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Synthesis, Properties and Spectroscopic Characterization of Some Diorganotin(IV) dithiocarbamates Complexes

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ABSTRACT

Reaction of diorganotin(IV) dichloride with carbon disulphide and primary amines in 1:2:2 molar ratio under stirring at 277 K yield product of the type $R_2Bu[S_2CNHR']_2$ where R= Me, Bu, Ph and R'= Me, Et, Prⁱ, Bu, Ph. These newly synthesized complexes are yellow crystalline solid, soluble in common organic solvents and non-volatile in nature. All these complexes have been characterized by elemental analysis (C, H, N, S, Sn), molecular weight determination, IR and NMR [¹H, ¹³C, ¹¹⁹Sn] spectral data. On the basis of above studies hexacoordinated nature of the tin atom and bidentate behavior of ligand have been established.

Keywords: Dimethyltin(IV) dichloride, dibutyltin(IV) dichloride, diphenyltin(IV) dichloride, primary amines, carbon disulphide.

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INTRODUCTION

In recent years considerable interest has been evinced in the field of chemistry of metallic moieties bonded with sulphur ligands such as dithiolates [1], thio- β -diketonates [2,3], O,O'-dialkyl and alkylene dithiophosphates [4,5], trithiophosphates [6,7] due to their interesting versatility in chemical bonding modes [uni, bidentate (chelating/ bridging)]. Besides this, a large number of N,N'-dialkyl dithiocarbamate derivatives of tin metals have also been synthesized [8-10], but the perusal of literature revealed that N-alkyl dithiocarbamate derivatives of tin metal have not been synthesized and characterized as yet. However N-alkyl derivatives of nickel is reported in the literature in which distorted square planar geometry of nickel atom have been established [11].

Dithiocarbamates ligands have a great tendency to bind the metal atom and it behaves as a monodentate, bidentate, anisobidentate ligands. Due to its various structural properties and coordination mode with tin metal, they show antifungal [12-14] and biological activity such as antibacterial [13,15], anticancer [14] and cytotoxic activity [16].

MATERIALS AND METHODS

Tin and Sulphur were estimated gravimetrically as tin oxide and barium sulphate (Messenger's method) [17]. A Knauer vapour pressure osmometer in chloroform was used for molecular weight determination. FTIR spectra were recorded on a Shimadzu 8201 PC spectrophotometer in the region of 4000-200 cm^{-1} using CsI cells. ^1H and ^{13}C NMR spectra (in CDCl_3) and ^{119}Sn NMR spectra (in C_6H_6) were recorded on Bruker DRX-300 spectrophotometer using TMS (For ^1H and ^{13}C) and Me_4Sn (For ^{119}Sn) as external references.

Since, all the ligand complexes of tin(IV) have been synthesized by a similar route and hence synthesis of only one representative member is described below.

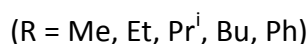
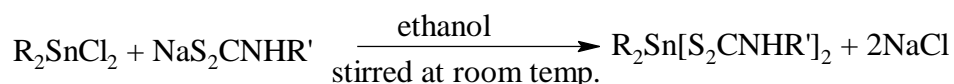
Synthesis of $\text{Me}_2\text{Sn}[\text{S}_2\text{CNHMe}]_2$ - Ethanolic solution of methyl amine (5.16 g ; 16.56 mmole) and carbon disulphide (12.65 g ; 16.56 mmole) was stirred at 298K. After one hour stirring the addition of dimethyltin(IV) dichloride (1.82 g ; 8.32 mmole) yielded to a clear solution and still left stirring for another hour a yellow solid was obtained which was filtered off and then washed 3-4 times with cold ethanol and dried in vacuo. Recrystallise with CHCl_3 : $\text{C}_2\text{H}_5\text{OH}$ (1:1) mixture yielded yellow crystalline solid (2.85 g, 95%) [Calcd. For $\text{C}_6\text{H}_{14}\text{N}_2\text{S}_4\text{Sn}$ Sn 32.77%, S 35.55%, C 20.00%, H 3.89%, N 7.77% found : Sn 32.45%, S 35.52%, C 19.92%, H 3.82%, N 7.70%]

Similar complexes have also been synthesized by alternative method.

Synthesis of $\text{Me}_2\text{Sn}[\text{S}_2\text{CNHMe}]_2$ - The solution of dimethyltin(IV) dichloride (1.79 g ; 5.89 mmole) in ethanol was added to the ethanolic solution of sodium N-methyldithiocarbamate (1.52 g ; 11.78 mmole) in 1:2 molar ratio and stirred for half an hour at room temperature. A yellow crystalline solid was obtained, filtered off and then washed 3-4 times with cold ethanol, then recrystallise with CHCl_3 : $\text{C}_2\text{H}_5\text{OH}$ (1:1) results in the formation of yellow crystalline solid.

