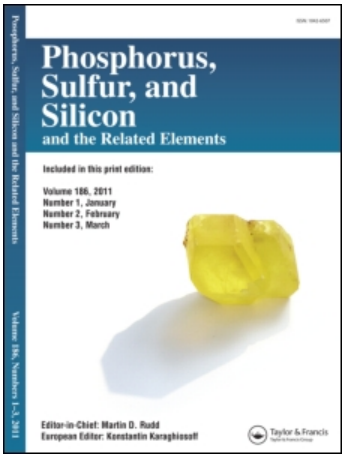

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SYNTHESIS AND CHARACTERIZATION OF 5- AND 6-COORDINATED MONOORGANOTIN(IV) COMPLEXES OF 2- AMINOCYCLOPENTENE-1-CARBODITHIOIC ACID AND ITS N-/S-ALKYL DERIVATIVE HAVING NS AND SS DONOR SYSTEM

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SYNTHESIS AND CHARACTERIZATION OF 5- AND 6- COORDINATED MONOORGANOTIN(IV) COMPLEXES OF 2- AMINOCYCLOPENTENE–1-CARBODITHIOIC ACID AND ITS N-/S-ALKYL DERIVATIVE HAVING $\widehat{NS}$ AND $\widehat{SS}$ DONOR SYSTEM

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Monoorganotin(IV) complexes of 2-aminocyclopentene-1-carbodithioic acid and its N-/S-alkyl derivatives of formula $BuSnCl_{3-n}[S(S)C\overset{(CH_2)_3}{=\!=}CN(H)R]_n$ (where n = 1,2; R=-H, $-CH_3$, $-C_2H_5$ and $-nC_4H_9$) and $BuSnCl_{3-n}[N(H)C\overset{(CH_2)_3}{=\!=}CC(S)SCH_3]_n$ (where n = 1,2) have been synthesised by the reactions of butyltintrichloride with corresponding ligands in different stoichiometric ratios. The plausible structures of these derivatives have been proposed on the basis of physico-chemical and spectral (IR, ^1H, ^{13}C and ^{119}Sn NMR) Studies.

Keywords: Monoorganotin(IV) complexes; FT-IR spectra; NMR spectra

INTRODUCTION

Interest in the synthesis of 2-aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives of monoorganotin(IV) species arises because of their most varied coordination chemistry, versatile structural features[1–5] and biological activity.[6,7] 2- aminocyclopentene-1- carbodithioic acid and its N-/S-alkyl derivatives constitute an interesting class of mono functional

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bidentate nitrogen and sulphur containing ligands owing to their biological activity[8] and ambidentate nature[9–13]. In the present paper we report the synthesis and characterization of some monoorganotin(IV) complexes of 2-aminocyclopentene-1-carbodithioic acid and its N-/S-alkyl derivatives.

RESULTS AND DISCUSSION

2-aminocyclopentene-1-carbodithioic acid (ACDA) and its N-/S-alkyl derivatives exist in various tautomeric forms[14,15]with preponderance of the isomer (I) in solution[12].

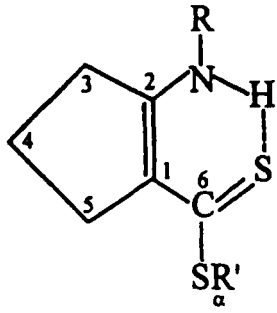


FIGURE I

where R^1 = H and R = H (HACDA), CH_3 (HMeACDA), C_2H_5 (HEt-ACDA), C_4H_9(HBuACDA); R = H and R^1 = CH_3(HACDE)

Butyltin(IV) complexes of general formula $BuSnCl_{3-n}[S(S)CC(CH_2)_3CN(H)R]_n$ and $BuSnCl_{3-n}[N(H)C(CH_2)_3CC(S)SR']_n$ have been synthesised by the interaction of butyltintrichloride with the sodium salt of 2- aminocyclopentene-1-carbodithioic acid and its N-/S alkyl derivatives in different stoichiometric ratios in refluxing benzene solution.

