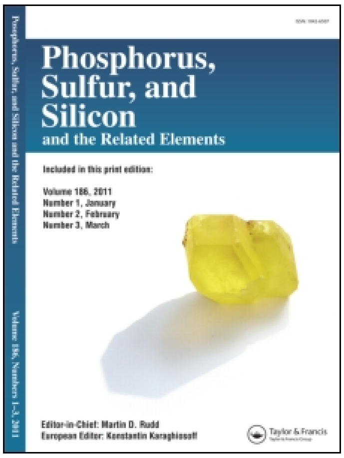

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF HETEROCYCLIC DITHIOCARBAMATE COMPLEXES OF TRIORGANOTIN (IV)

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF HETEROCYCLIC DITHIOCARBAMATE COMPLEXES OF TRIORGANOTIN (IV)

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Heterocyclic dithiocarbamate complexes of triorganotin (IV) having general formula,

$\overline{CH_2CH_2XCH_2CH_2N}CS_2SnR_3$ (where X = $>CH_2$, $>CH—CH_3$, $>N—CH_3$, $>O$; R = $—CH_3$ and $—C_6H_5$)

have been synthesized by the reaction of triorganotin chloride with the sodium salt of the corresponding ligand in 1:1 stoichiometry. These complexes have been characterized by elemental analysis, molecular weight measurements, IR and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy, suggesting that the methyl tin complexes are probably four coordinate, while the phenyl tin ones are probably five-coordinate with bidentate dithiocarbamate.

INTRODUCTION

The geometry and coordination number of the central tin atom in triorganotin (IV) derivatives of various ligands can mainly depend on the nature of organo groups attached to the central tin atom.[1,2] Studies on $R_nSn(S_2CNR'R'')_{4-n}$ reveal that the dithiocarbamate ring can act both as monodentate[3] (R = $—C_6H_5$, n-C_4H_9 and $—C_6H_5CH_2$; $n = 3$), bidentate[4,5] (R = CH_3, n-C_4H_9, $—C_6H_5$; $n = 1$ or 2) and chelating uninegative[6] (R = $—CH_3$; $n = 3$) ligand. Although the bidentate[4,5] as well as chelating uninegative[6] nature of dithiocarbamates are well established, the reported monodentate behaviour of dithiocarbamates is yet to be confirmed. Recently, ^1J (^{119}Sn, ^{13}C) coupling constants[4,5,7] along with the ^{119}Sn NMR data have been used to elucidate the structures of a variety of organotin (IV) compounds,[8] specially those of diorganotin dithiocarbamates.[9] No such report is yet available on the triorganotin (IV) derivatives of heterocyclic dithiocarbamate complexes. We now report the synthesis and characterization of triorganotin (IV) derivatives of some heterocyclic dithiocarbamates.

RESULTS AND DISCUSSION

The reactions of triorganotin chloride with the sodium salt of heterocyclic dithiocarbamates in 1:1 molar ratio in refluxing benzene solution yield the corresponding triorganotin (IV) derivatives.

$$\overline{\mathrm{CH_2CH_2XCH_2CH_2N}}\mathrm{CS_2Na}$$

$$+ \mathrm{R_3SnCl} \xrightarrow[\text{benzene}]{} \overline{\mathrm{CH_2CH_2XCH_2CH_2N}}\mathrm{CS_2SnR_3} + \mathrm{NaCl}\downarrow$$

(where X = >CH_2, >CH-CH_3, >N-CH_3, >O; R = —CH_3 and —C_6H_5)

Complexes where R = —CH_3 are viscous liquids and those having R = —C_6H_5 are crystalline solids with sharp melting points. Both are soluble in common organic solvents like benzene, chloroform, dichloromethane and CS_2. Vapour pressure osmometric molecular weight measurements in chloroform solution at 45°C confirm their monomeric composition.

