The Malaysian Journal of Analytical Sciences, Vol 15 No 1 (2011): 106 - 112

The Malaysian Journal of
ANALYTICAL
SCIENCES ISSN 1394-2506

SYNTHESIS AND CHARACTERIZATION OF DIPHENYLTIN(IV) DITHIOCARBAMATE COMPOUNDS

(Sintesis dan Pencirian Sebatian Difenilstanum(IV) Ditiokarbamat)

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Abstract

Ten compounds of diphenyltin(IV) with *N*-dialkyldithiocarbamate were successfully prepared using *in situ* methods. Elemental analysis data (C, H, N and S) showed an agreement with the general formula of $(\mathrm{C_6H_5})_2\mathrm{Sn}[\mathrm{S_2CN}R_1R_2]$ (R_1 = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_7H_7}$; R_2 = $\mathrm{C_2H_5}$, $\mathrm{C_4H_9}$, $\mathrm{C_6H_{11}}$, $i\mathrm{C_3H_7}$, $\mathrm{C_7H_7}$). The structures of these compounds have been examined by infrared spectroscopy, ultraviolet, ^{1}H, ^{13}C & ^{119}Sn NMR spectroscopy and X-ray crystallography. The infrared spectra of these compounds showed three important peaks for *v*(C$\overset{\text{- - -}}{\text{—}}$N), *v*(C$\overset{\text{- - -}}{\text{—}}$S) and *v*(C$\overset{\text{- - -}}{\text{—}}$S) bands that appeared in the region of 1474 -1499, 969 - 995 and 324 - 335 cm^{-1} respectively. Data for ^{13}C NMR spectroscopy showed an important peak in the region of 198 – 200 ppm that corresponded to the $\mathrm{NCS_2}$ group. Single crystal X-ray diffraction studies showed $(\mathrm{C_6H_5})_2\mathrm{Sn}[\mathrm{S_2CN}(\mathrm{C_2H_5})(\mathrm{CH_3})]_2$ (**1**) is six coordinated and adopted a *monoclinic* system with space group C*2/c*, while $(\mathrm{C_6H_5})_2\mathrm{SnCl}[\mathrm{S_2CN}(\mathrm{C_7H_7})(i\mathrm{C_3H_7})]$ (**2**) is five coordinated, crystallized in *monoclinic* system with space group P*b₁/n*. Meanwhile, six coordinated $(\mathrm{C_6H_5})_2\mathrm{Sn}[\mathrm{S_2CN}(\mathrm{CH_3})(i\mathrm{C_3H_7})]_2$ (**3**) adopted a *orthorhombic* system with a space group P*bcn*.

Keywords: diphenyltin(IV), dithiocarbamate.