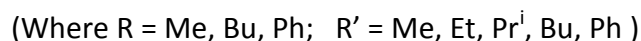
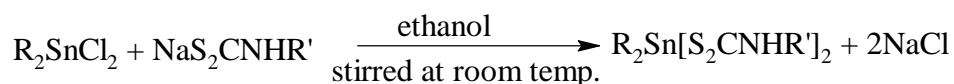
RESULT AND DISCUSSION

All these complexes have been synthesized by the addition of carbon disulphide to an ethanolic solution of alkyl amine under stirring at 277 K. After one hour stirring, the dropwise addition of dialkyltin(IV) dichloride yielded to a clear solution. The rate of addition is controlled to maintain a temperature of 277 K. The reaction mixture is stirred for another hour.



A yellow coloured solid is obtained which is filtered and washed with cold ethanol for 3-4 times and then recrystallize with chloroform-petroleum ether mixture (1:1).

Alternatively these complexes have also been synthesized by mixing and stirring of Diorganotin(IV) dichloride and sodium salt of dithiocarbamate in 1:2 molar ratio under stirring for half an hour at room temperature in the presence of ethanol. The NaCl formed is removed by filtration. The filtrate is evaporated to yield $\text{R}_2\text{Sn}(\text{S}_2\text{CNHR}')$, which is recrystallise from chloroform-petroleum ether mixture (1:1).



These newly synthesized complexes are yellow coloured crystalline solid which are non-volatile in nature, soluble in common organic solvents like benzene, chloroform etc., monomeric in nature and extremely sensitive towards atmospheric moisture.

I.R. spectra

Following characteristic absorption signal are obtained in newly synthesized compounds (table 2).

1. A sharp band in the region $959\text{-}971\text{ cm}^{-1}$ has been assigned to the $\nu(\text{C-S})$ bond which are suggests the chelating character of the dithiocarbamate ligand [18].
2. $\nu(\text{C-N})$ stretching vibration are obtained in region $1492\text{-}1510\text{ cm}^{-1}$ between the range of $\nu(\text{C=N})$ double bond ($1640\text{-}1690\text{ cm}^{-1}$) and $\nu(\text{C-N})$ single bond ($1492\text{-}1510\text{ cm}^{-1}$) [19], It indicates that the C-N bond in the complexes have partial double bond character. Besides this, $\nu(\text{C-N})$ vibration is shift to higher frequencies than the free ligand ($1450\text{-}1476\text{ cm}^{-1}$) shows that the dithiocarbamate attached with the metal ion in bidentate manner.

3. A strong band of primary amines appears at about $2999-3120\text{ cm}^{-1}$ shows the $\nu(\text{N-H})$ stretching vibrations.
4. The absorption band in the region $360-378\text{ cm}^{-1}$ is assigned to $\nu(\text{Sn-S})$ stretching vibrations, which is support the proposed coordination of the complexes.
5. Appearance of a weak band at $660-670\text{ cm}^{-1}$ has been assigned to $\nu(\text{Sn-C})$ linkage.

NMR Spectra

^1H NMR

Due to bonding between the dithiocarbamate ligand and tin metal, all the complexes shows downfield shift in comparison to the starting material (table 3). The PMR spectra of all these complexes (solution in CDCl_3) shows the characteristics resonance for alkyl, aryl protons on tin atom and alkyl, aryl protons of nitrogen atom. A singlet peak appears at δ 3.00-3.05 ppm shows the N-H proton. Phenyl protons attached with tin metal shows multiplet at δ 6.62-6.65 ppm while phenyl protons attached with nitrogen atom shows multiplet at δ 7.51-7.61 ppm.

^{13}C NMR (table 4)

1. CS_2 peak in ^{13}C NMR shows sharp singlet at δ 194 ppm in free ligand is shifted to higher frequency in all these complexes (δ 195-200 ppm) which shows that the ligand is attached with tin atom. The high value of thion carbon chemical shift could be explained by an increase of π -bond order in the whole NCS_2 moiety.
2. Due to electron donating groups present on the tin atom (Sn-R where $\text{R} = \text{Bu, Ph}$), CS_2 peak appears at δ 199-201 ppm which is slightly downfield shift as compare to the complex in which $\text{R} = \text{Me}$ (δ 197.2 – 197.5 ppm).
3. Carbons of aryl group which are attached to nitrogen group appears at δ 136 – 140 ppm and carbons of aryl group which are attached to tin atom shows multiplet at 128-198 δ ppm.