(i) $BuSnCl_3 + nR(H)NC(CH_2)_3CC(S)SNa \rightarrow$

$$BuSnCl_{3-n}[S(S)CC(CH_2)_3CN(H)R]_n + nNaCl\downarrow$$

(where R = -H, $-CH_3$, $-C_2H_5$ and $-nC_4H_9$; n = 1,2)

(where R = -H, $-CH_3$, $-C_2H_5$ and $-nC_4H_9$; n = 1,2)

(ii) $BuSnCl_3 + nNa(H)NC\overset{(CH_2)_3}{=\!=\!=}CC(S)SR' \rightarrow$

$$BuSnCl_{3-n}[N(H)C\overset{(CH_2)_3}{=\!=\!=}CC(S)SR']_n + nNaCl\downarrow$$

(where $R' = -CH_3$; n = 1, 2)

(where $R^1 = -CH_3$; n = 1,2)

After filtering off the sodium chloride formed and stripping off the volatile fractions under reduced pressure at room temperature, brown solids to sticky solids are obtained. These are found to be soluble in common organic solvents. Osmometric molecular weight measurements in chloroform solution at 45°C show their monomeric nature.

INFRARED SPECTRA

A broad absorption band observed at 2540–2440 cm^{-1}due to vSH mode in the IR spectra of parent ligands have been found to be absent in the spectra of the monobutyldichloro(N-alkyl derivatives of 2-aminocyclopentene-1-carbodithioic acid)tin(IV) as well as monobutylchlorobis (N-alkyl-2-amino-cyclopentene-1-carbodithioic acid) tin(IV) complexes, indicating the deprotonation of vSH group and the formation of Sn-S bond. The appearance of a new band at 450–405 cm^{-1} which may be assigned to vSn-S[16,17] further supports the tin-sulphur bonding. The presence of only one intense absorption band in the region 930–910 cm^{-1} assigned for vasym CSS[18] reveals the bidentate behaviour of the ligand moieties in complexation. The absorption band observed at 620–605 cm^{-1}, 350–310 cm^{-1} are being assigned to vsym CSS and vSn-Cl, respectively[19–21]. The absence of any appreciable shift in v NH_2/NHR(~ 3400 cm^{-1}) absorption band in complexes in comparison to its position in parent ligand depicts the non-involvement of NH_2/NHR group in bonding. The strong absorption band observed at 1610–1600 cm^{-1}, 1500–1475 cm^{-1}, 1365–1340 cm^{-1} and 1285–1275 cm^{-1} may be attributed to $\nu NH_2 + C=C$, $\nu CH_2 + C=C$, $\nu C=N + C=S$ and $\nu C=S + C=N$ modes,[12] respectively. No significant shift in these bands has been observed when compared to their position in corresponding ligands.

In S-alkyl-2-aminocyclopentene-1-carbodithioic acid derivatives, a shift of ~ 80–60 cm^{-1} in the position of NH_2 band towards lower wave number

indicates the involvement of amino nitrogen of the ligand moiety in the bonding. This Sn-N bonding is supported by the appearance of a new absorption band at 510–480 cm^{-1} which may be assigned to vSn-N mode[22]. The presence of two splitted bands for vasym CSS in the region 970–925 cm^{-1} indicates the participation of only one sulphur atom of the ligand moiety in complexation. A small shift(~ 10 cm^{-1}) towards lower side in the position of $\nu C=N+C=S$ and $\nu C=S+C=N$ absorption bands further supports the bidentate nature of the ligand.

^{1}H NMR SPECTRA

In the spectra of N-alkyl derivatives of ACDA, absence of any signal for -SH proton supports the deprotonation of-SH group and the formation of Sn-S bond. In the ^{1}H NMR spectrum of ACDA, the presence of two broad signals due to the NH_2 protons observed at δ 11.2 and 7.13 ppm, shows the non-equivalent nature of the amino protons, these signals shift downfield in the spectra of the corresponding complexes and appear at δ 8.60–8.62 and 6.67–6.98 ppm, respectively. One plausible explanation for this may be that when sulphur atom is involved in the bonding, the hydrogen bond (NH----S=) weakens. However, the presence of two signals even on complexation indicates that some weak interaction still persists between one of the NH_2 protons and the sulphur of dithiocarboxylate group (-C=S). A similar phenomenon has been observed in the ^{1}H NMR spectra of other N-alkyl derivatives of ACDA of monobutydichlorotin(IV) as well as monobutylchlorotin(IV) complexes and NH proton is observed in the range of δ 9.12–10.12 ppm. In complexes the position of protons attached to the ring carbon appear at δ 1.64–2.18 ppm [-CH_2(4)] as a quintet and δ 2.47–4.72 ppm [-CH_2,(3&5)] as a multiplet. The protons of alkyl group attached with nitrogen appear at their usual positions.[13]