Abstrak

Sepuluh kompleks daripada difenilstanum(IV) dengan *N*-dialkilditiokarbamat telah berjaya disediakan menggunakan cara *in situ*. Data analisis unsur (C, H, N dan S) terhadap semua kompleks telah menunjukkan persetujuan dengan formula umum $(\mathrm{C_6H_5})_2\mathrm{Sn}[\mathrm{S_2CN}R_1R_2]$ (R_1 = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_7H_7}$; R_2 = $\mathrm{C_2H_5}$, $\mathrm{C_4H_9}$, $\mathrm{C_6H_{11}}$, $i\mathrm{C_3H_7}$, $\mathrm{C_7H_7}$). Struktur kesemua sebatian dapat ditentukan dengan menggunakan spektroskopi inframerah, ultralembayung, ^{1}H, ^{13}C dan ^{119}Sn RMN dan kristalografi sinar-X. Spektrum inframerah bagi sebatian ini menunjukkan tiga jalur penting, iaitu jalur *v*(C$\overset{\text{- - -}}{\text{—}}$N), *v*(C$\overset{\text{- - -}}{\text{—}}$S) dan *v*(Sn-S) yang wujud masing-masing pada julat 1474 -1499, 969 - 995 dan 324 - 335 cm^{-1}. Data daripada ^{13}C RMN menunjukkan puncak pada julat 198 – 200 ppm yang menandakan wujudnya kumpulan $\mathrm{NCS_2}$. Struktur hablur tunggal $(\mathrm{C_6H_5})_2\mathrm{Sn}[\mathrm{S_2CN}(\mathrm{C_2H_5})(\mathrm{CH_3})]_2$ (**1**) dan $(\mathrm{C_6H_5})_2\mathrm{SnCl}[\mathrm{S_2CN}(\mathrm{C_7H_7})(i\mathrm{C_3H_7})]$ (**3**) mempunyai sistem *monoklinik* dengan masing-masing mempunyai kumpulan ruang C*2/c* dan *P2₁/n* dengan sebatian pertama mempunyai struktur enam koordinatan dan struktur kedua membentuk lima koordinatan. Manakala $(\mathrm{C_6H_5})_2\mathrm{Sn}[\mathrm{S_2CN}(\mathrm{CH_3})(i\mathrm{C_3H_7})]_2$ (**2**) menunjukkan sistem *ortorombik* dengan kumpulan ruang P*bcn* dengan membentuk struktur enam koordinatan.

Kata kunci: difenilstanum(IV), ditiokarbamat.

Introduction

Organotin(IV) compounds have received tremendous attention for their synthesis, characterization and biological activities and their ability to bind with sulfur ligand such as thione or dithiocarbamate [1]. Furthermore, tin compound has an ability to form stable bonds with carbon as well as heteroatoms that have received much attention both in academic and applied research [2]. X-ray crystallographic studies of the dithiocarbamate compounds of diorganotin(IV) have shown a variety of coordination environments around the central tin atoms such as molecular geometry, ranging from tetrahedral to distorted octahedral [3]. The ligands coordinated to the tin atom may also display interesting bonding capabilities as two sulfur atoms can act as an S,S-bridging ligand [4]. Organotin compounds are widely used in chemical industries such as antifouling agents, plastic stabilizers, wood preservatives, bactericides, fungicides and insecticides [5]. Furthermore, organotin(IV) dithiocarbamate compounds have been used in chemical vapour deposition processes, flame retardants, polymer stabilizers and non-linear optical materials [6]. In this paper we report the synthesis and structure determination of ten diphenyltin(IV) dithiocarbamates compounds of the type $(C_6H_5)_2Sn[S_2CNR_1R_2]$ (R_1 = CH_3, C_2H_5, C_7H_7; R_2 = C_2H_5, C_4H_9, C_6H_{11}, iC_3H_7, C_7H_7). The crystal structures of diphenyltin(IV) methylisopropyldithiocarbamate, $(C_6H_5)_2Sn[S_2CN(CH_3)(iC_3H_7)]_2$(**1**), (*N*-benzyl-*N*-isopropyldithiocarbamato)chlorido diphenyltin(IV) $(C_6H_5)_2SnCl[S_2CN(C_7H_7)(iC_3H_7)]$(**2**) and diphenyltin(IV) ethylmethyldithiocarbamate, $(C_6H_5)_2Sn[S_2CN(CH_3CH_2)(CH_3)]_2$ (**3**) have also been determined and will be briefly discussed.

Material and Method

Material

All chemicals and solvents that have been used in this experiment were purchased from Merck and used without purification due to their high purity as follows: *N*-methylethylamine, *N*-methylcyclohexylamine, *N*-ethylcyclohexylamine, *N*-methylisopropylamine, *N*-ethylisopropylamine, diphenyltin(IV) dichloride, carbon disulphide, chloroform and ethanol.