IR Spectra

The IR spectra of these derivatives exhibit a strong band in the region 1470 ± 30 cm^{-1} which may be attributed to the $\nu(C \overset{...}{—} N)$ mode. The presence of one intense absorption band at 1000 ± 10 cm^{-1} for $\nu(C \overset{...}{—} S)$ mode, with a weak shoulder at 1010 ± 20 cm^{-1} reveals that the dithiocarbamate ligand are monodentate[3] moieties in trimethyltin(IV) complexes. However, the appearance of only one strong band at 1000 ± 10 cm^{-1}, without a shoulder in the triphenyltin(IV) analogs indicates the bidentate behaviour by the ligand. Analysis of the position of $(C \overset{...}{—} N)$ mode further support such behaviour of ligands. This band, in fact, undergoes a shift towards a lower region or remains unchanged,[10] while for bidentate coordination the frequency of their stretching mode would undergo upward shift when compared with its position in the corresponding dithiocarbamate sodium salt. The absorption band observed at 370 ± 30 cm^{-1} has been assigned to ν Sn—S[11] mode. The bands observed at 520 ± 10 cm^{-1} and 560 ± 30 cm^{-1} are due to ν_{sym}(Sn—C) and ν_{asym}(Sn—C), respectively.[12,13]

NMR Spectra

The ^1H NMR spectra of the complexes (Tables I) display the characteristic signals due to —CH_3, ring-CH_2, >N-CH_3, >CH-CH_3, $O\begin{smallmatrix}/\,CH_2,\\ \backslash\,CH_2,\end{smallmatrix}$ —$N\begin{smallmatrix}/\,CH_2,\\ \backslash\,CH_2,\end{smallmatrix}$ protons. A singlet at δ 0.56 to 0.67 ppm in trimethyltin(IV) complexes may be assigned to methyl protons attached to tin. The observed tin proton coupling constants ^2J (^{119}Sn, ^1H) are about 28.12 Hz. This suggests that the tin atom in these complexes is four-coordinate.[14] A correlation between ^2J (^{119}Sn, ^1H) values and C—Sn—C bond angle θ is given by the relation[7]:

$$\theta = 0.0161[^2J]^2 - 1.32[^2J] + 133.4$$

Substituting the relevant coupling constant data in the above equation, the C—Sn —C angles are 109°, indicating a tetrahedral environment around the central tin atom. Phenyl protons are observed as a complex multiplet in the range δ 7.23–7.97 ppm, and no ^{119}Sn-^1H coupling was observed.

A comparison of the ^{13}C NMR spectra of the ligands[15] with the corresponding triphenyltin(IV) complexes (Tables II) shows an upfield shift in the position of CS_2 carbon signal indicating the chelating tendency of the dithiocarbamate moiety. How-

TABLE I

^{1}H NMR spectral data of heterocyclic dithiocarbamate complexes of triorganotin(IV) (values indicated in the table represents the protons in the bold letters) (δ) ppm

Complex	—CH$_3$	$CH_2\Big\langle{}^{CH_2^-}_{CH_2^-}$	>CH-Me	$Me—CH\Big\langle{}^{CH_2^-}_{CH_2^-}$	$Me—N\Big\langle{}^{CH_2^-}_{CH_2^-}$	$C—N\Big\langle{}^{CH_2^-}_{CH_2^-}$	$O\Big\langle{}^{CH_2^-}_{CH_2^-}$	Sn—R	$\lvert{}^2J(^{119}Sn,{}^1H)\rvert$	Me—Sn—Me Angle θ°
$(CH_3)_3Sn(Pipdtc)$	—	1.69(s) (6H)	—	—	—	4.15(t) (4H)	—	0.62(s) (9H)	28.12	109
$(CH_3)_3Sn(4\text{-}MePipdtc)$	0.96(d) (3H)	—	0.96–1.68(m) (1H)	3.13(t)(4H)	—	5.22(d) (4H)	—	0.56(s) (9H)	—	—
$(CH_3)_3Sn(N\text{-}MePzdtc)$	2.33(s) (3H)	—	—	—	2.49(t)(4H)	4.18(t) (4H)	—	0.56(s) (9H)	—	—
$(CH_3)_3Sn(Morphdtc)$	—	—	—	—	—	3.84(t) (4H)	4.24(t) (4H)	0.67(s) (9H)	28.12	109
$(C_6H_5)_3Sn(Pipdtc)$	—	1.68(s) (6H)	—	—	—	4.02(d) (4H)	—	7.31–7.95(m) (15H)	—	—
$(C_6H_5)_3Sn(4\text{-}MePipdtc)$	0.96(d) (3H)	—	1.20–2.25(m) (1H)	3.13(t)(4H)	—	4.90(d) (4H)	—	7.23–7.87(m) (15H)	—	—
$(C_6H_5)_3Sn(N\text{-}MePzdtc)$	2.25(s) (3H)	—	—	—	2.41(t)(4H)	4.10(t) (4H)	—	7.23–7.87(m) (15H)	—	—
$(C_6H_5)_3Sn(Morphdtc)$	—	—	—	—	—	2.41(t) (4H)	4.10(t) (4H)	7.31–7.87(m) (15H)	—	—