In S-alkyl derivatives, the signal observed at δ11.2 ppm in parent ligand and assigned to chelated -NH was found to be absent and the signal observed at δ 5.81 ppm and assigned to free -NH is shifted downfield to δ 5.99–6.20 ppm, indicating the removal of one of the protons of amino group on complexation and the formation of Sn-N bond. A downfield shift in the position of S-CH_3(δ 2.64 ppm in free ligand) signal further supports the participation of the -C = S group in bonding.

The butyl protons attached with central tin atom were observed as a complex multiplet in the range δ 0.86–2.38 ppm.

^{13}C NMR SPECTRA

The mode of bonding suggested above has been confirmed on the basis of ^{13}C NMR spectral data.

In the spectra of the ligands ACDA and its N-alkyl derivatives, the signal for C_6 appears at δ 189.07–196.12 ppm, which shifts downfield and is observed in the range of δ 197.62–202.06 ppm in their corresponding complexes. Such a large shift of δ 7.68–8.55 ppm [for C_6] may be due to the deshielding of the carbon atom because of the deprotonation of one thiol group and coordination through the other sulphur atom. The position of other signals in the spectra of the ligand and the corresponding monoorganotin(IV) complexes remains unaltered.[13]

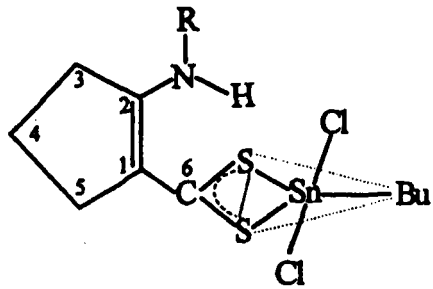
In the spectrum of HACDE the signal observed at δ 166.15 ppm for C_2 carbon attached with NH_2 group shows a shift of δ 1.08–1.32 ppm in the spectrum of the corresponding complexes. This shift indicates the bonding of nitrogen atom with tin in complexes. The signals for C_6 carbon [C(S)SMe] and $C_\alpha$carbon [-SCH_3] show appreciable shift of δ 1.99–3.60 ppm and δ 1.68–1.71 ppm, respectively. These shifts indicate the involvement of C(S)S(CH_3) group in bonding.

The signals for the butyl carbon attached with tin have been observed at δ 37.65–37.02 (C_1), 25.64–25.19 (C_2), 28.28–27.25 (C_3), and 13.76–13.38 (C_4) ppm, respectively.

^{119}Sn NMR SPECTRA

The ^{119}Sn NMR spectra of ACDA and its N-/S-alkyl derivatives of monobutyldichlorotin(IV) complexes are observed in the region δ (-) 223.34 to (-) 246.08 ppm which confirm a penta coordination environment around the central tin atom.[23]

On the basis of molecular weight measurements, IR and NMR spectral evidences described above, the following structures [Fig. 2 and Fig. 3]



where R = -H, - CH_3, - C_2H_5 and -nC_4H_9

FIGURE 2 Proposed structure for $BuSnCl_2[S(S)CC\overset{(CH_2)_r}{=\!=}CNHR]$

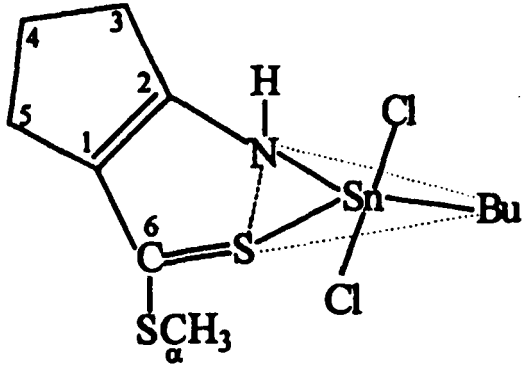
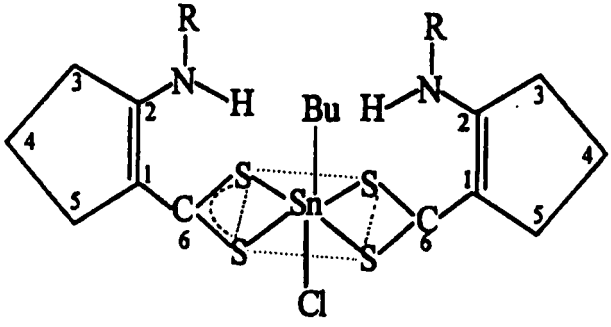