Instrumentation

The melting point was measured by using the Electrothermal IA 9100. Elemental analysis had been carried out on a Fison EA 1108. Perkin Elmer Model GX Spectrophotometer was used to record the infrared spectra by using KBr disc in the spectral range of 400-4000 cm^{-1} and nujol in polyethylene tablets in the range of 400-250 cm^{-1}. The ^1H, ^{13}C and ^{119}Sn NMR spectra were also recorded in $CDCl_3$ as solvent using JOEL JNM-LA 400 Spectrometer and tetramethylsilane (TMS) as an internal standard. Bruker SMART APEX diffractometer and Oxford Diffraction Xcaliber Eos Gemini were used to determine X-ray structure and carried out at the Department of Chemistry, University of Malaya and University Putra Malaysia respectively.

General Synthetic Procedure

The compounds (Table 1) were prepared by using direct reaction between 0.005 mol carbon disulphide and an ethanolic solution of amines (0.005 mol). The mixture was stirred for one hour at 277 K and added dropwise to diphenyltin(IV) dichloride (0.0025 mol) in 20 mL of ethanol. The white precipitate that was formed, filtered and washed with cold ethanol and dried in desiccators. Suitable crystals were afforded by slow crystallization from a ethanol:chloroform (1:2) mixture.

Results and Discussion

Ten diphenyltin(IV) dithiocarbamate compounds have been prepared by using the insertion technique [7], which are the reaction between diphenyltin(IV) dichloride, amines and carbon disulphide at 277 K in ethanol to give stable compounds. General scheme for the reaction involved in the synthesis is shown in Figure 1. All compounds exhibit as solids either white or yellowish in colour. Elemental analysis (C, H, N and S) showed that the experimental values are in agreement with theoretical values based on their general formula (Table 1).

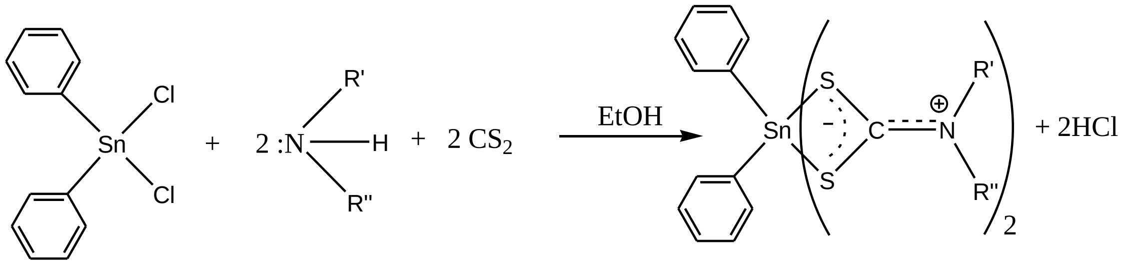


Figure 1: General reaction scheme between amines, carbon disulphide and diphenyltin(IV) dichloride.

Table 1: Physical and elemental analysis data for diphenyltin(IV) dithiocarbamate compounds.

Compound	**Yield (%)**	**Melting point (ºC)**	**Elemental analysis (%)**				
			C	**H**	**N**	**S**	**Sn**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_2H_5)]_2$	89	164-165	43.22	4.42	4.90	22.51	20.42
			44.37	**4.84**	**5.17**	**23.69**	**21.93**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_6H_{11})]_2$	92	141-143	49.27	4..50	4.17	18.84	17.72
			51.77	**5.90**	**4.31**	**19.74**	**18.28**
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(C_6H_{11})]_2$	83	117-119	52.99	5.71	3.80	17.57	17.13
			53.17	**6.25**	**4.13**	**18.93**	**17.52**
$(C_6H_5)_2Sn[S_2CN(CH_3)(iC_3H_7)]_2$	87	179-181	45.37	5.11	4.69	21.14	20.96
			46.40	**5.31**	**4.92**	**22.52**	**20.85**
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(iC_3H_7)]_2$	90	116-118	48.24	5.74	4.69	21.47	18.53
			48.50	**5.30**	**4.51**	**21.65**	**19.86**
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)(iC_3H_7)]$	72	197-199	51.41	4.55	2.64	10.63	20.41
			51.85	**4.54**	**2.63**	**12.04**	**22.28**
$(C_6H_5)_2SnCl[S_2CN(CH_3)(C_7H_7)]$	76	173-175	49.80	3.42	2.86	11.04	22.56
			49.98	**3.99**	**2.78**	**12.71**	**23.52**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_4H_9)]_2$	88	85-87	46.48	5.76	4.60	19.83	20.13
			48.24	**5.74**	**4.69**	**21.47**	**19.87**
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)_2]$	70	218-220	56.29	4.74	2.69	10.12	19.32
			55.84	**4.17**	**2.41**	**11.04**	**20.44**
$(C_6H_5)_2SnCl[S_2CN(C_2H_5)(C_7H_7)]$	74	187-189	50.53	4.49	3.03	11.17	11.45
			50.94	**4.27**	**2.70**	**12.36**	**12.89**