$CH_2CH_2XCH_2CH_2NCS_2SnR_3$: where X = >$CH_2$(Pipdtc); >CH—$CH_3$(4-MePipdtc); >N—$CH_3$(N-MePzdtc); >O(Morphdtc), respectively.

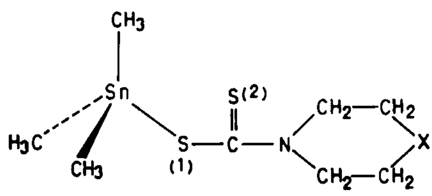
TABLE II

^{13}C and ^{119}Sn NMR spectral data of heterocyclic dithiocarbamate complexes of triorganotin(IV) (δ) ppm

Compounds	C^a	C^b	C^c	C^d	C^e	Sn-R	$\lvert ^1J(^{119}Sn, ^{13}Cl)\rvert$ Hz	Me—Sn—Me θ(°C) Angle	CN†	^{119}Sn δ,ppm
d c b a $CH_2CH_2(CH_2)CH_2CH_2NCS_2Sn(CH_3)_3$	211.08	52.60	25.35	23.24	—	−1.078	373.89	106.66	4	19.74
d c b a $CH_2CH_2(CH_2)CH_2CH_2NCS_2Sn(C_6H_5)_3$	194.21	53.85	25.62	22.97	—	142.58; 136.57*; 128.34; 128.93	—	—	—	(−)190.89
d e c b a $CH_2CH_2(CH—CH_3)CH_2CH_2NCS_2Sn(CH_3)_3$	211.10	51.62	33.26	29.52	20.75	−1.241	372.34	106.53	4	17.39
d e c b a $CH_2CH_2(CH—CH_3)CH_2CH_2NCS_2Sn(C_6H_5)_3$	194.48	53.20	33.69	29.63	21.02	142.64;136,62* 128.39;128.93	—	—	—	(−)190.60
e c b a $CH_2CH_2(N—CH_3)CH_2CH_2NCS_2Sn(CH_3)_3$	212.20	44.80	50.49	—	53.52	−1.403	375.02	106.75	4	22.65
e c b a $CH_2CH_2(N—CH_3)CH_2CH_2NCS_2Sn(C_6H_5)_3$	195.89	45.34	52.06	—	54.06	142.10;136.57 128.39;129.04	—	—	—	(−)175.54
c b a $CH_2CH_2(O)CH_2CH_2NCS_2Sn(CH_3)_3$	212.32	65.87	51.30	—	—	−1.132	373.64	106.64	4	34.48
c b a $CH_2CH_2(O)CH_2CH_2NCS_2Sn(C_6H_5)_3$	196.54	65.93	52.11	—	—	141.83;136.57* 128.50;129.15	—	—	—	(−)181.83

*Tin-phenyl values are given in the order C(i), C(o), C(m) and C(p), respectively.