FIGURE 3 Proposed structure for $BuSnCl_2[N(H)C\overset{(CH_2)_r}{=\!=}CC(S)SCH_3]$

may be proposed for monobutyldichlorotin(IV) complexes of N-alkyl derivatives of ACDA and S-alkyl derivative of ACDA, respectively.

However, in monobutylchlorobis(N-/S-alkyl derivatives of ACDA)tin(IV) complexes, ^{119}Sn chemical shifts are observed in the region δ (-) 440.25 to (-) 472.86 ppm. The appearance of ^{119}Sn chemical shift in this particular region has been earlier attributed to the existance of an octahedral geometry around tin atom[24] in the complexes. On the basis of above IR and NMR (^1H, ^{13}C and ^{119}Sn) spectral studies, the following



Where R = -H_2-CH_3-C_2H_5 and n-C_4H_9

FIGURE 4 Proposed structure for $BuSnCl[S(S)CC(CH_2)_nCN(H)R]_2$

structures [Fig. 4 and Fig. 5] may be proposed for monobutylchlorobis(N-alkyl derivatives of ACDA) tin(IV) complexes and monobutylchlorobis(S-alkyl derivative of ACDA) tin(IV) complex, respectively.

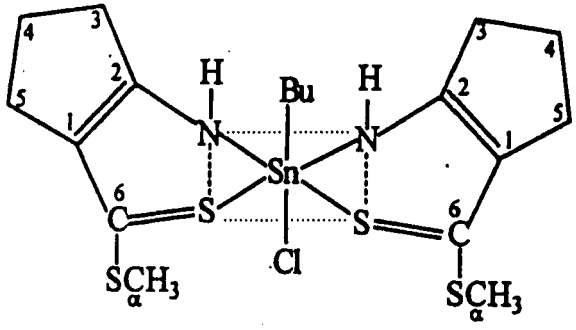


FIGURE 5 Proposed structure for $BuSnCl[N(H)C(CH_2)_nCC(S)SCH_3]_2$

EXPERIMENTAL

Butyltintrichloride (Fluka) was distilled (bp 93° / 10 mm) before use. Reactions were carried out under anhydrous conditions. Ligands were prepared by the literature methods.[14,15] Tin and sulphur were estimated gravimetrically, and by Messenger's method, respectively. Nitrogen and chlorine were estimated by Kjeldahl's and Volhard method, respectively[25]. Molecular weights were determined on a Knauer Vapour Pressure Osmometer in chloroform solution at 45°C. IR spectra were recorded in the range 4000–200 cm^{-1} on "Nicolet Magna 550" FT IR-spectrophotometer. ^{1}H, ^{13}C and ^{119}Sn NMR spectra have been recorded in $CDCl_3$ solution on a 90 MHz JEOL FX90Q spectrometer. TMS was used as an internal and external reference for ^{1}H and ^{13}C NMR, respectively. ^{119}Sn NMR spectra were recorded using Me_4Sn as an external reference.

All the complexes have been synthesised by the reactions of sodium salt of ligands with $BuSnCl_3$ in benzene solution. Since same procedure has been followed for the synthesis of organotin(IV) complexes and therefore, the preparation of a representative complex has been described in brief and the results of the analogous complexes have been summarised in Table-I.

Preparation of monobutyldichloro(2-aminocyclopentene-1-carbodithioic acid)tin(IV); BuSn (ACDA)Cl_2

A benzene solution of 2-aminocyclopentene-1-carbodithioic acid(HACDA) (0.69g, mmol) was added to a solution of sodium methoxide (0.10 g, mmol sodium in 10 ml of methanol) with constant stirring and refluxed for 3 h. A benzene solution of $BuSnCl_3$ (1.22 g, mmol) was then added to the above solution drop by drop with constant stirring and the reaction mixture was finally refluxed for about 4h. The precipitated sodium chloride was filtered off. Evaporation of excess of solvent lead to a brown solid (yield 74%). The solid product was recrystallised from chloroform-pet. ether (40–60°C) mixture. The compound on analysis was found to have: Sn, 29.14; N, 3.26; S, 15.66; Cl, 17.32%. Calcd. for $C_{10}H_{17}S_2NCl_2Sn$: Sn, 29.30; N, 3.45; S, 15.83; Cl, 17.51%.