Bold = experimental value

Important infrared of diphenyltin(IV) dithiocarbamate bands are listed in Table 2. Based on the spectral data, diphenyltin(IV) dithiocarbamates compounds exhibited peaks that can be assigned to thioureida band, $v(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{N})$ found in the region of 1470 - 1500 cm^{-1} [6]. By the introduction of more electronegative substituents, the band will move to higher frequency due to the sensitivity towards substitution on the tin atom. Meanwhile, peaks in the region of 970 - 995 cm^{-1} are attributed to $v(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{S})$ [8]. Existence of a single v(C=S) band at 960 – 1005 cm^{-1} inferred that the ligand chelated as a bidentate entity [9]. Strong absorption bands which appeared in the region of 325 - 384 cm^{-1} was attributed to Sn-S stretching frequency that indicated the existence of metal-ligand bond [10].

Table 2: The infrared absorption bands of diphenyltin(IV) dithiocarbamate (cm^{-1}).

Compound	**Wavenumber (cm^{-1})**			
	v(C-H)	**$v(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{N})$**	**$v(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{S})$**	**v(Sn-S)**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_2H_5)]_2$	2976, 2931	1493	985	354
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_6H_{11})]_2$	2929, 2854	1478	970	384
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(C_6H_{11})]_2$	2933, 2856	1474	995	358
$(C_6H_5)_2Sn[S_2CN(CH_3)(i\text{-}C_3H_7)]_2$	2973, 2929	1478	969	354
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(\mathrm{i}\text{-}C_3H_7)]_2$	2977, 2933	1475	993	386
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)(iC_3H_7)]$	2979s, 2980s	1478s	964s	325s
$(C_6H_5)_2SnCl[S_2CN(CH_3)(C_7H_7)]$	2849s, 2928s	1495m	995s	326s
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_4H_9)]_2$	2929s, 2954s	1499s	975m	326s
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)_2]$	2930m	1496m	997w	326s
$(C_6H_5)_2SnCl[S_2CN(C_2H_5)(C_7H_7)]$	2910s, 2789m	1496m	995s	327s

The protons for the phenyl groups exhibited chemical shifts in the range 7.27-8.07 ppm (Table 3) as multiplets due to deshielding on complexation similar to what has been reported by Yin et al. (2004) [11]. The -CH_2- protons from the ethyl group resonated as a quartet at 3.69-3.83 ppm, while -CH_3 protons resonated as a triplet at 1.22 - 1.29 ppm [12]. The *N*-methyl protons signal was observed as a singlet at 3.19 - 3.34 ppm, while mutiplets at 1.12 - 1.95 ppm and 4.50 - 4.65 ppm were attributed to *N*-cyclohexyl protons [13]. While for the isopropyl group, the multiplet signal at 5.08 - 5.10 ppm and doublet signal at 1.21-1.26 ppm were attributed to methyne and methyl proton respectively [14]. The important data of ^{13}C NMR of the compounds are depicted in Table 4. The assignment of ^{13}C signal for NCS_2 group for all compounds appeared in the region of 198 – 200 ppm and indicated the coordination between sulfur and tin atom [15].