†Coordination number.



(where X = >CH_2, >CH-CH_3, >N-CH_3, >O)

FIGURE 1

ever, in trimethyltin(IV) complexes this signal does not show any shift in its position when compared with the spectra of the corresponding ligands. This may be interpretated for the monodentate behaviour of ligand. In trimethyltin(IV) complexes, a singlet for methyl carbon occurred in the range δ 1.07–1.40 ppm. The tin-carbon coupling constants, ^1J (^{119}Sn, ^{13}C), were observed in the range of 372–375 Hz, which indicates that the central tin atom is four-coorrdinate.[16] A correlation between ^1J (^{119}Sn,^{13}C) values and C—Sn—C bond angle (θ) in trimethyltin(IV) complexes is given by[7]:

$$^1J = 11.4\theta - 875$$

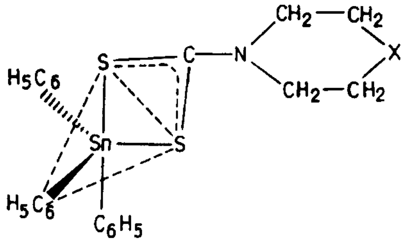
or

$$\theta = 0.0877[^1J] + 76.7543$$

Substituting the coupling constant data in the above equation, the C—Sn—C angles are found to be in the range of 106.5°–106.8°, suggesting a distorted tetrahedral environment around the tin atom.[7]

^{119}Sn chemical shifts for trimethyltin(IV) complexes are in the range δ (−) 17–35 ppm (Table II). The appearance of a ^{119}Sn signal in this region is consistent with tetrahedral bonding[8] around the central tin atom (Figure 1).

In all the organotin(IV) dithiocarbamates the geometries are distorted. In diorganotin(IV) bisdithiocarbamates, the ligand behave as bidentate moiety and Me—Sn—Me bond angle in trans geometry are found[4,5] to be in the range of 136–144°. The two modifications of $Me_3Sn\ S_2CNMe_2$ show the average Me—Sn—Me bond angles of 111° (orthorhombic)[17] and 113.7° (monoclinic)[6] in distorted tetrahedral geometry. The behaviour of ligands may be is best described as chelating uninegative



(where X = >CH_2, >CH-CH_3, >N-CH_3, >O)

FIGURE 2

TABLE III

Analytical and physical data of triorganotin(IV) complexes

Reactants in g		Molecular Formula (% Yield)	NaCl g Found (Calc.)	M.P. (±1°C)	Analysis		MW Found (Calc.)	V(C $\overset{\cdots}{-}$ N) cm^{-1}	V(C $\overset{\cdots}{-}$ S) cm^{-1}
NaS$_2$CNCH$_2$CH$_2$ X CH$_2$CH$_2$	R$_3$SnCl				Sn% Found (Calc.)	S% Found (Calc.)			
X=>CH$_2$ 2.22	R=-CH$_3$ 2.02	C$_9$H$_{19}$NS$_2$Sn (92)	0.58 (0.59)	-	36.00 (36.62)	19.32 (19.78)	322.12 (324.06)	1450	1010 1020
X = >CH-CH$_3$ 2.32	R = -CH$_3$ 2.10	C$_{10}$H$_{21}$NS$_2$Sn (94)	0.60 (0.61)	-	35.08 (35.10)	18.52 (18.96)	335.42 (338.09)	1470	990 1010
X = >N-CH$_3$ 2.09	R = -CH$_3$ 1.93	C$_9$H$_{20}$N$_2$S$_2$Sn (85)	0.54 (0.56)	-	34.96 (35.00)	18.62 (18.90)	338.74 (339.08)	1440	1000 980
X = >O 2.06	R = -CH$_3$ 1.86	C$_8$H$_{17}$NOS$_2$Sn (90)	0.53 (0.54)	-	36.32 (36.40)	19.28 (19.66)	325.92 (326.03)	1470	1010 1000
X = >CH$_2$ 1.29	R = -C$_6$H$_5$ 2.27	C$_{24}$H$_{25}$NS$_2$Sn (92)	0.33 (0.34)	150	23.20 (23.26)	12.38 (12.56)	510 (510.27)	1490	1010
X = >CH-CH$_3$ 1.32	R = -C$_6$H$_5$ 2.36	C$_{25}$H$_{27}$NS$_2$Sn (86)	0.33 (0.35)	140	22.58 (22.63)	12.18 (12.22)	510 (524.30)	1500	1010
X = > N-CH$_3$ 1.42	R = -C$_6$H$_5$ 2.53	C$_{24}$H$_{26}$N$_2$S$_2$Sn (89)	0.37 (0.38)	164	22.52 (22.59)	12.16 (12.20)	525 (525.29)	1480	990
X = >O 1.30	R = -C$_6$H$_5$ 2.28	C$_{23}$H$_{23}$NOS$_2$Sn (90)	0.33 (0.34)	168	23.12 (23.17)	12.44 (12.51)	512.16 (512.25)	1470	1000