TABLE I Synthetic and analytical data of monoorganodichlorotin(IV) and monoorganochlorotin(IV) complexes of 2- aminocyclopentene-1-carbodithioic acid and its N-/S- alky derivatives

S.No.	*Reactants in gms.*			*Product Molecular Formula % yield*	*NaCl Found (Calcd.)*	*State/Colour/m.p.(°C)*	*M.Wt. Found (Calcd.)*	*Elemental Analysis % Found (Calcd.)*			
	Sodium	*Ligand*	*Organotin chlorides*					*Sn*	*N*	*S*	*Cl*
1.	0.10	ACDA 0.69	$BuSnCl_3$ 1.22	$C_{10}H_{17}S_2NCl_2Sn$ 74%	0.22 (0.25)	Solid/Brown/ 104	402 (404.98)	29.14 (29.30)	3.26 (3.45)	15.66 (15 83)	17.32 (17.51)
2.	0.09	MeACDA 0.67	$BuSnCl_3$ 1.10	$C_{11}H_{19}S_2NCl_2Sn$ 72%	0.20 (0.22)	Solid/Brown/ 104	417 (419.10)	28.12 (28.32)	3.20 (3.34)	15.12 (15.30)	16.68 (16.92)
3.	0.11	EtACDA 0.89	$BuSnCl_3$ 1.34	$C_{12}H_{21}S_2NCl_2Sn$ 75%	0.25 (0.28)	Solid/ Yellowish Brown/60	431 (433.03)	27.22 (27.41)	3.04 (3.23)	14.64 (14.80)	16.14 (16.37)
4.	0.09	BuACDA 0.84	$BuSnCl_3$ 1.10	$C_{14}H_{25}S_2NCl_2Sn$ 70%	0.21 (0.23)	sticky solid/wine/ –	460 (461.09)	27.08 (27.48)	3.04 (3.24)	14.58 (14.84)	16.26 (16.41)
5.	0.12	ACDE 0.90	$BuSnCl_3$ 1.47	$C_{11}H_{19}S_2NCl_2Sn$ 74%	0.27 (0.30)	sticky solid/greenish/ –	421 (419.01)	28.14 (28.32)	3.18 (3.34)	15.14 (15 30)	16.68 (16.92)
6.	0.14	ACDA 0.96	$BuSnCl_3$ 0.85	$C_{16}H_{25}S_4N_2ClSn$ 73%	0.32 (0.35)	solid/brown/ 107	525 (527.79)	22.26 (22.48)	5.16 (5.30)	24.14 (24.29)	6.52 (6.71)
7.	0.12	MeACDA 0.90	$BuSnCl_3$ 0.73	$C_{18}H_{29}S_4N_2ClSn$ 71%	0.27 (0.30)	solid/brown/ 108	533 (555.85)	21.16 (21.35)	4.96 (5.04)	22.94 (23 07)	6.18 (6.37)
8.	0.13	EtACDA 1.05	$BuSnCl_3$ 0.79	$C_{20}H_{33}S_4N_2ClSn$ 74%	0.31 (0.33)	solid/yellowish green/134	580 (583.90)	20.18 (20.32)	4.52 (4.79)	21.78 (21.96)	5.96 (6.07)
9.	0.12	BuACDA 1.12	$BuSnCl_3$ 0.73	$C_{24}H_{41}S_4N_2ClSn$ 70%	0.28 (0.30)	solid/dark brown/ 118	639 (640.01)	18.26 (18.55)	4.18 (4.38)	19.88 (20.04)	5.38 (5.54)
10.	0.15	ACDE 1.13	$BuSnCl_3$ 0.92	$C_{18}H_{29}S_4N_2ClSn$ 75%	0.35 (0.38)	sticky solid/yellowish brown/-	557 (555.85)	21.18 (21.35)	4.94 (5.04)	22.96 (23.07)	6.16 (6.37)

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