Table 3: ^1H NMR spectra data of organotin(IV) dithiocarbamate compounds (δ, ppm).

Compound	**Chemical shift, δ (ppm)**		
	Sn-C_6H_5	**-NR'; R' = CH_3, C_2H_5**	**-NR''; R'' = C_2H_5, C_6H_{11}, *i*C_3H_7**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_2H_5)]_2$	7.27-7.89(m)	3.34(s)	3.83(qt), 1.28(t)
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_6H_{11})]_2$	7.27-7.88(m)	3.22(s)	4.65(m), 1.91(m), 1.39(m), 1.12(m)
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(C_6H_{11})]_2$	7.33-8.07(m)	3.72(qt), 1.29(t)	4.50(m), 1.95(m), 1.83(m), 1.65(m)
$(C_6H_5)_2Sn[S_2CN(CH_3)(iC_3H_7)]_2$	7.34-7.86(m)	3.19(s)	5.10(m), 1.21(d)
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(iC_3H_7)]_2$	7.30-7.85(m)	3.69(qt), 1.22(t)	5.08(m), 1.26(d)
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)(iC_3H_7)]$	7.24-7.38(m)	5.03(s), 7.45-7.54(m)	5.08(m), 1.25(d)
$(C_6H_5)_2SnCl[S_2CN(CH_3)(C_7H_7)]$	7.27-7.35(m)	3.29(s)	5.05(s), 7.39-7.44(m)
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_4H_9)]_2$	7.27-7.49(m)	3.34(s)	0.95(t), 1.36(m), 1.70(m), 3.75(t)
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)_2]$	7.27-7.40(m)	5.02(s), 7.41-7.54(m)	5.02(s), 7.41-7.54(m)
$(C_6H_5)_2SnCl[S_2CN(C_2H_5)(C_7H_7)]$	7.27-7.41(m)	3.75(qt), 1.28(t)	5.06(s), 7.45-7.52(m)

The coordination number of organotin(IV) dithiocarbamate compounds can be identified by using ^{119}Sn NMR spectroscopy [16]. The R substitute from dithiocarbamate groups that bind to the Sn atom affects the ^{119}Sn chemical shifts even though each compound have the same coordination due to the sensitivity of the chemical environment of the tin atom [17]. Only five compounds were afforded for ^{119}Sn NMR and the chemical shift for the compounds are tabulated in Table 5. This chemical shifts indicated those compounds having a six coordination environment around the tin atom with octahedral structure [16].

