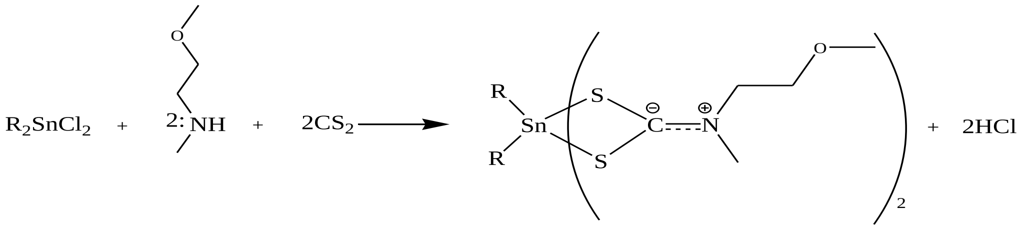
Instruments

The melting points were determined in open capillary tubes using an electrothermal 9300 digital melting point apparatus. The composition percentage of carbon, hydrogen, nitrogen, and sulphur were determined using an elemental analyser (CHNS−O), Model LECO 932. Solid-state infrared spectra of the compounds were recorded in the range of 4000–370 cm^{-1} and 350–200 cm^{-1}. The infrared spectra were recorded using a Perkin-Elmer Spectrum GX and Perkin-Elmer Spectrum BX. The ^{1}H, ^{13}C, and ^{119}Sn nuclear magnetic resonance spectra were recorded in $CDCl_3$ using Bruker Avance III 400.Tetramethylsilanewas used as an internal standard.

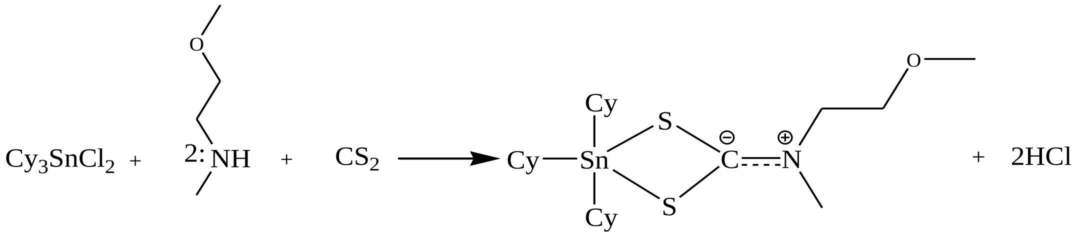
General Synthesis of Organotin(IV) (2-Methoxyethyl)-methyldithiocarbamate Complexes (Complex 1 and 2)

All complexes from di- and triorganotin(IV)(2-methoxyethyl)methyl dithiocarbamate were prepared using a direct reaction by mixing the metal and ligand with 1:2 and 1:1 molar ratio, respectively. The secondary amine dissolved in ethanol was stirred with ammonia as a catalyst before the addition of carbon disulphide(CS_2). The solution was continuously stirred for 2 h. After that, organotin(IV) chloride dissolved in a suitable solvent was added to the solution and stirred for another 2 h. The precipitate formed was filtered and washed with cold ethanol and dried in desiccator. The general reaction between secondary amine, carbon disulphide, and phenyltin(IV) trichlorideis illustrated in the following figure:

Reaction mechanism of Complex 1 (R=Bu) and Complex 2 (R=Ph)



Reaction mechanism of Complex 3 (tricyclohexyltin)



Synthesis of $Bu_2Sn[S_2CN(C_3H_7O)(CH_3)]_2$ (complex 1)

(2-methoxyethyl)methyl amine(1.1 mL, 10mmol) dissolved in 30mL ethanol was stirred in an ice-bath condition (below 4°C) for 30 min. 1–2 mL of 25% ammonia solution was added to provide a basic condition. Then, a cold ethanolic solution of carbon disulphide (0.6 mL, 10mmol) was added into the solution and stirred for about 2 h. Next, dibutyltin(IV) dichloride (1.52 g, 5mmol) dissolved in ethanol was added into the solution and further stirred for 2 h. After that, the precipitate formed was filtered and washed a few times with a cold ethanol to remove the impurities. Finally, the precipitate was dried in a desiccator. The $Bu_2Sn[S_2CN(C_3H_7O)(CH_3)]_2$complex was white in colour.