^{119}Sn NMR

^{119}Sn NMR spectra shows the sharp singlet at about δ 246.7-262.4 ppm which shows six coordination number of the tin atom (Table 3).



Table 1: Synthesis and characterization of diorganotin(IV) bis(N-alkyl dithiocarbamate)

S.No.	Reactant			Product R ₂ Sn[S ₂ CNHR'] ₂ g... % yield	Analysis					Molecular weight Found (Calcd.)
	R ₂ SnCl ₂ g... mmole	CS ₂ g... mmole	R'NH ₂ g... mmole		S% Found (Calcd.)	Sn% Found (Calcd.)	C% Found (Calcd.)	H% Found (Calcd.)	N% Found (Calcd.)	
1	R=Me 1.82 8.32	12.65 16.65	R'=Me 5.16 16.65	R=Me R'=Me 2.85 95.48	35.52 (35.55)	32.45 (32.77)	19.92 (20.00)	3.82 (3.89)	7.70 (7.77)	----
2	R=Me 1.88 8.32	13.07 17.19	R'=Et 13.07 17.19	R=Me R'=Et 2.83 88.16	33.86 (34.22)	31.50 (31.55)	25.60 (25.67)	4.76 (4.81)	7.42 (7.49)	356 (374)
3	R=Me 1.76 8.04	12.23 16.09	R'=Pr ⁱ 12.23 16.09	R=Me R'=Pr ⁱ 2.89 92.67	32.59 (32.98)	29.69 (30.41)	30.85 (30.93)	5.61 (5.67)	7.14 (7.21)	-----
4	R=Me 1.99 9.09	13.83 18.19	R'=Bu 13.83 18.19	R=Me R'=Bu 3.34 91.76	31.62 (31.84)	28.99 (29.35)	35.74 (35.82)	6.42 (6.47)	6.91 (6.97)	-----
5	R=Me 1.86 8.49	12.19 16.99	R'=Ph 12.19 16.99	R=Me R'=Ph 3.86 93.99	26.40 (26.44)	23.98 (24.38)	39.62 (39.67)	3.67 (3.72)	5.71 (5.79)	472 (484)
6	R=Bu 2.03 6.70	1.02 13.40	R'=Me 1.02 13.40	R=Bu R'=Me 2.84 95.62	27.87 (28.82)	26.12 (26.51)	32.37 (32.43)	5.80 (5.86)	6.22 (6.31)	429 (444)
7	R=Bu 1.62 5.35	8.13 10.70	R'=Et 8.13 10.70	R=Bu R'=Et 2.09 95.62	27.59 (27.94)	25.52 (25.76)	36.61 (36.68)	6.49 (6.55)	6.02 (6.11)	----
8	R=Bu 1.85 6.09	9.26 12.19	R'=Pr ⁱ 9.26 12.19	R=Bu R'=Pr ⁱ 2.63 91.64	26.78 (27.11)	24.77 (25.00)	40.60 (40.68)	7.12 (7.20)	5.86 (5.93)	-----
9	R=Bu 1.88 6.19	9.42 12.39	R'=Bu 9.42 12.39	R=Bu R'=Bu 2.70 89.70	26.00 (26.33)	23.98 (24.27)	44.38 (44.44)	7.74 (7.82)	5.69 (5.76)	473 (486)
10	R=Bu 2.34 7.70	11.71 15.41	R'=Ph 11.71 15.41	R=Bu R'=Ph 4.05 92.68	22.24 (22.53)	20.54 (20.77)	46.43 (46.48)	5.21 (5.28)	4.88 (4.93)	-----
11	R=Ph 1.81 5.28	8.03 10.56	R'=Me 8.03 10.56	R=Ph R'=Me 2.46 96.09	26.10 (26.39)	24.29 (24.53)	39.51 (39.59)	3.67 (3.71)	5.71 (5.77)	-----
12	R=Ph 2.08 6.05	9.19 12.10	R'=Et 9.19 12.10	R=Ph R'=Et 2.58 85.43	25.40 (25.65)	23.65 (23.84)	43.21 (43.29)	4.37 (4.41)	5.54 (5.61)	-----
13	R=Ph 1.71 4.99	7.58 9.98	R'=Pr ⁱ 7.58 9.98	R=Ph R'=Pr ⁱ 2.34 91.41	24.36 (24.95)	22.72 (23.19)	46.69 (46.78)	5.01 (5.01)	5.34 (5.46)	498 (513)
14	R=Ph 1.87 5.45	8.29 10.91	R'=Bu 8.29 10.91	R=Ph R'=Bu 2.58 89.99	23.89 (24.28)	22.12 (22.58)	50.00 (50.09)	5.60 (5.69)	5.25 (5.31)	-----
15	R=Ph 1.85 5.37	8.17 10.75	R'=Ph 8.17 10.75	R=Ph R'=Ph 3.06 93.57	20.77 (21.01)	19.11 (19.54)	51.16 (51.23)	3.54 (3.61)	4.50 (4.59)	-----