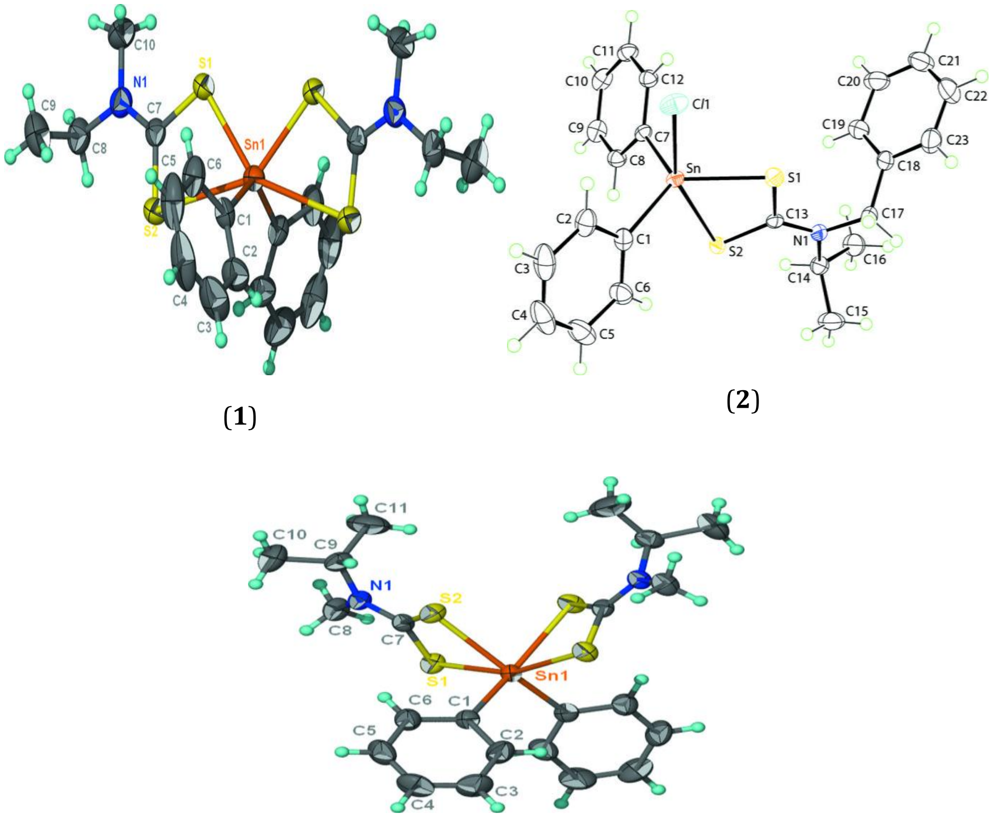
Table 4: ^{13}C NMR data of diphenyltin(IV) dithiocarbamate compounds (δ, ppm).

Compound	**Chemical shift, δ (ppm)**			
	$N^{13}CS_2$	**$Sn\text{-}C_6H_5$**	**-NR'; R' = CH_3, C_2H_5**	**-NR'; R' = C_2H_5, C_6H_{11}, *i*C_3H_7**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_2H_5)]_2$	199.0	128.4, 134.5, 128.6	42.9	53.5, 12.0
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_6H_{11})]_2$	198.6	129.0, 134.4, 128.4	36.6	65.2, 30.2, 25.5, 25.6
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(C_6H_{11})]_2$	198.4	129.0, 134.4, 130.3	44.9, 14.2	65.7, 30.9, 25.6, 30.7
$(C_6H_5)_2Sn[S_2CN(CH_3)(i\text{-}C_3H_7)]_2$	198.6	128.5, 134.5, 128.3	35.3	56.9, 19.9
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(i\text{-}C_3H_7)]_2$	198.4	128.2, 134.4, 128.3	43.8, 14.2	57.4, 20.5
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)(iC_3H_7)]$	198.0	128.5, 135.9, 129.1	58.67, 135.5, 130.1, 128.8, 126.5	53.0, 20.4
$(C_6H_5)_2SnCl[S_2CN(CH_3)(C_7H_7)]$	201.1	128.1, 134.3, 128.9	42.5	61.4, 135.7, 127.6, 128.9, 128.5
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_4H_9)]_2$	199.2	134.3, 128.4, 128.2	43.35	13.8, 19.9, 28.9, 58.4
$(C_6H_5)_2SnCl[S_2CN(C_7H_7)_2]$	199.0	128.8, 133.4, 128.1	57.4, 135.8, 129.2, 128.9, 127.9	57.4, 135.8, 129.2, 128.9, 127.9
$(C_6H_5)_2SnCl[S_2CN(C_2H_5)(C_7H_7)]$	197.1	135.7, 129.2, 128.9,	50.1, 11.7	58.8, 133.6, 128.7, 128.8, 127.9

Table 5: ^{119}Sn NMR data of diorganotin(IV) dithiocarbamate compounds (δ, ppm).