Yield: 66.31%, melting point 59.7–62.9 °C. Elemental Analysis %: Anal. (calculated): C, 40.26 (38.50); H, 7.33 (6.82); N, 4.98 (5.04); S, 23.65 (22.84). ^{1}H NMR [$CDCl_3$] δ(ppm): 2.043–1.439 (m, 6H, Sn–CH_2–CH_2–CH_2–), 0.984 (t, 3H, –CH_3), 3.397 (s, 3H, N–CH_3), 3.463 (s, 3H, O–CH_3), 3.711 (t, 2H, N–CH_2–R’-), 4.066 (t, 2H, N–R–CH_2–). ^{13}C NMR [$CDCl_3$] δ(ppm): 34.28–13.87 (Sn–C), 44.48 (N–CH_3), 56.56 (N–CH_2–R’-), 59.06 (O–CH_3), 70.13 (N–R–CH_2–), 201.17 (NCS_2). ^{119}Sn NMR [$CDCl_3$] δ (ppm): −338.59. IR (KBr, cm^{-1}): 1490 (v C–N), 2921 (v C–H), 990 (v C–S), 351(v Sn–S), 553(v Sn–C).

Synthesis of $Ph_2Sn[S_2CN(C_3H_7O)(CH_3)]_2$ (complex 2)

(2-methoxyethyl)-methylamine (0.22 mL, 2mmol) dissolved in 10mL ethanol was stirred in an ice-bath condition (below 4°C) for 30 min. 1–2 mL of 25% ammonia solution was added to provide a basic condition. Then, a cold ethanolic solution of carbon disulphide (0.12 mL, 2mmol) was added into the solution and stirred for about 2 h. Next, diphenyltin(IV) dichloride (0.34 g, 1mmol) dissolved in ethanol was added into the solution and further stirred for 2 h. After that, the precipitate formed was filtered and washed a few times with a cold ethanol to remove the impurities. Finally, the precipitate was dried in a desiccator. The $Ph_2Sn[S_2CN(C_3H_7O)(CH_3)]_2$ complex was white in colour.

Yield: 78%, melting point109.1–111.1°C. Elemental Analysis %: Anal. (calculated): C, 44.7 (43.93); H, 5.12 (5.03); N, 4.26 (4.67); S, 20.24 (21.33).^{1}H NMR [$CDCl_3$] δ(ppm): 8–7.28 (m, 5H, Sn–C_6H_5), 3.364 (s, 3H, N–CH_3), 3.444 (s, 3H, O–CH_3), 3.69 (t, 2H, N–CH_2–R’–), 3.966 (t, 2H, N–R–CH_2–). ^{13}C NMR [$CDCl_3$] δ(ppm): 151.238–128.24 (Sn–C aromatic), 45.45 (N–CH_3), 57.84 (N–CH_2–R’–), 59.06 (O–CH_3), 69.96 (N–R–CH_2–), 199.88 (NCS_2). ^{119}Sn NMR [$CDCl_3$] δ (ppm): −499.85. IR (KBr, cm^{-1}): 1497 (v C–N), 2892 (v C–H), 988 (v C–S), 389 (v Sn–S), 523(v Sn–C).

Synthesis of $Cy_3Sn[S_2CN(C_3H_7O)(CH_3)]$(complex 3)

(2-methoxyethyl)-methyl amine (0.22 mL, 2mmol) dissolved in 10mL ethanol was stirred in an ice-bath condition (below 4°C) for 30 min. 1–2 mL of 25% ammonia solution was added to provide a basic condition. Then, a cold ethanolic solution of carbon disulphide (0.12 mL, 2mmol) was added into the solution and stirred for about 2 h. Next, tricyclohexyltin(IV) chloride (0.81 g, 2mmol) dissolved in chloroform was added into the solution and further stirred for 2 h. After that, the precipitate formed was filtered and washed a few times with a cold ethanol to remove the impurities. Finally, the precipitate was dried in a desiccator. The $Cy_3Sn[S_2CN(C_3H_7O)(CH_3)]$complex was white in colour.