Table 2: I.R. spectral data of diorganotin(IV) bis(N-alkyl dithiocarbamate) in cm^{-1}

S.No.	Compound $\text{R}_2\text{Sn}[\text{S}_2\text{CNHR}']_2$	$\nu(\text{C-H})$	$\nu(\text{N-C})$	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{N-H})$	$\nu(\text{Sn-S})$	$\nu(\text{Sn-C})$
1	R=Me R'=Me	2950 m	1145	1490	955	3109	345	663
2	R=Me R'=Et	2972 m	1160	1495	967	2995	340	662
3	R=Me R'=Pr ⁱ	2968 m	1152	1499	958	3128	348	664
4	R=Me R'=Bu	2972 m	1158	1500	957	3130	352	662
5	R=Me R'=Ph	3045 m	1147	1510	965	3122	354	664
6	R=Bu R'=Me	2971 m	1150	1505	961	3136	344	669
7	R=Bu R'=Et	2973 m	1155	1502	959	3111	347	670
8	R=Bu R'=Pr ⁱ	2965 m	1156	1497	960	3109	350	672
9	R=Bu R'=Bu	2967 m	1152	1498	970	3130	355	670
10	R=Bu R'=Ph	3055 m	1157	1504	965	3132	352	671
11	R=Ph R'=Me	2970 m	1158	1508	957	2998	347	665
12	R=Ph R'=Et	2973 m	1160	1506	955	3119	352	664
13	R=Ph R'=Pr ⁱ	2968 m	1163	1499	958	3117	353	665
14	R=Ph R'=Bu	2970 m	1143	1497	965	3120	348	667
15	R=Ph R'=Ph	2974 m	1147	1507	962	3123	347	668

Table 3: ^{119}Sn NMR and ^1H NMR data of Diorganotin(IV) (N-alkyl dithiocarbamates) in δ ppm

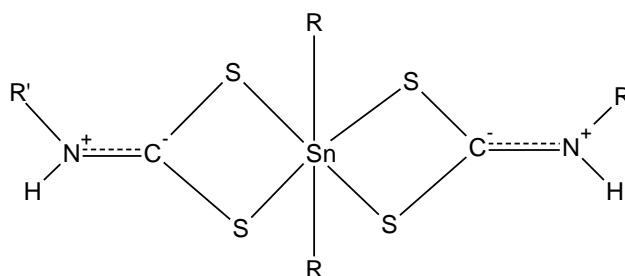
S.No.	Compound $\text{R}_2\text{Sn}[\text{S}_2\text{CNHR}']_2$	^{119}Sn NMR (δ ppm)	^1H NMR (δ ppm)
1	R=Me R'=Me	248.6	1.42 s, 6H (SnMe), 3.06 s, 2H (NH), 3.28 s, 6H (NMe)
2	R=Me R'=Et	246.7	1.29 t, 6H (NMe), 1.39 s, 6H (SnMe), 3.26 q, 4H (NCH ₂), 3.04 s, 2H (NH)
3	R=Me R'=Pr ⁱ	243.2	1.28 d, 12H (NMe), 1.40 s, 6H (SnMe), 3.35 m, 2H (NCH), 3.04 s, 2H (NH)
4	R=Me R'=Bu	251.9	1.30 t, 6H (NMe), 1.39 s, 6H (SnMe), 1.92 m, 8H (CH ₂), 3.02 s, 2H (NH), 3.10 t, 4H (NCH ₂)
5	R=Me R'=Ph	260.3	1.41 s, 6H (SnMe), 3.02 s, 2H (NH), 7.61 m, 10H (C ₆ H ₅)
6	R=Bu R'=Me	250.4	1.45 t, 6H (SnMe), 1.67 t, 4H (SnCH ₂), 1.89 m, 8H (SnCH ₂), 3.05 s, 2H (NH), 3.27 s, 6H (NMe)
7	R=Bu R'=Et	247.9	1.31 t, 6H (NMe), 1.42 t, 6H (SnMe), 1.66 t, 4H (SnCH ₂), 1.87 m, 8H (SnCH ₂), 3.06 s, 2H (NH), 3.27 q, 4H (NCH ₂)
8	R=Bu R'=Pr ⁱ	245.8	1.28 d, 12H (NMe), 1.44 t, 6H (SnMe), 1.67 t, 4H (SnCH ₂), 1.90 m, 8H (SnCH ₂), 3.03 s, 2H (NH), 3.36 m, 2H (NCH)
9	R=Bu R'=Bu	253.4	1.42 t, 6H (SnMe), 1.45 t, 6H (NMe), 1.65 t, 4H (SnCH ₂), 1.89 m, 8H (SnCH ₂), 1.92 m, 8H (NCH ₂), 3.03 s, 2H (NH), 3.19 t, 4H (NCH ₂)
10	R=Bu R'=Ph	262.5	1.44 t, 6H (SnMe), 1.67 t, 4H (SnCH ₂), 1.85 m, 8H (SnCH ₂), 3.03 s, 2H (NH), 7.50 m, 10H (C ₆ H ₅)
11	R=Ph R'=Me	252.4	3.04 s, 2H (NH), 3.26 s, 6H (NMe), 6.64 s, 10H (SnC ₆ H ₅)
12	R=Ph R'=Et	249.7	1.30 t, 6H (NMe), 3.24 s, 4H (NCH ₂), 3.03 s, 2H (NH), 6.62 s, 10H (SnC ₆ H ₅)
13	R=Ph R'=Pr ⁱ	247.2	1.29 d, 12H (NMe), 1.40 s, 6H (SnMe), 3.34 m, 2H (NCH), 3.02 s, 2H (NH), 6.63 s, 10H (SnC ₆ H ₅)
14	R=Ph R'=Bu	254.9	1.31 t, 6H (NMe), 1.90 m, 8H (CH ₂), 3.03 s, 2H (NH), 3.12 t, 4H (NCH ₂), 6.65 s, 10H (SnC ₆ H ₅)
15	R=Ph R'=Ph	264.2	3.01 s, 2H (NH), 6.66 s, 10H (SnC ₆ H ₅), 7.61 m, 10H (C ₆ H ₅)