moiety. The central tin atom acquire 5-coordination through weak Sn—S dative bond.[6,17] The average bond angle of 107° in the present case however indicates further weakening or absence of Sn—S(2) interaction (Figure 1) in solution. But it has to be borne in mind that the structure in solution and solid state may be different, and in organotin derivatives the bond angles in solution are generally less than in solid state as they are free of solid state packing constraints.[4] Thus, the possibility of weak interaction between Sn and S(2) atoms can not be completely ruled out in the absence of X-ray structural data in solid state.

In contrast to the above, the ^{119}Sn NMR signals of triphenyltin(IV) complexes are in the range δ (−)175–191 ppm. The appearance of a ^{119}Sn signal in this region is consistent with 5-coordination around the central tin atom[8] (Figure 2).

These results are not surprising in view of the enhanced electronegativity of R group in phenyl derivatives.[18] A five coordination around central tin atom in compounds where R = —C_6H_5 is likely to be favoured with trigonal bipyramidal geometry with ligand acquiring axial-equatorial positions in a highly distorted structure.[18]

Although we conclude that the dithiocarbamates behave as monodentate ligands when three methyl groups are attached to the central tin atom and as bidentate ligands in presence of three phenyl groups, we recognize that X-ray diffraction studies are essential to confirm bonding modes and geometries in the solid state.

EXPERIMENTAL

The ligands used in this investigation were prepared by literature method.[19] Me_3SnCl was distilled at 153°C and Ph_3SnCl was recrystallised from benzene-hexane solution. Tin and sulfur were estimated gravimetrically as tin oxide and barium sulphate (Messenger's Method), respectively.[20] Molecular weights were determined with a "Knauer vapour pressure osmometer," using chloroform solutions at 45°C.

Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Perkin Elmer 577 spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ and $CHCl_3$ solutions respectively on a 90 MHz JEOL FX 90 Q spectrometer using TMS as an internal reference. ^{119}Sn NMR spectra of complexes were recorded in $CHCl_3$ solution using Me_4Sn as an external reference. ^{13}C NMR spectra of four samples in $CDCl_3$ solution were recorded on a Bruker WH 270 MHz spectrometer using TMS as an internal reference.

Since all complexes were synthesized in the same way, experimental details of a representative complex are given below. Analytical results are summarised in Table III.

Synthesis of $(CH_3)_3Sn(Pipdtc)$; $(C_{19}H_{19}NS_2Sn)$

A benzene solution of Me_3SnCl (2.02 g, 10.2 mmol) was added drop by drop to the benzene suspension of the sodium salt of piperadine dithiocarbamate (2.22 g, 10.2 mmol). The reaction mixture was stirred for ~4 hours at room temperature and then refluxed for ~6 hours to ensure complete reaction. The NaCl formed was filtered off and excess solvent was removed from the filtrate under reduced pressure. The crude product was recrystallized from chloroform-hexane.

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