Compound	**δ(^{119}Sn), ppm**	**Coordination No.**
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_2H_5)]_2$	-324.2	6
$(C_6H_5)_2Sn[S_2CN(CH_3)(C_6H_{11})]_2$	-318.0	6
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(C_6H_{11})]_2$	-316.8	6
$(C_6H_5)_2Sn[S_2CN(CH_3)(i\text{-}C_3H_7)]_2$	-317.8	6
$(C_6H_5)_2Sn[S_2CN(C_2H_5)(i\text{-}C_3H_7)]_2$	-316.9	6

Only three compounds, bis(*N*-ethyl-*N*-methyldithiocarbamato-κ^2S,S')diphenyltin(IV) (**1**), (*N*-benzyl-*N*-isopropyldithiocarbamato)chlorido diphenyltin(IV) (**2**) and bis(*N*-isopropyl-*N*-methyldithiocarbamato-κ^2S,S')diphenyltin(IV) (**3**) produced single crystals by slow evaporation of ethanol:chloroform 1:2 mixture. The ORTEP plots are shown in Figure 3. The single crystal studies of bis(*N*-ethyl-*N*-methyldithiocarbamato-κ^2S,S')diphenyltin(IV) (**1**) [18] and bis(*N*-isopropyl-*N*-methyldithiocarbamato-κ^2S,S')diphenyltin(IV) (**3**) [19] adopted *monoclinic* system with a space groups C*2/c* and P*2i/n* respectively, both with six-coordinated in a skew-trapezoidal-bipyramidal geometry. Both structures (**1** and **3**) have short thioureide C-N distance, 1.336(2) and 1.323(3) Å respectively, suggesting partial double bond character [6]. The compound (*N*-benzyl-*N*-isopropyldithiocarbamato)chlorido diphenyltin(IV) (**2**) adopted a *orthorhombic* system with space group P*bcn*, the Sn atom is penta-coordinated by an asymmetrically coordinating dithiocarbamate ligand, a Cl and two ispo-C atoms of the Sn-bound phenyl groups [20]. The resulting C_2ClS_2 donor set defines a coordination geometry intermediate between square-pyramidal and trigonal-bipyramidal with a slight tendency towards the latter.



(**1**)

(**2**)

(**3**)

Figure 3. ORTEP plot of (**1)** bis(*N*-ethyl-*N*-methyldithiocarbamato- *κ*^{2}S,S')diphenyltin(IV), (**2**) (*N*-benzyl-*N*-isopropyldithiocarbamato)chlorido diphenyltin(IV) and (**3**) bis(*N*-isopropyl-*N*-methyldithiocarbamato-κ^{2}S,S')diphenyltin(IV) at the 50% probability level.

Conclusion

The elemental and spectroscopic data showed that ten diphenyltin(IV) dithiocarbamate compounds are successfully synthesized and pure compounds were obtained. Further, the crystallographic studies of bis(*N*-isopropyl-*N*-methyldithiocarbamato-*κ*^{2}S,S')diphenyltin(IV) and bis(*N*-isopropyl-*N*-methyldithiocarbamato-*κ*^{2}S,S') diphenyltin(IV) showed that the dithiocarbamate ligands are bonded to the tin atom in six coordinate symmetry with bidentate manner having skew trapezoidal bipyramidal geometry. While (*N*-benzyl-*N*-isopropyldithiocarbamato)chlorido diphenyltin(IV) is penta-coordinated by an asymmetrically coordinating dithiocarbamate ligand, a Cl and two ispo-C atoms of the Sn-bound phenyl groups.

Acknowledgement

We would like to thank Universiti Kebangsaan Malaysia for UKM-GUP-NBT-08-27-111 and the Government of Malaysia for the Science Fund 06-01-02-SF0539 grants. Thank you also to Prof Ng Seik Weng and Prof E. R. T. Tiekink, UM and Dr Mohamed Ibrahim Mohamed Tahir, UPM for the crystal structures. We would also like to thank all faculty members that have contributed to this research.

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