Table 4: ^{13}C NMR spectral data of Diorganotin(IV) bis(N-alkyl dithiocarbamate) in δ ppm

S.No.	Compound $\text{R}_2\text{Sn}[\text{S}_2\text{CNHR}']_2$	CS_2	NR'	SnR
1	R=Me R'=Me	197.3	R'= Me 34.62	R= Me 14.09
2	R=Me R'=Et	197.5	R'= Et 48.70 12.09	R= Me 14.11
3	R=Me R'=Pr ⁱ	197.2	R'= Pr ⁱ 55.06 19.68	R= Me 14.13
4	R=Me R'=Bu	197.3	R'=Bu 27.84 27.19 26.20 13.49	R= Me 14.12
5	R=Me R'=Ph	197.4	R'= Ph 136.62 128.19 185.95 129.29	R= Me 14.11
6	R=Bu R'=Me	200.5	R'= Me 34.67	R= Bu 32.06 26.54 28.52 13.98
7	R=Bu R'=Et	200.7	R'= Et 48.27 12.25	R= Bu 32.07 26.52 28.40 13.98
8	R=Bu R'=Pr ⁱ	200.6	R'= Pr ⁱ 55.12 19.60	R= Bu 31.87 25.50 28.82 12.96
9	R=Bu R'=Bu	200.7	R'=Bu 27.60 27.18 26.37 13.55	R= Bu 32.04 26.57 27.33 13.88
10	R=Bu R'=Ph	200.4	R'= Ph 136.75 128.12 184.64 129.39	R= Bu 32.00 26.55 28.35 13.99
11	R=Ph R'=Me	199.7	R'= Me 34.70	R= Ph 195.79 136.80 142.66 128.79
12	R=Ph R'=Et	199.2	R'= Et 48.32 12.10	R= Ph 195.72 136.66 142.62 128.59
13	R=Ph R'=Pr ⁱ	199.3	R'= Pr ⁱ 55.16 19.79	R= Ph 195.24 136.90 142.40 128.45
14	R=Ph R'=Bu	199.4	R'=Bu 27.59 27.18 26.37 13.40	R= Ph 195.59 136.29 142.50 128.57
15	R=Ph R'=Ph	199.5	R'= Ph 136.59 128.14 184.97 129.35	R= Ph 195.76 136.45 142.39 128.50

CONCLUSION

All the above evidences suggests that in these complexes dithiocarbamate ligand act as a bidentate and forms the hexacoordinate complexes with the central metal atom.


 Proposed structure of $\text{R}_2\text{Sn}(\text{S}_2\text{CNHR}')_2$

(Where R = Me, Bu, Ph; R' = Me, Et, Prⁱ, Bu, Ph)



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