Yield: 76.39%, melting point102.7–104.4°C. Elemental Analysis %: Anal. (calculated): C, 52.4 (51.89); H, 8.05 (8.14); N, 2.53 (2.63); S, 12.47 (12.05). ^{1}H NMR [$CDCl_3$] δ(ppm): 2.019–1.272 (m, 11H, Sn–C_6H_{11}), 3.383

(s, 3H, N–CH_3), 3.54 (s, 3H, O–CH_3), 3.725 (t, 2H, N–CH_2–R'–), 4.137 (t, 2H, N–R–CH_2–). ^{13}C NMR [$CDCl_3$] δ(ppm): 34.62–27.01 (Ccyclohexyl), 45.24 (N–CH_3), 57.23 (N–CH_2–R'–), 59.04 (O–CH_3), 70.31 (N–R–CH_2–), 199.5 (NCS_2). ^{119}Sn NMR [$CDCl_3$] δ(ppm):−370.12 IR (KBr, cm^{-1}): 1485 (v C–N), 2911 (v C–H), 990 (v C–S), 355(v Sn–S), 584(v Sn–C).

RESULTS AND DISCUSSIONS

Three new complexes of organotin(IV) (2-methoxyethyl)-methyl dithiocarbamate with the general formula of $R_nSn[S_2CN(C_2H_4OCH_3)(CH_3)]n{-}_2$(R=Bu and Ph for n= 2; R= Cy for n= 3) were successfully prepared in situ between secondary amine, (2-methoxyethyl)-methyl amine with carbon disulphide,CS_2 in the presence of ammonia to provide a basic solution [2].All the complexes were in white powder form and stable with the melting point ranging from 60 to 111°C.Theyields were above 65%. The calculated percentages for the elements were in good agreement with the experimental values. All the compounds were also easily dissolved in chloroform.

Infrared (IR) Spectroscopy

IR spectroscopy is a useful technique in structural determination of coordination complexes [15]. In all the complexes, a sharp peak appeared in the spectra in the region of 1485–1495 cm^{-1}. This band is called "thioureide band", arisingin the region of 1470–1500 cm^{-1}[2]. The thioureide band is simply a combination of v(C–N) and v(C=N). Due to the presence of electron-rich sulphur atoms, delocalisation of electrons occurs over the entire NCS_2 region, resulting in the partial double bond character of thioureide band [1]. This thioureide band is sensitive towards the presence of substituent groups on tin (Sn) atom in which the more electronegative substituent will give ahigher frequency of vibration [5]. Besides, resonance has the effect of reducing the force constant, K, and the absorption then moves to a lower frequency [14]. This scenario could explain the reason diphenyltin complex exhibits the highest frequency at 1497.39 $cm^{-1}$for this band as phenyl is the most electronegative group than butyl and cyclohexyl. Thus, the electron density on metal is reduced in this complex, leading to decreased electron back donation from metal to sulphur. It results in the weakening of resonance effect in NCS_2 region. Hence, absorption moves to a higher frequency.

On the other hand, the appearance of the single band for v(C–S) in the 950–1050 cm^{-1} region was indicative of the bidentate behaviour of the dithiocarbamate ligand[9]. The spectra showed the presence of a single peak in theregion of988–990 cm^{-1}, suggesting that the dithiocarbamate ligands in all the complexes were in bidentate mode. Diphenyltin(IV) complex showed a lower frequency for this band at 988.7 cm^{-1}compared to both dibutyltin and tricyclohexyltin(IV) complexes. This phenomenon can be associated with the electronegative property of diphenyl group that has reduced the density of delocalised electrons in the C–S bond, thus leading to the lower vibration frequency.

The Sn–S bands existed in the far infrared region (250–450 cm^{-1}) [4]. The bonding of tin with sulphur atom of (2-methoxyethyl)-methyl dithio carbamate ligand was observed with the presence of peak absorption at 351–389 cm^{-1}, indicating the coordination between the ligand and metal bond via the sulphur atom [16]. The vibration band due to v (Sn-C) stretching usually appeared in the range of475–625 cm^{-1}, determining that the tin was still in contact with the organic groups [16]. The vibration band of our complexes was observed in the spectra at 523–584 cm^{-1}.

Nuclear Magnetic Resonance (NMR) Spectrospcopy

^{1}H NMR spectra were recorded in $CDCl_3$ solution. Tetramethylsilane was used as an internal standard at room temperature. Generally, the ^{1}H NMR spectra of the complexes contained absorptions in two regions assignable to the dithiocarbamate ligand(3–4 ppm) and organic groups attached to Sn atom for nonaromatic group(1–2 ppm) and for phenyl group(7–8 ppm). Two types of methylene protons in methoxyethyl chain attached to nitrogen atom showed triplet signals around 3.7–4 ppm, while the methyl protons bound to oxygen showed signals around 3.5 ppm in all the complexes. Methyl protons bound to nitrogen atom resonated at 3.4, 3.36, and 3.38 ppm in complexes**1**,**2**, and **3**, respectively. As all the three complexes were from the same series of dithiocarbamate ligand, the protons in the ligand were expected to arise at almost the same chemical shifts. The difference in organotin used to form each complex might not influence the resonance of those protons because the influence of the substituents dropped rapidly with distance [14].

In the case of dibutyltin, four sets of signal for methyl protons and broad signals for the methylene protons were observed in the range of 0.984–2.042 ppm. A shielding effect could be experienced through the carbon chain due to the attachment of the butyl group to the electropositive Sn atom via carbon nuclei [12]. The signals with a complex multiplet at 7.28–8.00 ppm were assigned to aromatic protons of phenyl group [17]. Meanwhile, in the case of tricyclohexyltin, four sets of signal were observed in the range of 1.272–2.019 ppm with one of them overlapping with the other one. The resonance could be assigned to the methylene protons of tricyclohexyl group, which is in agreement with the previous report [3].

Next, for ^{13}C NMR spectra, the (2-methoxyethyl)-methyl dithiocarbamate ligand of all the three complexes exhibited signals for the N–CH_2 and N–R–CH_2 carbons at 70 ppm and 56–57 ppm, while the methyl carbons bound to nitrogen atom were found to resonate at 44–45 ppm. The methyl carbons of methoxy resonated at 59 ppm in all the three complexes. The signals of butyl carbon atoms attached to Sn atom in complex **1** appeared at 13.87, 26.47, 28.56, and 34.28 ppm. For phenyl carbon atoms in complex **2**, the signals appeared at 128.24, 128.51, 134.29, and 1151.24 ppm, while the signals for carbon atoms of cyclohexyl in complex **3** appeared at 27.01, 29.33, 32.05, and 34.62 ppm. A single peak of $N^{13}CS_2$ carbon at 201.17, 199.88, and 199.50 ppm was observed in all the complexes, which was associated with the backbone carbon of the dithiocarbamate[8]. All the carbon positions were in agreement with the previously reported values on the similar organotin(IV) of other dithiocarbamate complexes[3,12].

^{119}Sn NMR spectra were also recorded in $CDCl_3$ to support the structures deduced from the ^{1}H and ^{13}C NMR spectra. ^{119}Sn NMR spectra can be used as an indicator of the coordination number of the tin atom. In the range of δ 200 to −60, δ −90 to −190, δ −210 to −400, δ −440 to −540 ppm, the coordinate numbers of the tin were four, five, six, and seven, respectively [15]. Based on the data, complex **1** exhibited the ^{119}Sn spectra at −338.59and complex **3** at−370.12, namely under the range from−210 to −400, indicating that the tin atom had six coordination numbers. Next, in complex **2,**the signal appeared at −499.85, which indicated the seven coordination number of tin atom. One of the additional coordination numbers of tin in complex **2** and **3** might be due to chloride that did not dissociate from the tin atom upon complexation as one additional band was observed in the IR spectroscopy at 283.11 and 281.95, which might be assigned to the Sn–Cl bond [6].

CONCLUSION

Three new organotin(IV) complexes with ligand (2-methoxyethyl)-methyldithiocarbamate were successfully synthesised in situ. All the new complexes were characterised by elemental and spectroscopic analyses. It is suggested that Sn atom has six coordination numbers in complex **1** and **3** while seven coordination numbers in complex **2.** The exact structure will be further confirmed using X-ray crystallography analysis.

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